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"DEVELOPMENT OF SUSTAINABLE TANNIN WITH LOW CARBON FOOTPRINT TO OBTAIN HIGH QUALITY LEATHER"

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Abstract

Today we are experiencing an “eco friendly boom”; which includes the developing of ecological processes that have a smaller impact in the environment. This is the reason that prompted me to carrying out this thesis; the aim is to use a vegetable extract as a sustainable product for the pre-tanning processes. This study considers the use of the fruit of the Tara tree as a raw material source of tannins with low carbon footprint and proposes alternatives to avoid or reduce the use of commercial vegetable extracts, synthetic products and mineral salts that require non sustainable processes. Various experimental designs have been developed as to obtain new tailored Tara tannins by both chemical and physical modification, in order to obtain a higher percentage of tannins, and therefore improve its tanning capability, also reducing the astringency and improving the penetration of the tannin molecules through the leather structure. In chemical modifications, several aqueous extractions at different temperatures and combined with some chemicals, have been developed and optimized in order to increase the tannin content and reduce the astringency. The degree of hydrolysis has controlled by measuring the Gallic acid content by means of HPLC (High performance liquid Chromatography). In the physical modification part, the Tara has been milled and sieved, at several particle sizes, with the aim of obtaining a smaller molecular size.

Both chemical and physical modifications were tested in hides, in a wet-white pre-tanning process, combining them with the fewest possible commercial vegetable extracts and syntans. The formulations have been optimized by experimental design. All the resulting leather products and final baths have been analyzed with physical and chemical tests respectively, to determine if they comply with the parameters established by the IULTCS (International Union of Leather Technologists and Chemists Societies). Finally, a life cycle assessment has been developed, in order to determine the environmental improvement of the new modified product, obtained in this thesis.

Keywords: Modified Tara, tannins, pre-tanning, vegetable tanning, re-tanning, Gallic acid, Wet-white, sustainable, carbon footprint.

Resumen

Hoy estamos viviendo un "boom ecológico", esto significa desarrollar procesos con un menor impacto ambiental y tratar de hacerlos lo más ecológico posible. Ésa es la razón de llevar a cabo esta tesis, se trata de usar un extracto vegetal como producto sostenible para procesos de pre-curtido, curtido y re-curtido. Esta tesis considera el fruto del árbol de Tara como materia prima y fuente de taninos con baja huella de carbono, además de propone alternativas para evitar o disminuir el uso de extractos vegetales comerciales, productos sintéticos y sales minerales que son preparados por procesos no sostenibles. Varios diseños experimentales han sido desarrollados para obtener un nuevo tanino de Tara modificado química y físicamente, con el fin de obtener un porcentaje más alto de taninos y por lo tanto mejorar su capacidad de curtición, además se busca mejorar la penetración de la molécula de tanino dentro de la estructura de la piel. En las modificaciones químicas, varias extracciones acuosas a diferentes temperaturas, combinadas con algunos productos químicos, han sido desarrolladas y optimizadas con el fin de reducir la astringencia y aumentar el contenido de tanino. El grado de hidrólisis se ha controlado mediante la medición del contenido de ácido gálico por Cromatografía en fase liquida de alto rendimiento (HPLC por sus siglas en ingles). En la modificación física, la Tara se ha molturado y tamizado, en varios tamaños de partícula, con el fin de obtener un tamaño molecular más pequeño.

Ambas modificaciones químicas y físicas se han probado en la piel, en un proceso de pre-curtición wet-white, combinándolos con la menor cantidad posible de extractos vegetales comerciales y taninos sintéticos. Las formulaciones se han optimizado por diseño experimental. Todos los cueros producidos y baños finales de curtido han sido analizados con ensayos físicos y químicos respectivamente, para determinar si cumplen con los parámetros establecidos por los estándares de la Unión Internacional de Tecnólogos y Sociedades de Químicos del Cuero (IULTCS por sus siglas en ingles). Se ha desarrollado un análisis de ciclo de vida, con el objetivo de determinar la mejora ecológica del nuevo producto modificado, obtenido en esta tesis.

Palabras Clave: Tara modificada, taninos, pre-curtición, curtición vegetal, re-curtición, Ácido gálico, Wet-white, sustentable, huella de carbono.

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Introduction

Throughout history, tanning processes have been used as a means to prevent the skins from rotting, so, these could be used in everyday life; at first, natural extracts from trees or plants were used, without actually knowing their composition or what the reaction with the skins really was.

It is not till the 20th Century that leather production became an industry, thanks to the increasing demand for of articles made from leather. This industry has survived due to the intrinsic properties of leather, because an article made from leather has always been considered a quality item.

In addition, leather is a by-product of meat industry; this means that if we do not process all the amount of skin that is generated, we would have a serious problem with wastes and pollution.

According to the IPPC (Integrated Pollution Prevention and Control, 2013),[1] chromium is the most widely used tanning agent; about 80 to 95% of the tannin processes performed in the world, are done with chromium. This is due to the properties that this agent gives to the leather, such as elasticity, high temperature shrinkage, smoothness, etc.

However, the use of chromium in the tanning industry has been more restricted by environmental issues, which have been discussed enough, so alternatives have been sought to replace this material.

A significant part of the whole leather production, is being processed by wet-white and vegetable tanning procedures, such as the automotive upholstery leather, as well as an important percentage of the shoe upper industry and the leather goods market.

It is also thanks to sustainability of the processes of raw materials, that we keep in road with new investigations to reach more environmental friendly developments. These is the reason why it is necessary to use the Tara tannins as a source of sustainable raw material and try to prevent the use of materials chemically processed as much as possible.

Tara tannin is an alternative to reduce the use of metallic salts and some vegetable extracts. Attempts have been made to use Tara tannins and some synthetic tannins in different tanneries due to the interest in developing chrome-free leathers, because of the tightening restrictions on chrome contained in floats and in waste disposal.

At present, tara is used mostly as a retanning in manufacturing processes of automotive upholstery, this is because it provides light-colored, has a higher light fastness, and gives a vegetable character to the leather.

The Tara is an extract, in which the relation between tannin and non-tannin is the highest with a strong natural acidity, thus giving the most astringent tannin in the market. This property is interesting to produce skins levanted or coarse grain.[2]

This thesis proposes to design new tailored functional pre-tanning recipes to promote the sustainability and manufacture of high quality leather articles, through the **chemical** and **physical** modification of the Tara tannins.

The Tara tannin by itself is not a good tanner because of its high astringency, which produces a low penetration trough the skin; this is why such modifications have been developed, to improve the penetration.

The physical and chemical modifications of commercial Tara tannin have been carried out on the basis of the research and development activities, with the corresponding experimental designs.

Tara tannins have been used for their light fastness properties in the tanning industry; however, the activities proposed in this thesis will optimize innovative formulations by using new modified products. These new fractions, combined with the formulations of modified Tara with pre-tanning materials will improve the penetration and bonding with the collagen matrix.

The use of Tara tannins has increased, in the last decades, and the leather production for automobile upholstery, is currently experiencing its highest demand.[3] However, there are no specific promotions for the use of Tara tannins as pre-tanning agent.

Additionally, this thesis is supplemented with some SEM photos (Scanning Electron Microscope), of the final leather articles to see the compacted fibers, and the penetration of the tannins through the leather structure.

This thesis is also supported with articles published in magazines specialized in the Leather sector. There are two articles published in the Journal of the American Leather Chemists Association (JALCA), named:

- *Low carbon products for the design of innovative leather processes. Part I: determination of the optimal chemical modification of tara. . (JALCA, Vol. 108, pag. 386-391, 2013)*

- *Low carbon products for the design of innovative leather processes. Part II: determination of the optimal physical modification of tara. (JALCA, Vol. 109, pag. 25-31, 2014)*

One article pending to be published in the Journal of AQEIC (Spanish Leather Chemists Association).

- Application of Sustainable tannins with Low carbon footprint

And presented in the 62nd Congress of AQEIC, Lorca (Murcia), May 10th and 11th, 2013

Presentation: 'Aplicación de taninos sostenibles con baja huella de carbono'
Author: Jorge Gerardo Díaz Muñoz.

Objectives

Although, the leather industry is subjected to social and political attacks due to the pollution that it can cause, not all of what is believed is true; this is the reason why the leather industry is in the constant search of decreasing its pollution rates.

We must take into account that, the tanning process, is not the only one contaminating the environment, but also those products used through out the whole tanning process, as discussed later in the life cycle analysis of a product.

A product such as Tara tannin, found in nature, which does not need to cut down and does not require undergoing chemical processes for its preparation, could replace products used in the tanning industry, whose use or manufacture is not considered environmentally friendly.

This thesis is focused in modifying the Tara tannin to increase its tanning power and reduce its astringency, and to attempt to reduce syntans and other kind of auxiliaries, enhancing the use of the modified natural product.

The aim of this thesis is the design of new pre-tanning formulations by using the fruit of the Tara tree (Cæsalpinia Spinosa) as a source of vegetable tannin, which is physically or chemically modified to promote sustainability in the manufacture of high quality leather articles.

In terms of innovative aspects, this thesis will use new tailored Tara products that are able to facilitate the penetration of the tannin molecules through the leather section, avoiding or reducing the use of aldehydes, syntans, common vegetable tannins and other mineral salts. The existing technologies promote the use of glutaraldehyde and syntans in wet-white leathers to guarantee a complete degree of penetration.

Another objective is reducing or replacing the use of pre-tanning agents like aldehydes and synthetic type, used in the production of wet-white leather, by using sustainable vegetable tannins. In addition, the new modified tannins may replace some of the commercial vegetable extracts used, which are linked to deforestation.

The evaluation of new designed products shall consist of their application on hides where physical-chemical parameters will determine the final quality of the leather, in addition to the pollution load of waste effluents.

There are some steps that support the research of innovative new Tara products, whose description and objectives are as follows:

- **First Step: Modifications of original Tara.**

New products based on physically and chemically modified Tara tannin, to enhance the penetration on the hide.

By increasing the degree of exhaustion of vegetable tanning in final floats, the presence of total dissolved solids and suspended solids is reduced, resulting in a reduction in COD values which decreases the environmental impact of vegetable tanning baths.

Modifications of Tara tannin are divided in two main ways.

1. - **Chemical modifications**: there are a few sources of commercial Tara tannin that have been modified by means of water extraction with temperature. The aim of the project will be to study which of the aqueous extraction process that require the application of temperature is the least aggressive. The degree of hydrolysis will be controlled by means of the acid Gallic content by HPLC. The expected results will consist on obtaining a liquid Tara extract using temperatures between the ranges of 20-130ºC. On the other hand, a series of sulphitation tests with Tara tannins will help to decrease their astringency and facilitate the penetration of the tannin molecules through the leather structure. In summary, the chemical modification was conducted in the following order:

- Aqueous extraction at different temperatures
- Chemical extraction using acid and alkali
- Chemical modification process by sulphitation
- Optimization of aqueous extraction
- Application in hides

2. - **Physical modifications:** the commercial Tara extracts has a particle size ranges of 75-125 microns. The aim is to separate the commercial Tara in different fractions by means of physic procedures. There's no other available solid Tara tannin whose particle size are smaller 75 microns. The aim is to determine, by means of a thorough characterization, which of the solid fractions is the most adequate to be used as a tanning product, based on its capability of penetration and final tannin yield. Finally, and most importantly, we will pursue to reduce the particle sizes as much as possible through milling, seeking to obtain the smallest particle size in order to achieve a better penetration through the leather structure.

With the aim of optimizing the best formulations, the new modified product shall be applied with the intention of finding the best wet-white pre-tanning process. The experimental part of this thesis is divided into the following steps:

Second Step: Use of New Tara tannin as pre-tanning agent.

1- **Combination of Modified Tara with different commercial products:** Vegetable tannins (quebracho, mimosa), dispersants, and synthetic tannins. An experimental design has been developed for the application of the Tara products on hides at pilot scale, in order to determine their tanning power, analyzing their degree of penetration and stabilization on the skin structure and the physical and organoleptic properties acquired.

The mixtures of the Tara tannin with other pre-tanning or re-tanning products, such as naphthalene sulphonic acid syntans, phenol syntans or commercial vegetable extracts will improve the penetration ability of the new designed products, protecting the leather of the current astringency caused by the acidic nature of the Tara tannin.

Reduce Tara tannin astringency and avoid the formation of large molecular aggregates as much as possible, to facilitate penetration of tannin molecules in the hides.

2- **Optimization of wet-white recipe using modified tara (pre-tanning):** The other technical focus consists on the design of new recipes for pre-tanning, by using the best combination of modified Tara with the best resultant product of section 1, which will improve the final results in leather. These new designs will be considered in the field of new wet-white formulations where new tailored Tara tannins will be applied on the pelt.

Pre-tanned leathers of this section have been re-tanned, to manufacture a type of final article: Automotive upholstery leather; with the aim of determining if it meet the standard values for chemical and physical assessments.

Avoid the formation of complexes of iron (III) that are present in the Tara itself, or during the machining processes of wet-white leather processed with Tara, through various complex agents, the presence of iron in these processes causes dark spots on the leather processed with Tara tannin.

Reduce or replace the use of synthetic products and some other products with low sustainability as much as possible.

An ultimate goal is to manufacture final leather articles, with the optimized pre-tanning recipe, that meet the standards and specifications set by different directives and agencies that regulate the use of leather. Also, carry on a comparative economic, quality and environmental assessment, between the regular processes and the new optimized ones, obtained in this thesis, with the modified tara.

Determine, through a life cycle assessment (LCA), environmental benefits and savings of the new process obtained in this thesis.

Chapter 1: Description

1.1 Tara: General description

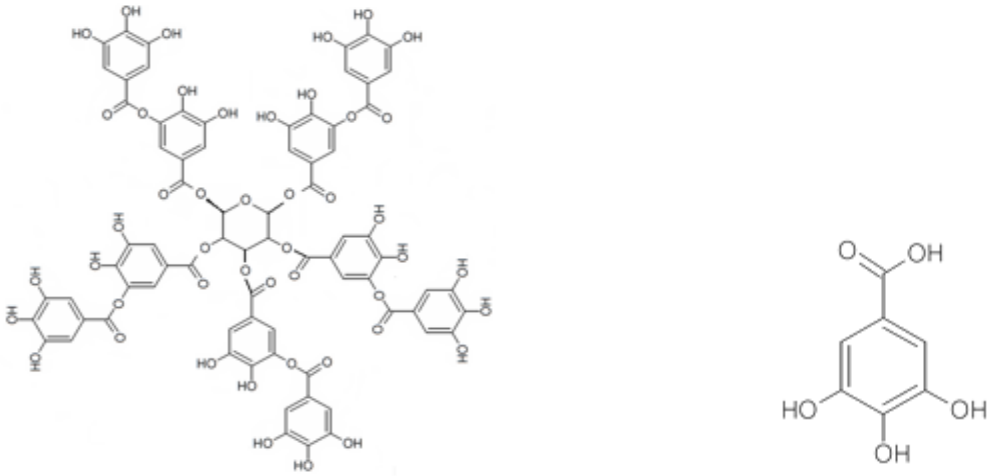
The Tara tannin powder comes from the fruit of the Tara tree, which can be obtained without the need to deforest entire areas, unlike many of the vegetable extracts used in the Tanning industry that come from wood. The latter proves that this raw material is a sustainable, environmentally friendly source; which does not mean that all vegetable tannins are not sustainable.

Cæsalpinia spinosa (Molina) Kuntze (known as Spiny holdback in Europe),[4] better known as Tara tree, is a small leguminous tree or thorny shrub, native from Peru.[5] This tree has survived in a dry environment by literally sucking water out of the air. Excess water, that Tara trees do not need, runs off the trees and replenishes groundwater that has been lost due to years of drought. It also provides a convenient source of fresh drinking water for locals.

Tara is cultivated as a source of tannins based on a galloylated quinic acid structure.[6]

To know about the chemistry of Tara tannins, it is important to say that it is a hydrolysable tannin formed by a core of sugar molecules such as glucose, coupled with phenol carboxylic acids, like gallic acid and its derivatives. The ester linkages are formed between the alcohol groups (-OH) of the sugar molecule and the carboxylic groups (-COOH) of the molecules of phenol-carboxylic acids. The number of ester linkages in a molecule of tannin depends on the sugar molecules present at the core of the tannin molecule.

In the image below, it can be seen the gallic acid (right) and its derivatives surrounding the core of sugar in the tannic acid (left).



Tannic Acid or Gallotannic

Gallic acid

Figure 1: Tannic Acid and Gallic acid

In turn, according to Horler and Nursten (1961), there are Quinic acid molecules with gallic acids binds replacing the-OH of its structure that coexist within the structure of Tara tannin, as shown in Figure 2; Giovando et. al,[7]have also said that this is the main structure of gallotannin, present in Tara tannins.

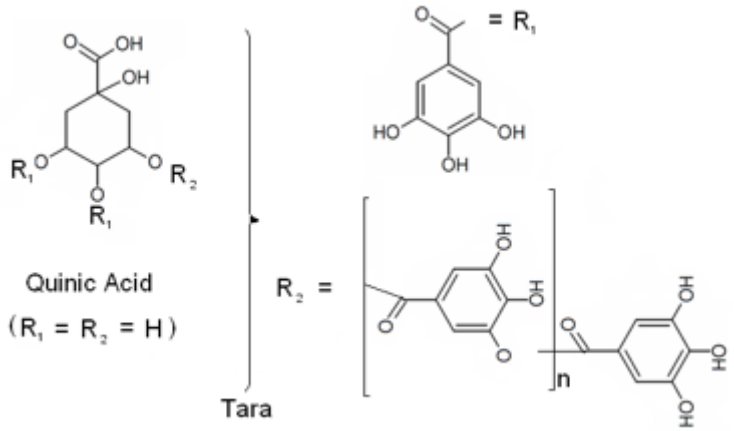


Figure 2: Galloylated quinic acid structure of Tara tannin.

Tara tannins are very astringent and react strongly when in contact with the skin, leaving the material surface unable to penetrate through the entire skin. As a result of these properties, this thesis is focused in chemically and physically modifications of the Tara tannin, to increase its tanning power, decrease its astringency, and to attempt to reduce the use of syntans and other kind of auxiliaries, thus increasing the use of natural products.

The modified Tara, is pretended to be used as a pre-tanning (wet-white) agent, combined with the minimum of auxiliaries.

Other studies have been performed regarding the use of Tara, but were rather focused on economic analysis and a general idea of their behaviour as pre-tanning.[8] However, there has never been a study seeking to improve their performance as tanning agent by modifying their nature.

Bibliography from studies examining the use of Tara combined with other inorganic salts (aluminum, chromium) or with organic products (glutaraldehyde, syntans, quaternary phosphonium salts) show the improvement of its tanning powder by means of penetration and the block of the reactive groups of collagen to facilitate the penetration to avoid an excess of tanning on the leather surface.[9,10,11] However, an industrial application has not been generated.

Ultrasound application in vegetable tanning processes could improve the diffusion rate and generate an appreciable reduction in the particle size,[12] but the overall results are not very

practical. As to the application of bacterial enzymes, which is also studied, the use of bacterial colagenasa as an auxiliary agent in tanning bath has increased tanning absorption and better diffusion into leather[13].

As it comes from the fruit of the tree, Tara is a sustainable source of tannins compared with some conventional commercialized vegetable extracts that come from wood that requires deforestation.

Besides its light fastness and light colors, tara tannins are much appreciated in the industry because the leather articles derived from it could be full, soft, with a firm and smooth grain. Tara is soluble in water and does not contain color substances, as it is the case with other vegetable tannins.

The general specifications for commercially available Tara powder for tanning applications are around of 48% of tannin content, a maximum of 13% of water content, and a pH (at 6.9ºBè) of 3 – 4.[14] Tara powder can be used to pre-tan and tan all kind of hides and skins and to re-tan chrome tanned leathers to improve grain tightening. Being the re-tanning process in the manufacture of leather for car seats its main application.

Every part of the Tara fruit can be commercialized, resulting in a more feasible supply chain. See annex 3 for photographs and a brief description of the tara as a botanic plant.

1.2 Sustainability

> As minimum, sustainability requires that everybody's basic needs be satisfied.
> (Mathis Wackernagel)

Over the last few decades the word sustainability and its definition have become stronger in almost all aspects of society.

It is said that while the nature and seriousness of the threat are not confirmed, there is a general awareness of deterioration in the planet's health[15], because, essentially, reputable scientific sources are in agreement that we are facing serious environmental problems.

The economic activities and that level of consumption cannot be sustained by the Earth's ecosystems, and it is necessary to establish some boundaries to ensure the integrity of the environmental and to reduce the pressure to which the ecosystem is submitted.[16]

In this context, because some companies cause many environmental impacts and even catastrophes, society has begun to demand that they accept their responsibility, but also society is aware and want a role in this issue.[17]

With all the changes that have occurred on the planet, it is clear that we have to take actions in order to have a more sustainable environment. But what is sustainability?

According to the EPA (United States Environmental Protection Agency)[18], Sustainability is based on a simple principle: Everything that we need for our survival and well-being depends, either directly or indirectly, on our natural environment.

Sustainability is responsible to maintain and create a balance between nature and man to ensure a stable and durable relationship, which permits fulfilling the social, economic and other relevant requirements of present and future generations.

It is therefore important to ensure that we will have enough water, materials, and resources to preserve our environment for future generations.

M. Wackernagel said that sustainability requires living within the productive capacity of nature. Therefore, we need to know how to identify and measure nature's productivity.[19]

In summary, nature has to be able to grow back what men take from it. After examining the characteristics of the Tara tree, we can say that the use of this tree is completely sustainable, since the tanning would be extracted from the fruits, which are regenerated each year; on top of that, it shall be noted that a Tara tree has a life span of approximately 80 years.

Unlike the cases of the more widely used vegetable extract tannins, which are obtained from wood or bark; where no effective chain-wide renovation or reforestation is successfully achieved in every case.

Behinds these definitions of sustainability are the people who realize that change in the way we produce and consume needs to be undertaken, i.e. the way of thinking has changed and we are more aware of the need of our consumption habits to me more friendly to the environment in order for these be regenerated in the shortest time possible.

This is why; many of the current researches are mainly focused on the search processes of sustainable, high-quality raw materials and end items that meet the needs of consumers.

1.3 Carbon Footprint

The term “low carbon footprint” is used to qualify the tanning used in this study. It is important to first clarify the definition of what the carbon footprint is, and then to determine why the Tara tanning is a low carbon footprint material.

Being the climate change a popular subject among the public, political, and corporate claim, the use of the term ‘Carbon footprint’ has become a widely used concept in the public debate.

Despite being a widely used term, there is not a concrete definition of it, and there are disputes regarding the measurement units that should be used. However, the common baseline is that the carbon footprint refers to a certain amount of gaseous emissions, which are responsible for climate change and associated to the production or consumption activities of humans. From this point on, there are some disagreements.

It is important to establish a difference between the terms ecological footprint, human footprint and carbon footprint; ecological footprint refers to the impact made to the environment by every process or consumption undertaken by both humans and animals; whereas, human footprint refers to the impact made to the environment by the human beings. However, in the context of this thesis, Carbon footprint refers to the Carbon gasses emitted into the atmosphere by any process undertaken.

The wide range of definitions goes from direct CO_2 emissions to full life-cycle greenhouse gas emissions and not even the units of measurement are clear. Thomas Wiedmann and Jan Minx collected a series of Definitions of 'carbon footprint' from the literature. [20] As shown in the following table.

Source	Definition
BP (British Petroleum) (2007)	"The carbon footprint is the amount of carbon dioxide emitted due to your daily activities – from washing a load of laundry to driving a carload of kids to school."
British Sky Broadcasting (Sky) (Patel 2006)	The carbon footprint was calculated by "measuring the CO2 equivalent emissions from its premises, company-owned vehicles, business travel and waste to landfill." (Patel2006)
Carbon Trust (2007)	"… a methodology to estimate the total emission of greenhouse gases (GHG) in carbon equivalents from a product across its life cycle from the production of raw material used in its manufacture, to disposal of the finished product (excluding in-use emissions). "… a technique for identifying and measuring the individual greenhouse gas emissions from each activity within a supply chain process step and the framework for attributing these to each output product (we [The Carbon Trust] will refer to this as the product's 'carbon footprint')." (Carbon Trust 2007, p.4)
Energetics (2007)	"… the full extent of direct and indirect CO2 emissions caused by your business activities."
ETAP (2007)	"…the 'Carbon Footprint' is a measure of the impact human activities have on the environment in terms of the amount of greenhouse gases produced, measured in tonnes of carbon dioxide."
Global Footprint Network (2007)	"The demand on bio-capacity required to sequester (through photosynthesis) the carbon dioxide (CO2) emissions from fossil fuel combustion." (GFN 2007; see also text)
Grub & Ellis (2007)	"A carbon footprint is a measure of the amount of carbon dioxide emitted through the combustion of fossil fuels. In the case of a business organization, it is the amount of CO2 emitted either directly or indirectly as a result of its everyday operations. It also might reflect the fossil energy represented in a product or commodity reaching market."
Paliamentary Office of Science and Technology (POST 2006)	"A 'carbon footprint' is the total amount of CO2 and other greenhouse gases, emitted over the full life cycle of a process or product. It is expressed as grams of CO2 equivalent per kilowatt hour of generation (gCO2eq/kWh), which accounts for the different global warming effects of other greenhouse gases."

Table 1: Definitions of 'Carbon footprint' from literature[21] [22]

Thomas Wiedmann and Jan Minx (2008) proposed one of the most acceptable definitions of "carbon footprint":[20]

"The carbon footprint is a measure of the exclusive total amount of carbon dioxide emissions that is directly and indirectly caused by an activity or is accumulated over the life stages of a product."

They refer to every activity made by persons, group of people, companies, organizations, processes, and industry sectors etc. Products include goods and services. In any case, all direct (on-site, internal) and indirect emissions (off-site, external, embodied, upstream, and downstream) need to be taken into account.

But what if a product derives from the deforestation of thousands of trees, or if a thermo-chemical process is needed, and certain chemicals is added to reach the final product. There are certain things that these definitions of carbon footprint do not include.

For this thesis, it is important to know that we have to take into account the manufacturing process of Tara, from its collection, grinding, and transportation, to its final disposal.

At the end, a life cycle assessment will be conducted, to determine the emission of Carbon footprint when using the Tara tannin as opposed to the other products intended to be replaced.

1.4 Life Cycle Assessment (LCA)

In the past few decades, it has become necessary to tangibly determine how much waste does a product truly generates, from the moment it is being produced, to the moment the product itself becomes a waste.

There are a several techniques to measure the ecological impact of a product; being the life cycle assessment (LCA) is one of the most widely used. LCA tests the product from its initial stage (cradle stage) to its final stage (grave stage), also named ´from cradle to grave´, covering its entire life cycle, and also evaluating the product in terms of the environmental impact during its lifetime.[23]

In fact, LCA and Product Carbon footprint (PCF) go hand in hand; that is, in order to calculate the carbon emissions of a product, an analysis of a product life cycle is conducted. The result obtained from the LCA of a product indicates the total amount of Greenhouse Gases (GHG) produced by a product or process of any kind.

Nowadays, climate change is one of the most popular topics in society, and this has generated interest in estimating the total amount of GHG produced during the different stages of the life cycle of goods and services; i.e. their production, process, transportation, sale, use and disposal.[24] But, this also stimulates the studies on how to reduce said GHG gases.

For the tanning process, knowing where the carbon footprint measuring limits has become rather confusing, this is because there is not a universal measure or parameter set, as there are some analysis that commence from the slaughterhouse, whereas others start from the food production chain.

Based on the premise that the manufacturing of all leather products has an impact on the planet; therefore, before any endeavor to reduce it begins; it is crucial that we quantify such impact.

A study made by Brugnoli and Brondi[24], shows the results of different articles, reporting the boundary selection of different LCA on leather production and leather products. (Fig. 3).

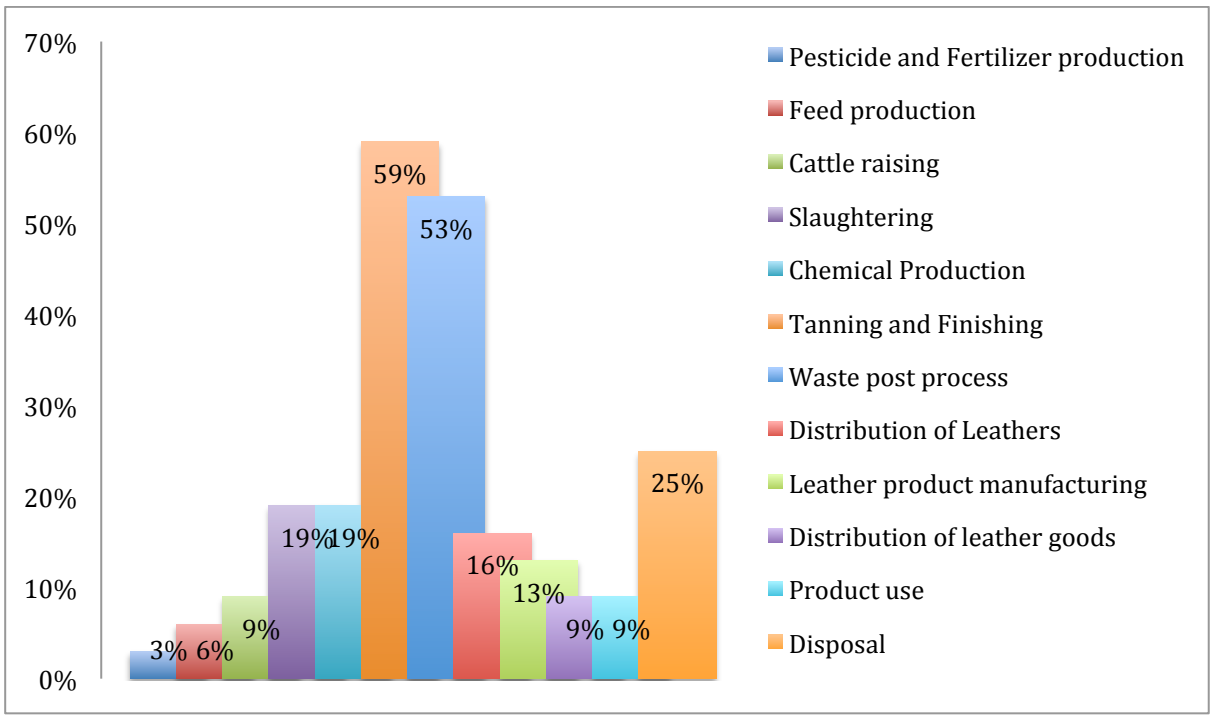


Figure 3: Literature percentage according to the examined phases of leather Life Cycle.[24]

First studies seem particularly focused only on the tanning process only, while the recent ones have been shifting the subject of the study on other life cycle phases like leather final disposal and auxiliary materials production.

Many of the life-cycle analysis conducted, are usually hard to understand and lack accuracy, which leads to a lack of understanding by employers or final customers.

It is necessary to establish for the evaluation of LCA in the leather industry, this could be done by analysing each step separately, and bringing them together; this way, the analysis of a stage could be used for a different industry. For example, the LCA and Carbon footprint for Cattle rising could either serve for tanning industry or for the meat or dairy industry.

1.5 Leather Industry and the environment

One of the implicit goals of this thesis is to use products that do not pose a threat neither to the environment nor to human health in any form, whether components used directly in the tanning industry or lack management of waste from the tanning.

The use of wood from trees in not looked as environmentally sustainable, because in most cases the tree's speed of grow this too low to even consider it as an appropriate source. For example, quebracho grows slowly and it takes100 years for it to grow to maturity, it takes40 years for the chestnut to do so, and approximately 10 years for the mimosa.[25] Avoiding the cutting down of some tree species, has a positive environmental impact, and makes the final product more sustainable.

However, this work does not aim to completely eliminate the use of those products that may pose a threat to the environment; however, it is expected to replace or reduce the use of some products that can be considered as contaminants in wastewater, or whose manufacture requires a non-friendly or unsustainable environment.

The leather industry is a well known as a high water consumer (30 to 80 m3 for I ton of processed raw hides).[26] At the same time, this industry is known for producing wastewater. The main analyses of wastewater generated from tanneries, are: high salinity, high organic loading (COD, BOD_5), high content of ammonia and organic nitrogen, colorant content, as well as the presence of specific pollutants (sulphide, chromium).

As mentioned above, nowadays approximately 85-90% of hides are tanned with chrome. Tannery effluents containing chromium (III) salts have to be treated to reduce the chromium concentration in the final effluent to reduce the value specified in the permitted discharge conditions.[26] The toxicity of chromium is perhaps the most debated topic among the tanning industry and the authorities.

For hides tanned with other products, the demand is expected to increase, including vegetable and synthetic tanning, etc. Even the upholstery leather for cars, whose recycling requirements are very important, has increasingly been using chrome-free leather. [27]

It is important to notice that the Tara products are not subject to review by REACH, and the exemption from such registration is due to the following definition:

"Substances occurring in nature, if they are not chemically modified, unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC". [28]

REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the **R**egistration, **E**valuation, **A**uthorization and Restriction of **Ch**emical substances. This law entered into force on 1 June 2007.[29]

REACH was created to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance the innovation and competitiveness of the EU chemicals industry. The benefits of the REACH system will come gradually, as more and more substances are phased into REACH.

Manufacturers and importers are required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database controlled by the European Chemicals Agency (ECHA) in Helsinki.

REACH has to regularize a large number of substances that have been manufactured and placed in the European market for many years, sometimes in very large amounts, and there is insufficient information on the risks that they pose to human health and the environment.

Not being a threat to human health or the environment and being a natural product, the Tara could be a better choice to be used in the tanning industry.

Additionally, there is a directive that tries to settle the final disposes of vehicles, including the leather on their seats. The Directive on End-of Life Vehicle (ELV) 2000/53/EC, is the first EU waste directive with which the EU Commission has introduced the concept of Extended Producer Responsibility. The directive aims at the reduction of waste arising from end-of-life vehicles.[30]

The directive covers the aspects of the whole life cycle of a vehicle, as well as aspects related to treatment operations. Such as:

- Preventing the use of certain heavy metals such as cadmium, lead, mercury and hexavalent chromium,
- Collection of vehicles at suitable treatment facilities,
- De-pollution of fluids and specific components,
- Coding and/or information on parts and components
- Ensuring information for consumers and treatment organizations
- Achieving reuse, recycling and recovery performance targets

The directive involves four major stakeholders, the producer, the recycling industry, the last holder and the authorities. Each has a responsibility within their own possibility.

In order to measure the actual performance of the countries, targets were defined with the ELV Directive. The EU Member States and EFTA (European Free Trade Association) countries are obliged to ensure that economic operators (i.e. authorities, treatment operators and producers) meet the following minimum targets as part of their shared responsibility:

	As of Jan 1, 2006	As of Jan 1, 2015
Reuse & Recycling	80%	85%
Reuse & Recovery	85%	95%

Table 2: Percentages pretended to be achieved in 2015 by REACH.

It is intended that these percentages are achieved, within the deadlines set, so the tanning industry has to be aware that it need to use other products in the tanning process, so the final use of automotive leather could be reused, recycled or simply not pose a threat to the environment.

The chart in annex 2, includes a description of the inputs and outputs that are needed for the tannin process.

1.6 Global market and possibilities of Tara (Supply and Demand)

Today, there is a great interest and demand of more sustainable products, like those that come from the Tara tree; this is the reason for the growing international demand for Tara.

The modified Tara obtained from this thesis is targeted to the pre-tanning and tanning processes of products such as automobile upholstery, footwear and leather goods.

It is also known that there are other products available that can be used as alternative for the Tara, like vegetable extracts or other species from natural organic synthesis. However, this thesis aims at developing new ways to improve the current Tara product, and to enhance its quality via some chemical or physical modifications.

This could be an opportunity to replace or minimize the use of the before mentioned chemical products, which have a high carbon footprint and are less sustainable, and slowly improve the image that people have of the leather industry.

As in any process and product to be marketed, it is important to consider the supply and demand it generates, as well as the price of the product.

Much has been talked about the growing demand for Tara products, due to the multiple benefits already mentioned above; however, in this regard, the increases in exports and sales are the ones that speak for themselves.

According to industry sources, currently the supply of Tara does not meet demand. This is reflected in the price raise of the Tara powder, which depends on the seasons.[31]

Peru is the world's largest producer of Tara, in 2008 it reported a currency income of approximately $42 million from the export of Tara powder. It likewise indicates that the

global unmet demand is 35.6%; this demand shall be increased by 21.2%. It is expected that this offer is based on the exploitation of forest plantations and natural or wild so there must be a technical management.[32]

In a Recent article about the Tara exports in Peru, published in November 2012[33],it is stated that the Tara gum exportations have increased by181%. Also, Tara powder increased its shipments by 11%, being Germany and China the main destination of these products.

Between January and October of 2012, exports of Tara gum were worth $ 18.9 million, which represents a growth of 181% in the monthly average (U.S. $ 1.8 million) with respect to last year (U.S. $ 676.432).

Meanwhile, the export of tara powder grew 11% in the same period, up from U.S. $ 25 million, at an average price downward by 4% (USD $ 1.76 per kilo), regarding the previous year.

According the website Agrodataperu,[34] the next table shows the Tara exportation from Peru, comparing 2011 and 2012, with their FOB, kilograms and average price month by month; there was a 13% increase in exports by 2012; and sales for USD $30.8 million, with an average price going down to US $ 1.75 /kilo.

TARA EXPORT						
Month	2012			2011		
	FOB	Kilograms	Average Price	FOB	Kilograms	Average Price
January	1,881,619	1,051,720	1.79	1,472,824	1,065,020	1.38
February	1,525,980	833,000	1.83	1,166,384	791,000	1.47
March	1,335,599	766,715	1.74	1,104,356	696,960	1.58
April	2,145,309	1,230,654	1.74	1,044,391	565,500	1.85
May	2,421,130	1,381,880	1.75	1,639,520	900,587	1.82
June	2,968,270	1,664,300	1.78	2,028,358	1,054,400	1.92
July	2,506,757	1,375,945	1.82	3,185,263	1,603,200	1.99
August	3,515,719	1,966,425	1.79	3,735,337	1,857,380	2.01
September	3,839,889	2,245,000	1.71	3,777,283	1,947,400	1.94
October	3,310,260	1,959,075	1.69	2,758,501	1,462,700	1.89
November	3,167,669	1,816,550	1.74	3,645,522	1,976,781	1.84
December	2,188,250	1,263,200	1.73	1,606,870	888,938	1.81
TOTALS	30,806,452	17,554,464	1.75	27,165,620	14,809,866	1.83
Month average	2,567,204	1,462,872		2,263,802	1,234,155	
% Average Grow	13%	19%	-4%	0%	-32%	47%

Table 3: Comparison between 2012 and 2011 for total exportation of Tara from Peru (Source: AgrodataPeru.com).[34]

As can be seen there is a great market, with an increasing demand, with great opportunity to increase the production and to get into the market with a new modified product that offers more quality and diversity.

Exports to China are worth USD $ 7.5 million (24% of total), followed by Brazil USD $ 6.3 million (20%) and Italy USD $ 4.0 million (13%), plus30 other countries.

Figure 4: Main countries that import Tara from Peru (Source: AgrodataPeru.com)[34]

As we have already mentioned, the possibility of using the new modified product derived from Tara as a substitute for more products currently used in the tanning industry, or the reduction of them. Therefore it is important to mention the amount of skin that is processed in the world and therefore the potential for the use of this product.

Although we have already mentioned that the current supplies do not meet the demand, it is important to emphasize the possibility of a greater exploitation of this sustainable product.

The next table shows the raw hides and skins processed, and the footwear production around the world.[35]

	RAW HIDES AND SKINS				LEATHER						FOOTWEAR WITH LEATHER UPPERS[3/]		
	Livestock Population	Production	Net Trade[1/]	Apparent Availability[2/]	Production		Net Trade[1/]		Apparent Availability		Production	Net Trade[1/]	Apparent Availability
					Heavy	Light	Heavy	Light	Heavy	Light			
	million head	(..... thousand tonnes .....)			thousand tonnes	million sq.ft.	thousand tonnes	million sq. ft.	thousand tonnes	million sq. ft.	million pairs		
BOVINE HIDES AND SKINS													
World	**1 616.6**	**6 428.0**	**- 228.1**	**6 656.1**	**551.0**	**14 137.6**	**+ 3.2**	**+ 1 176.7**	**547.8**	**12 960.9**	**4 478.3**	**- 151.8**	**4 630.1**
Developing Countries	1 305.3	3 950.7	- 1 232.6	5 183.2	405.2	9 103.1	+ 16.8	+ 333.2	388.4	8 770.0	3 494.0	+ 1 083.6	2 410.4
Developed Countries	311.3	2 477.1	+ 1 004.5	1 472.6	145.8	5 034.5	- 13.6	+ 843.5	159.4	4 190.9	984.3	- 1 235.4	2 219.7
SHEEPSKINS*													
World	**1 083.5**	**400.2**	**- 22.1**	**422.3**		**5 276.0**		**- 52.2**		**5 328.2**	-	-	-
Developing Countries	762.5	216.6	- 114.1	330.7		4 152.5		+ 270.8		3 881.7	-	-	-
Developed Countries	321.0	183.6	+ 92.1	91.6		1 123.5		- 323.0		1 446.5	-	-	-

[1/] Theoretically, net trade at the global level should be close to zero, but in practice due to shipping time and reporting discrepancies the difference can be significant.
[2/] Wet salted for bovine, dry without wool for sheep and dry for goat
[3/] While there is a certain quantity of leather from sheep and goat going into footwear, leather shoes balances have only been shown against the bovine part of the table for reasons of simplicity and lack of data.
Apparent Availability = Production + Imports - Exports.
Net Trade = Exports - Imports
* Data on goatskins are not shown (see Foreword).

Table 4: Raw hides, leather and footwear production around the world[35]

The chart above shows the average production, trade, and apparent availability balance at all levels of processing during 2008-2010 of raw hides and skins, leather, and leather footwear.

As can be seen in this chart, there is a large production of leather around the world, and, as it has been previously stated around 80-85% of the world's leather production is done with chromium. Nevertheless, this thesis is focused in trying to substitute or reduce the use of these mineral salts, so here is a market with a great potential to exploit.

Chapter 2: Theoretic fundamentals

2.1 The Tanning process

2.1.1The collagen stabilization

The skin is an organ that protects animals from the environment, acting as a barrier from external factors, including the weather, and helping to maintain the proper temperature of the body.[36]

Skin is divided in three layers: the epidermis, dermis, and subcutaneous tissue. The epidermis is the outer layer of skin and is composed of 5 layers were the outer of which is named 'stratum corneum'. The intermediate layer, the dermis or *corium*, is the most valuable for the tanners; mostly a protein called collagen constitutes it. The subcutaneous tissue is a layer of fat and connective tissue that houses larger blood vessels and nerves.[36]

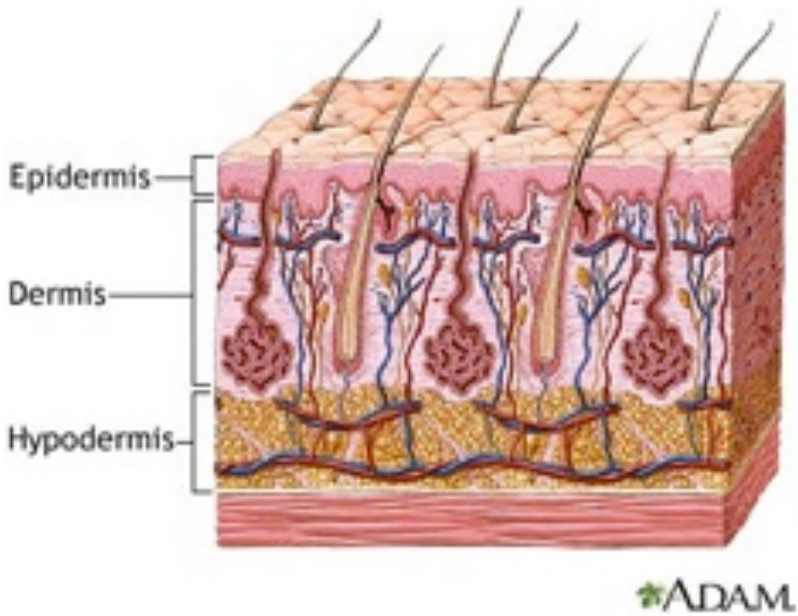


Figure 5: Diagram of Skin Layers (Picture taken from adam.about.net)[37]

The first step in the tanning process, is called 'beamhouse' operations, and consists of removing the two outer layers (epidermis and subcutaneous tissue) among other proteins from the intermediate layer (corium). This is done in order to purify, as much as possible, the structure of the collagen.

The process of tanning is focused on maintaining the skin's natural properties, to stabilise its structure (collagen) and at the same time to chemically process it, so it will no longer be subject to putrefaction.

Essentially, the process consists of the transformation of raw animal hides and skins, and residues of the food industry into leather, a stable material, which can be used in the manufacture of a wide range of products.

The whole process involves a sequence of complex chemical reactions and mechanical processes. Amongst which, tanning is the fundamental stage, as it gives leather its stability and essential character.[38] That is why we will not describe the other stages of the overall process, and we will only focus on the tanning process itself (Stabilization of collagen). In annex 1, there is a brief description of all tannin process, from raw material until final leather article.

Leather has a great stability to water, bacteria, heat and abrasion and consequently, it has a wide range of domestic and industrial applications.[39] These include shoes, clothing, leather goods, furniture, upholstery for cars, and many other items. All these different applications require different types of leather and different tanning methods or tanning agents.

The main tanning agents are within the following groups.

- Mineral tannages
- Vegetable tannins
- Syntans
- Aldehydes
- Oil tannage.

Preserving hides and skins (hides- for larger animals; skins- for smaller animals) by tanning and performing various steps of preparation and finishing, generates a final product with specific properties: stability, appearance, water resistance, temperature resistance, elasticity and permeability for perspiration and air, etc.

Collagen is the most abundant structural protein in vertebrates.[40] Type I collagen, the main one in skins and hides, is a sclero-protein consisting of aminoacids linked by –CO-NH- groups to form peptide chains.[41]

The Type I collagen molecule is distinguished by its unusually high content of glycine, proline and hydroxyproline which together account for over 50% of the amino acid content of the protein.

Table 5 shows all amino acids included in type I collagen. This composition is crucial to the structure and reactivity.

Amino acids	Content in %	Number per molecule
Glycine	33.53	1056
Proline	11.97	377
Hydroxyproline	11.18	352
Aspargine	1.19	37
Aspartic acid	3.07	97
Glutamine	2.57	81
Glutamic acid	4.75	150
Lysine	3.17	100
Hydroxilysine	0.40	13
Arginine	5.04	159
Histidine	0.20	6
Serine	3.46	109
Trypophane	0.20	6
-CO-NH-		3147

Table 5: Collagen Type 1: content of amino acids. (Source: Dr. G. Reich) [41]

Collagen is composed by three chains of polypeptides in an α-helix form, as protofibrils and each one contain approximately 1.000 aminoacids, every third amino acid is glycine (GLY). The other two amino acids (X and Y) in the triplets consist of about 10% proline, 10% hydroxyproline, 10% alanine and the rest a distribution of the other naturally occurring amino acids.[42]

A collagen fibril is the union of 7.000 – 8.000 protofibrils and they come together to form fibers of about 5 µm of diameter (Figure 6)[43]. The content of acidic and basic amino acids, aminoacids containing OH groups and peptide groups is important and decisive for the reactivity of the collagen, which is a requirement for its transformation into leather.

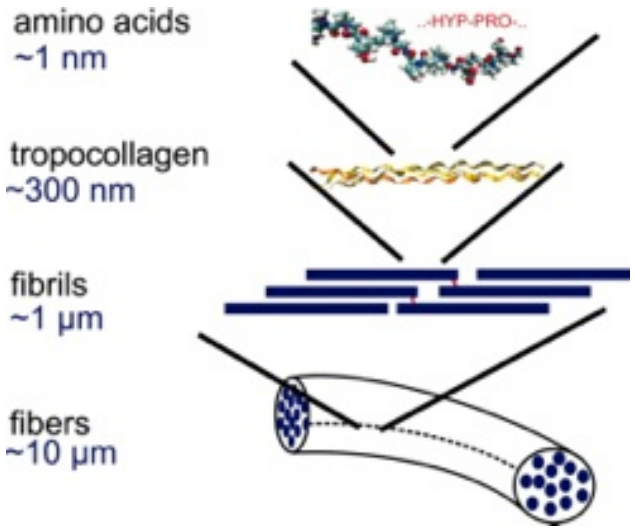


Figure 6: Diagram of collagen structure (Picture taken from www.sciencedaily.com)

To explain the chemistry of the basis of the tanning processes, we must know that all the reaction coordination and links with the tanning products are produced in the surface of the collagen molecules formed by fibrils, by means, between the chemicals agents and the lateral chains of aminoacids of collagen[44].

The basic chromium sulphate (Cr(OH)SO4) salts are, by far, the most used in the tanning process worldwide. The second most commonly used tanning agent, are the Vegetable tannins, natural products of relatively high molecular weight, which have the ability to strongly complex with carbohydrates and proteins. The most common vegetable extracts come from mimosa, quebracho and chestnut.

It is important to know, that each tanning agent or tanning process causes different reaction within the collagen structure. The following table summarizes the types of tanning or tanning agent types and bond types that occur within skin.

Functionality	**Bond type**	**Typical tanning agents**
Carboxyl groups	Complex bonding	Metallic salts, in particular basic chromium (III) sulphates
Basic groups	Covalent bonding	Aldehydes, diisocyanates, etc.
Peptide groups	Hydrogen bonds	Phenolic natural and synthetic tanning agents
Surface overall	Hydrophobic, "Van der Walls" bonds	Including polymers, tensides
Pores/capillarites	Fillers	Various substances

Table 6: Potential reactions on collagen during leather making[45]

To allow a bond between tanning agents and collagen in the pre-tanning process, it is necessary to remove the bond between the carboxyl and the amino groups, to allow the possibility for chemical tannins or another tannin agent to bond with these groups. Otherwise if not combined with any product, and should amino-carboxyl bonds remain, when the skin dries it becomes hard and translucent.

To use a tannin, we should know that it has more than one chemical function, this means that it has the ability to react with more than one collagen molecule simultaneously (reactivity), in order to ensure a cross-linking (tanning process).

There are two important features to consider when using the tannins, one being its molecular size, because as we previously mentioned, the tannins are materials of very high molecular weight, and this can hinder their penetration in the microstructure of collagen.

The second of these features is the solubility in water, since the tanning process is made in aqueous baths.

There have been talks about bonds and the reactivity of tannins with the collagen structure of the skin; however, this can be counterproductive because if the tannins have too much affinity with the skin, the contact will create an immediate reaction and tannins will remain on the skin surface, producing an over-tanning and preventing penetration. That is why the spread of tannins in the skin structure is important in the tanning process.

Another fact that constrains the diffusion of the substances in the leather is the formation of aggregates. All tanning agents with an affinity for collagen and whose ability to form hydrogen bonds tend to form aggregates of larger particles due to such dipolar or "secondary valence" character, which increases their particle size and reduce the penetration.

This is one of the main issues of this thesis, because Tara tannin by itself is very astringent and has a big molecular size, which prevents it from penetrating into the leather structure properly; this issue is expected be reduced with the chemical or physical modifications.

Hydrothermal Stability

As can be seen in table 5, hydroxyproline and proline are two of the main components of the collagen structure, the role of hydroxyproline is to stabilise the fibrils via interstrand hydrogen bonding interactions rather than intra-fibril stabilisation. In the collagen Xxx-Yxx-Gly triad (where Xxx and Yxx are any amino acid), a proline occupying the Yxx position is hydroxylated to give a Xxx-Hyp-Gly sequence. This modification of the proline residue increases the stability of the collagen triple helix.[46]

Breaking the hydrogen bonds in the triple helix may degrade the collagen structure; this is achieved if the wet collagen is subjected to high temperatures, causing the gelatinization. The temperature at which this collagen degradation occurs is known as "Shrinkage Temperature" (Ts), which can be modified depending on the tanning process or tanning agent type.

The effects of some of these chemical modifications (tanning processes) can be summarized in the next table, where the denaturation temperature is typically measured by the perceptible onset of shrinking:[47]

Chemical tanning	Denaturation temperature or Shrinkage temperature (Ts) ºC
None	60
Metal salts: Al(III), Ti(IV), Zr(IV)	70-85
Plant polyphenol gallotannin or ellagitannin	**75-80**
Plant polyphenols: flavonoid	80-85
Synthetic tanning agent: polymerized phenols	75-85
Aldehyde: formaldehyde or glutaraldehide	80-85
Aldehyde: phosphonium salt or oxazolidine	80-85
Basic chromium (III) sulphate	105-115
Combination: gallotannin + Al(III)	105-115
Combination: flavonoid polyphenols + oxazolidine	105-115

Table 7: Effects of chemical modifications on Shrinking Temperature.[47]

It could be said that, since a high shrinkage temperature results in greater stability of collagen, therefore, this latter would be less susceptible to denaturalization; however, obtaining the highest temperature is not the most important, as it will depend on the final article desired and the final manufacturing process to be undergone.

Once the tanning process is done, the leather is wet, and the shaving process is required to be done by machine, the shrinkage temperature must be taken into consideration, as the shaving process can raise the temperature on leather by friction and cause shrinkage. For practical purposes it is considered that a68-70 ° C temperature is enough to conduct the shaving process on pre-tanned leather.

Some studies mention the fact that in the collagen chemically treated and untreated, the hydrothermal stability is directly dependent on moisture, ie. reducing the water content causes the fibers to approach more closely, preventing them from collapsing into the interstices and this effect is correlated with elevated denaturation temperature.[48]

Therefore, a reduced ability to shrink is the same as increased hydrothermal stability. Consequently, chemical modification may reduce the ability of collagen to shrink, which results in higher observed denaturation temperature (Ts).[47]

2.1.2 Vegetable Tanning process

Vegetable tannins are products derived from plants. The plants have a particular ability to synthesize aromatic compounds. In the next section (2.2), there is a more extensive description of tannins and their composition.

During the preparation of the skin, carboxylic acids on the proline and hydroxyproline side chains of the collagen molecules become deprotonated, creating carboxylates. The resulting carboxylates bind with the phenol groups on any number of tannic acids. This tanning process creates a strong skin that is resistant to decay.[49]

In essence the process of vegetable tanning is pretty much the same as the one described before, because they can react with more than one side chain of collagen, resulting in their stabilization.

There are several types of vegetable tanning systems, and the characteristics of the leathers produced with these systems are not comparable to chrome tanned leathers, e.g. resistance to high temperature and flexibility. Instead some of the qualities of vegetable tanned leathers, e.g. natural color, toughness, stiffness can only be found in this type of leather.[50]

In a nutshell, the vegetable tanning process occurs as follows:

- The pre-tanning process (with syntans) starts with delimed skins (bated or not) to help the penetration of tannins.
- The tanning itself, where penetration is achieved and the reaction of tannins in the whole structure of the skin occur.
- A fixing stage follows, where tannings are intended to be less leachable with water.
- Finally, a finishing step takes places, which includes dying, re-tanning, or bleaching and greasing (on a greater or lesser degree).

2.1.3 Pre-tanning, tanning and re-tanning

It could be an attempt to use the new modified Tara in three different stages: pre-tanning, tanning and re-tanning. It doesn´t mean that they have to be used for the same final leather.

All testings have been done with the aim to increase the use of natural sustainable products, in this case the Tara, and to reduce the use of synthetic products as much as possible, such as metallic salts or no sustainable products that represents a threat to environment or human health.

During the pre-tanning process, the Tara is intended to be used to stabilize the collagen for it to be able to be mechanized without any kind of problem, like shaving. This stage is known as wet-white, better described in 2.1.4. These processes has been optimized with an experimental design, in chapter 4 section 2, with the aim of obtaining the best possible combination with an auxiliary product and improve the penetration.

The tanning process is referred to a vegetable tanning, where the objective is to pre-tan the skins with a combination of syntans, and then make a standard vegetable tanning combining vegetable extracts: such as Tara, Mimosa, Quebracho, chestnut, etc.

In re-tanning process the tara tannin is commonly used to re-tan most of the Automotive leather, both chrome tanned leathers or wet-white leathers (tanned with glutaraldehyde).

In general vegetable re-tannins plays a significant role in avoiding chromate formation. Besides mimosa and quebracho, chestnut and tara also showed a positive influence even when the leathers were exposed to extreme conditions like heat and UV radiation. Tara is particularly effective; on some leathers, an offer below 1% was sufficient to suppress chromate formation.[51]

2.1.4 Wet white

Today the term "wet white" (WW) is commonly referred to a pre-tanned either tanned with aldehydes, or glutaraldehyde and oxazolidine (which are more commonly used); however, WW could generally refer to leather that does not use chromium in tanning or "chrome-free". In this case, it is intended to reduce the load of aldehydes; therefore, a vegetable tanning (modified Tara) is used as an agent for wet white pre-tannins, and syntan auxiliary.

Other WW systems use metals, syntans or vegetable tannins (molecules obtained by organic synthesis with specific properties similar to the vegetable tannins).

However, calling it "wet-white" is not very accurate, since some aldehydes or synthetic pre-tanning leather are not white; and rather tend to be yellowish.

This fairly new method of tanning has been gaining popularity, partially due to the increased concern for water treatment systems and the environment.

Wet Blue (WB) consists of a tanning process where chrome is used to process the leather from rawhide to finished leathers. This process causes the semi-finished leather to look blue-tinted.

The leather trimmings from wet white tanned leather in the form of shavings can be recycled or used as a fertilizer, in contrast to wet blue tanning methods.

The WW is a pre-tanned material with the following properties:

1. A suitable temperature that allows for shrinkage and lowered divided.
2. The leather trimmings are free of chromium, metal salts and phenol.
3. It has a high degree of flexibility with respect to subsequent tanning method.

4. Pre-tanning material, due to the relatively low level of tanning is then subject to re-tanning process, giving the opportunity to change the vegetable character and make it appear more synthetic or flexible.

2.1.5 Light fastness and some quality assessments

It is said that the Tara tannin is used in leather industry because it has a good light fastness and light color, and it is well known that the individual color properties of vegetable tannins, as well as the colors they confer to resultant leathers have great importance when natural colored leather manufacture is taken in consideration. Additionally, these types of leathers should preserve their colors without change during their usage time in manufactured products.

It is well known that hydrolysable tannins are more stable to light than condensed tannins. Therefore it is essential to be aware of their light fastness behaviour.

Leathers tanned with mimosa, shows less color change than the other condensed tannins for about 6 hours. However, after 6 hours, the color of the leather increasingly changes and attains values similar to the other condensed tannins after 24 hours. [52] It is thought that this behaviour is related to the chemical structure of the mimosa tannin. Pasch et al, [53] have shown that mimosa is composed of prorobinetinidins while quebracho is composed of profisetinidins; Mimosa is heavily branched while quebracho is almost completely linear, which make it more easily hydrolysable; mimosa is completely stable to hydrolysis because of its inter-flavonoid link.

Considering that the hydrolysable tannins, chestnut and valonea, show similar behaviour against light color changing due to the fact that they have a very similar chemical structure; the leather tanned with Tara shows less color change than the other hydrolysable tannins in the first 8 hours. However, the color change then begins to increase and attains values similar to the other hydrolysable tannins after 16 hours. After 24 hours, no significant color difference is observed among the leathers tanned with hydrolysable tannins[54].

The light fastness determination method, used in this thesis, is obtained from regulations: EN ISO 105-B02 / IUF 402 / VESLIC C 4020. This regulation determines the resistance to color of leather to the action of a standard artificial light source.

The method say that he side to be tested of the leather sample is exposed to light from a Xenon Lamp, under controlled conditions, along with eight blue dyed wool standards (blue scale). Comparing the fading of the leather with the fading of the blue standards assesses the light fastness.

To better understand this method, there are some photos of the real tests, throughout this

thesis.

For almost every trial performed for this thesis, physical parameters have been taken into account to determine the better process to be used. In section 4.2 there is a description of some standard parameters and some directives that these final articles have to reach.

2.2 General view of tannins

2.2.1 Tannins: chemical analysis

Tannins description:

Tannins are polyphenols naturally derived from plants, with relatively high molecular weight (in the range of 500 – 3000), and astringent.

Tannins have been known and used for centuries for their property of being able to convert the skin in leather, that is, tanned hides. This is due to their ability to bind to macromolecules such as proteins and carbohydrates, precipitate with heavy metal salts, proteins, and alkaloids.

The earliest known use of these substances is in the tanning industry. They got their name from their ability 'to tan'. Tannins are deposited between the collagen molecules and their ability to react with other complex transversely shaped molecules, which allows the skin to stabilize and become resistant to temperature, water, etc.

These have a bitter taste and tend to accumulate in some fruits, roots, barks and to a lesser extent, leaves. The may have several uses, such as precipitation of the gelatine through the tannins; clarification of wine; the ability to precipitate proteins; and it is also used for tanning leather.

Real tanning is understood as the crosslinking of the skin's collagen chains, while synthetic tanning entails the filling of hollow spaces between the skin's collagen chains.[55]

Classification of tannins:

Tannins were divided into two groups: hydrolysable tannins (HT) and condensed tannins (CT), but now one of the most accepted classifications is the one proposed by Khanbabaee and Van Ree,[55] who, based on the molecular structures and properties, distribute tannins in four groups: gallotannins, ellagitannins , condensed tannins and complex tannins.

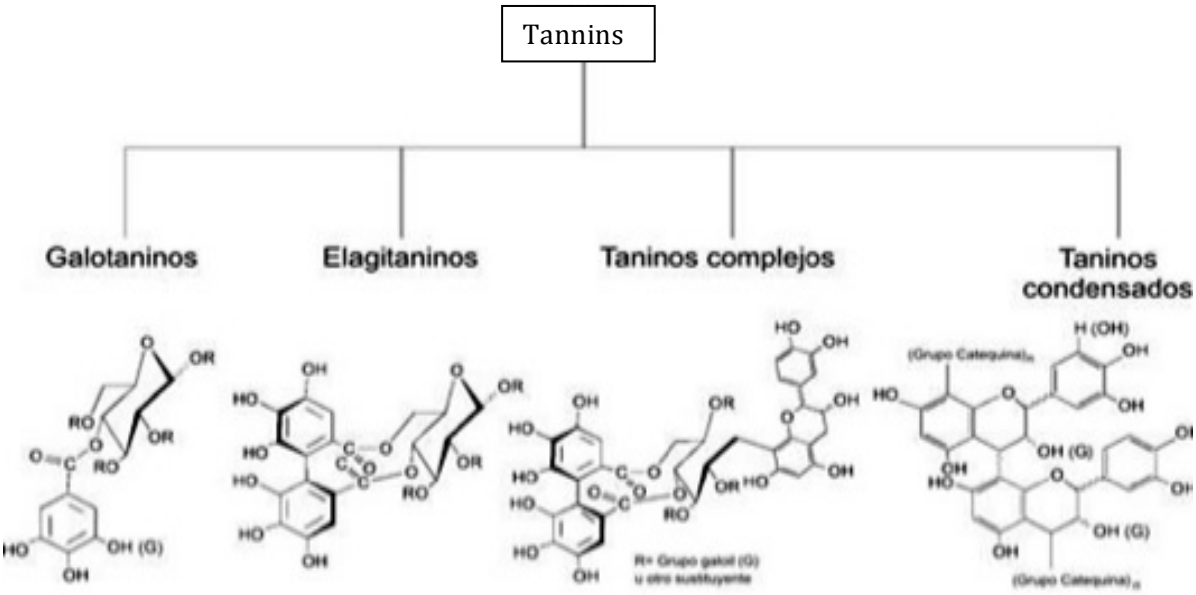


Figure 7: Tannins classification by Khanbabaee and Van Ree. [55]

However, the tanning industry still refers to two major groups:

- Hydrolysable tannins or pyrogallic: are those soluble products by hydrolysis in acidic or basic, enzymatic and boiling water. Its constitution is characterized by the fact that the benzene ring is attached to the second intermediate compound by oxygen atoms. Hydrolysable tannin extracts can be classified into two groups: (Fig. 8)

    a) Those that form gallic acid and glucose via hydrolysis, called Gallic extracts.
    b) Those others who form ellagic acid and glucose called ellagic extracts.

Hydrolysable esters are readily formed by a sugar molecule (generally glucose) linked to a variable number of molecules of phenolic acids (gallic acid or its dimmer, ellagic acid).

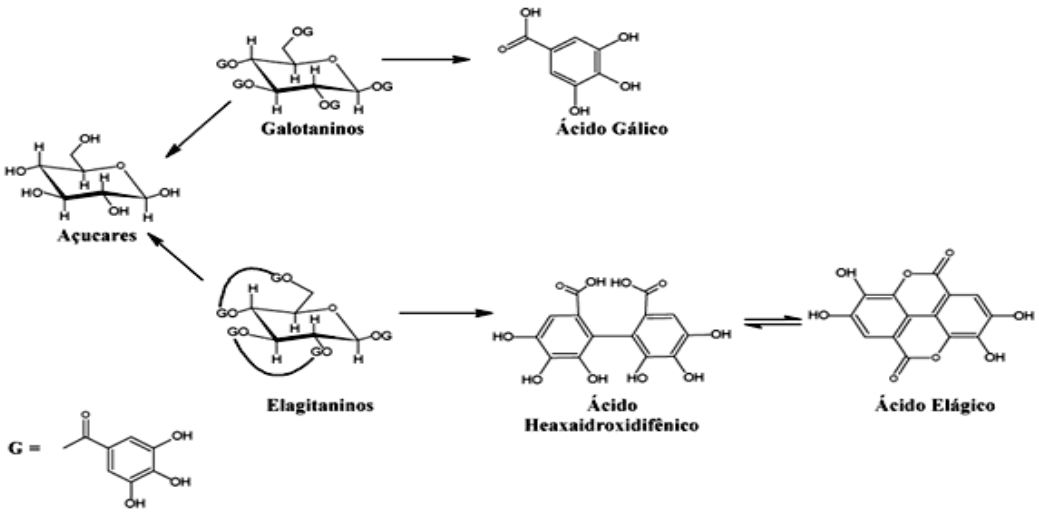


Figure 8: Hydrolysable tannins and ellagitannins.[56]

- Non-Hydrolyzable or condensed tannins: The condensed tannins or proanthocyanidins are poliflavonoids in nature,[57] consisting of chains of flavan-3-ol units. The most common class of proanthocyanidins are the procyanidins that consist on chains of catechin and/or epicatechin (Fig. 9). Catechin or condensates extracts in the same conditions form precipitates. Their cores constituents are united together with carbon atoms intervention.

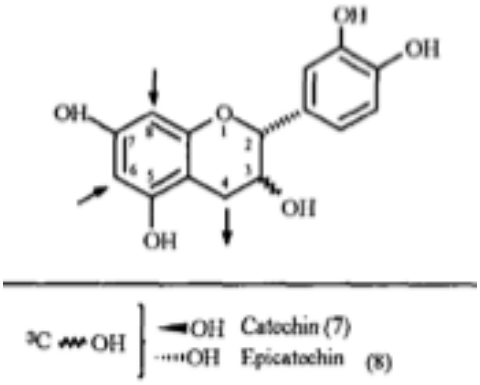


Figure 9: Catechin and/or Epicatechin.[6]

Now that the various types of tannin have been described, it is important to mention how tanning occurs. By establishing links between the collagen fibers of the skin and macromolecules tannins by the combination of the phenolic groups of the first forming hydrogen bridges, while establishing covalent bonds, are those that ensure that the binding will endure over time. This requires that the molecular mass has well defined limits, not too high so it can intercalate between inter-fibrillar spaces, nor too small, because in that case there would not be a sufficient number of links as ensure the stability of the union in the time.

Since Tannins have a high astringency, these are also used in the field of medicine. Used internally (oral), it has functions as an anti-diarrheal, favouring certain antiseptic effect.

Tannins also possess vasoconstrictor properties; therefore, these are used both internally and topically in the treatment of conditions such as varicose veins or haemorrhoids and small wounds. Tannings are indicated for topical uses are in the treatment of various skin problems; they are also used in certain skin diseases as well as in cosmetic astringents tonics.

Tannins determination method

There are several methods to determine the tannin content of a vegetable extract, such as the Protein Precipitation Method,[58] a gravimetric method based on the precipitation of tannins with copper acetate, and the colorimetric method [59]. However, the method that we used is the skin powder method, which is based on the quantitatively determination of the polyphenols that remain in the solution after the adsorption of tannins on skin powder takes place. Tannins are determined by difference.

The method used for determining the tannin content of the samples of Tara or changes is "The method of the hood". Listed below is a short summary, but a better description of this procedure is described in Annex 4.

This procedure is conducted to determine the concentration of tannins using the method of the filter, which consists in determining the tannin by filtration placing a tannin solution on a hood containing a leather powder slightly chromed, the tannic part of the sample is retained within the hood, no-tannins part can be evaluated from the liquid taken from this filtering process.

To determine the quality of the vegetable tannins the following parameters are examined:

- Tannin content: To characterize the content of tannins in the Tara powder, a standard method has not been determined yet, but a proposal is being submitted based on the filter method (Annex 4). It determines the substances that chemically combine with hide powder in analytical conditions.
- Non-tannin content: They are organic compounds with low molecular weight and, therefore, they do not have tanning capacity. Free gallic acid and other organic acids content in the powder are non-tannins compounds, as well as carbohydrates. They are determined by gravimetry.
- Insoluble matter: these are non-soluble particles or aggregates, but are component of the powder as lignin and cellulose. The gravimetric method is used after filtering the sample with a membrane of 0.45 microns.
- Total solids: is the quantity of substances no volatile at 100ºC. They are calculated by gravimetry
- Soluble Solids: Amount of water-soluble solids. Unlike total solids and insoluble.

2.2.2 Characterization of Tara tannin

For Tara, the greatest tannin concentration is found in the pods, which are pale yellow and/or red and are crushed to produce the Tara powder that is commercialized. As mentioned in the Background section of this document, this environmentally friendly

tanning agent is mainly used in the manufacturing of Automotive and furniture upholstery, specially for light colors.

Horler and Nursten[60] carried out a study demonstrating that principal components of Tara tannin were based on a galloylated quinic acid structure (Fig. 10). This is a notable difference from other members of the hydrolysable tannin group, which are based upon a galloylated or ellagoylated hexose.

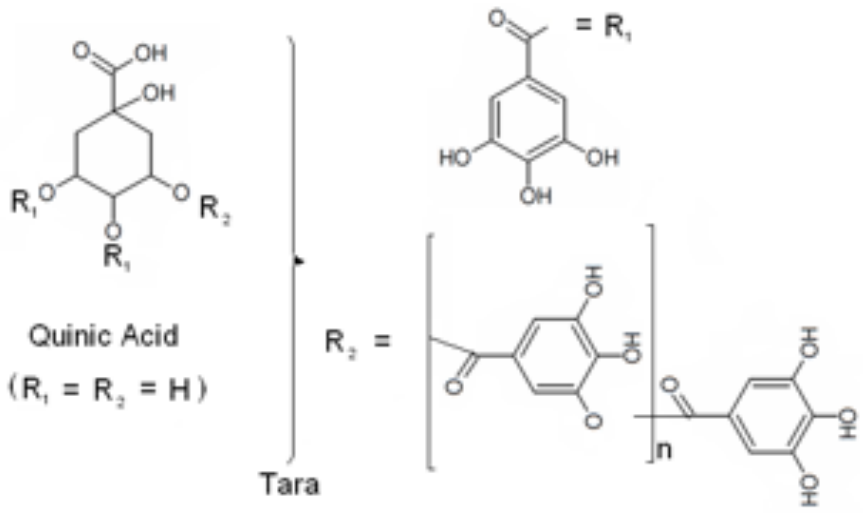


Figure 10: Galloylated quinic acid structure of Tara tannin.

The Tara tanning agent is extracted from the fruit husks of the small Tara tree. During the harvest, the trees are not damaged. The population in Peru developed a remedy against sore throat that used the precious content of the yellow-red Tara husks centuries ago. Various other fields of application of the husks and their content are known and mentioned: as a basic raw material for the production of colours, as a reduction agent in the chemical industry or as decantation agent in the production of alcohol.

Tara powder can be used to tan all kind of hides and skins and to re-tan chrome tanned leathers to improve the grain tightening. The general specifications for commercial tara powder for tanning application are: [61]

- Tannin content: min. 48%
- Water content: max. 13%
- pH (at 6.9°Be): 3-4

As previously mentioned in the background section of this thesis, Tara powder in addition to the Galloylated quinic acid structure, also coexists with tannic acid, which is formed by a core of sugar molecules such as glucose, coupled with phenol carboxylic acids, for instance gallic acid and its derivatives. The ester linkages are formed between the alcohol groups (-OH) of the sugar molecule and the carboxylic groups (-COOH) of the molecules of phenol-carboxylic acids. The number of ester linkages in a molecule of tannin depends on the sugar

molecules present in the core of the tannin molecule.

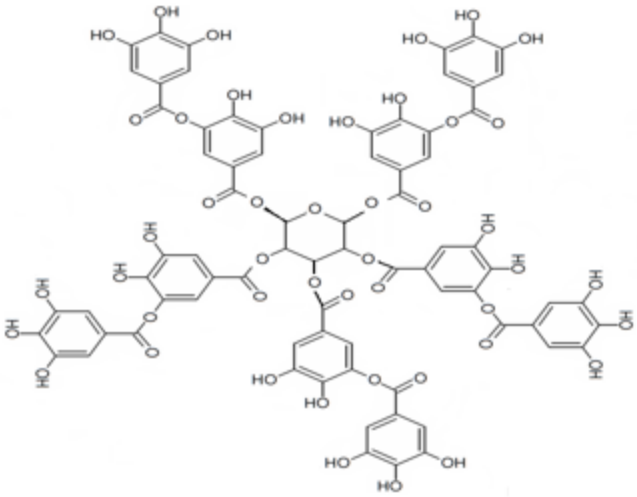


Figure 11: Tannic or Gallotannic acid.

Their properties can be summarized as:

- Low stability to hydrolysis and microorganisms: Hydrolysis of the ester bonds by acids and enzymes (esterase) causes the loss of tannin.
- High acidity: Tara solutions have a pH 3.0 - 3.5 due to the high concentration of acids.
- Slow penetration in the hide structure.
- Light fastness.
- High salt concentration buffers: these are salts of weak organic acids, which provide good protection to the leather before ageing and acid hydrolysis.

2.2.3 Tannins use

The conversion of raw animal hides into leather has traditionally been carried out with plant-derived tannins. The compounds that bind to the plant proteins are called (by definition) tannins. [62]

Through history, many different cultures have developed the process of tanning. Leather sandals have been found in Egyptian excavations from 3,300 years ago. Clearly tanning was being done before that time.[62]

Tannins are found in most plants, especially most woody plants and the quantities vary, but often about 1 to5% is encountered. There are two major types of tannins: condensed and hydrolysable. Both have been used for tanning. The most important commercial tannins are condensed tannins.[62]

There is, without a doubt, three species that leads the vegetable extract exploitation: Quebracho, Mimosa and Chestnut.

- Quebracho is probably the best quality tannin material for many purposes. The wood of this tree from Argentina, Paraguay, and Brazil (the Chaco) is usually conformed of about 20% (up to 40%) tannins. The tannins are extracted in water and then spray dried. Quebracho is wild harvested at present.[63]

- Mimosa, this tanning extract is derived from the bark of the Black Wattle tree, a species of Acacia native to Australia. The species was introduced to South Africa in 1871, initially used as shelterbelts for stock and the wood for fuel and fencing. Later, it was discovered that the bark contained high levels of tannin, which could be used for treating hides for leather production. This led to the tree being widely planted to produce tanning extract for the leather industry. [53]

- Chestnut tree. Chestnut wood is a source of natural tannin and was used for tanning leather before the introduction of synthetic tannins.[63] On a 10% moisture basis, the bark contains 6.8% tannin and the wood 13.4%[64]. The bark imparts a dark colour to the tannin, and has higher sugar content, whereas, chestnut tannin has a naturally low pH value, relatively low salts content and high acids content. It is one of the pyrogallol classes of tannins (also known as hydrolysable tannin). The wood seems to reach its highest tannin content after the trees reach 30 years old. The southern European chestnut wood usually contains at least 10 to 13% more tannin than chestnut trees in northern climates. Today, the largest producer of extract for tanning is Italy.

Other uses of tannins account for about 15% of the total market. In the past tannins and iron salts were used to make ink. Gums were also added. Tannins are sometimes used medicinally and are used in oil field drilling sludge.

2.2.4 The Syntans.

The syntans are, as their name implies, tannins that are synthesized artificially. But despite their name, these do not have the capacity to tan, but are rather used primarily to accompany vegetable tannins to accelerate the tanning and as fillers in re-tannins. E. Stiasny in 1912 created the first synthetic tanning.

After 1930, it was possible to produce other synthetic tannins with excellent tanning properties, which allowed replacing many vegetable tannins without noticeable differences in leather, but incorporating specific characteristics, such as:

- Clarification of vegetable tanning solution;
- Pre-tanning, to accelerate the penetration of vegetable tanning agents;
- Clarify the color of the leather tanning with vegetable extracts;
- Clarify the color of chrome tanned leather;
- Smooth, soft to the touch;
- Production of soft tanning effect and open;
- Enhance the penetration of dyes;
- Facilitate the ground
- Provide greater flexibility

For this thesis, the syntans are used to enhance or facilitate the penetration of the vegetable extract (Modified Tara). The main syntans that have been tried are phenolic syntan and naphthalene sulphonic syntan.

The phenol sulphonic acid is able to condensate and reacts with the protein to produce leather, and its synthesis is made with a phenol sulphonated with sulphuric acid to obtain a sulphonic acid (fig. 12).

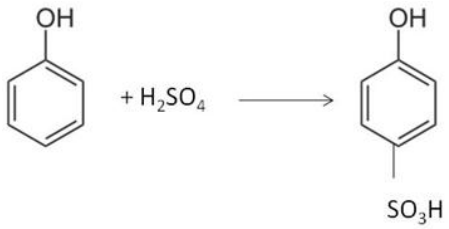


Figure 12: Phenol Sulphonation

The phenol sulphonic acid is condensed with formaldehyde (Fig. 13). The sulphonic groups have the ability to enhance the solubility of the molecule. Syntans based on phenolic groups are classified as ´replacement syntans´, because they are able to replace the vegetable tannins in a certain way.

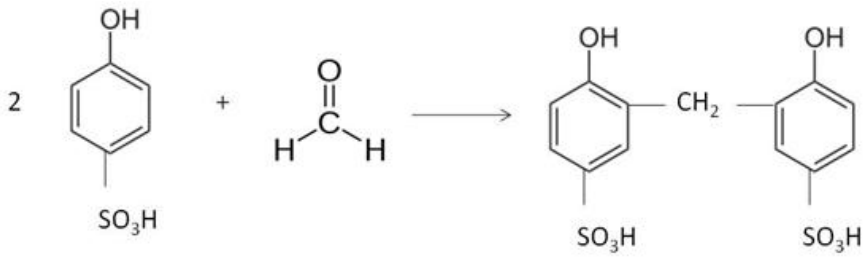


Figure 13: Condensation of phenol sulphonic acid.

The second syntan mostly used in the leather industry, is the naphthalene sulphonic syntan. This syntan has the characteristic of facilitating the penetration and helping to spread the vegetable tannin through the leather structure.

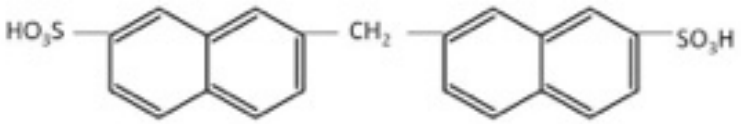


Figure 14: Naphthalene sulphonic acid.

This synthetic tannin follows the same principles of condensation and sulphonation, naphthalene syntans are the simplest and easiest to make. This material is very acid, and can be sold that way or neutralized to form a neutral salt (which is the most common).

Naphthalene sulphonic syntans are classified as ´auxiliary syntans´ and are mainly used mainly to confer supplementary properties to the main tanning agents. This syntan can be removed, and it does not have leather-forming properties. There is no real permanent stabilization of the hide fiber and only a slight raising of the shrink temperature.

It is clear that these syntans are important in leather industry, as they confer some properties to vegetable tannins; however, the main goal of this thesis is the use of sustainable tannins with low carbon footprint. This means that we pretend to use natural source materials as much as possible and less non-sustainable synthetic products.

In annex 5, there is a much wider explanation and description of tannins and their uses.

Chapter 3: Experimental Part

3.1 Chemical modifications of Tara tannins

The aim of this chapter is to develop several processes of chemical, physical, and even some thermo-chemical modification in order to obtain a modified Tara with a higher percentage of tannins, and therefore, improving their tanning ability. But the objective in this particular section is to carry out some chemical modifications on Tara tannin.

First of all, the characterization of commercial tara was performed, then different modification processes has been studied.

Several aqueous extractions with tara at different temperatures have been developed and optimized, as well as aqueous extractions with sulphitation processes, in acid and alkaline medium, in order to decrease it astringency and facilitate the penetration of the tannin molecules through the leather structure. A liquid of Tara extract has been obtained.

As discussed before, the Tara tannins are hydrolysable tannins, and some processes or the application of high temperature could produce this hydrolysis by releasing free acid Gallic. The degree of hydrolysis has been controlled by means of the gallic acid content in HPLC (High Performance Liquid Chromatography).

Various extracts obtained were characterized and, depending on the result, were optimized or not, and a pre-tanning process is applied.

Experiments have been conducted to apply the modified Tara during the tanning process at laboratory scale, in order to determine their tanning capacity and, evaluating the degree of penetration, thermal stability of leather structure, and the physical and organoleptic properties acquired.

Method

This part 3.1 was conducted in three stages:

- 1st stage. Several samples of the original tara powder were analysed to learn about the concentration of tannin using the filter method.
- 2nd stage. Development of several thermo-chemical extraction processes from commercially available tara as provided by a chemical supplier in order to obtain a tara extract with high tannin contents and low insoluble matter.
- 3rd stage. Optimization of the aqueous tannin extraction process and application to the leather.

3.1.1 Analytical characterization of tara

Several samples of original tara powder were analyzed to know about the concentration of tannin following the filter method, further described on Annex 4 of this thesis. To determine the quality of the vegetable tannins, the following parameters are examined:

- Tannin content by the filter method.
- Non-tannin content by the gravimetric method.
- Insoluble matter by the gravimetric method.
- Total solids by the gravimetric method.
- Soluble solids by the gravimetric method.
- Iron content by the atomic absorption method.

Table 8 shows the results of the analysis performed on the different tara samples.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4	Average
Soluble Solids (%)	58.9	67.9	59.7	60.1	61.6
Total Solids (%)	85.9	92.2	92.9	84.8	88.9
Non-Tannins (%)	12.0	17.9	14.7	13.7	14.6
Tannins (%)	46.9	50.1	45.0	46.5	47.1
Insoluble Matter	27.0	24.2	33.2	24.6	27.2
Water (%)	14.1	7.8	7.1	15.2	11.0
Iron (mg/Kg)	182.0	204.0	388.9	159.0	233.5

Table 8: Characterization of commercially available samples of Tara powder

As can be observed, there is variability between different samples. The tannin content ranges are between 45% and 50%. The concentration of insoluble matter, which is a negative factor for tanning process conducted with tara due to the large amount of insoluble material remaining in the wastewater, also presents a significant variability. Concerning iron content, no major differences were found between the samples observed except for sample 3, which has a remarkably high content.

3.1.2 Extraction processes of tara

Three types of extraction processes were carried out to try to obtain a tara extract with high tannin content and low content of insoluble matter.

3.1.2.1 Aqueous extraction at different temperatures

To perform this thermal process, solutions of tara at 10% content were prepared and treated at 70°C and 136°C by autoclave for 6 and 3 hours, respectively. After that, the solutions were filtered by means of a fabric filter and finally the content of tannins was determined.

Table 9 shows the results of the analysis of the Tara solutions concentrated at approximately 9% of water after the thermal processes of extraction.

Determination	70°C	136°C	Initial Tara powder
Soluble Solids (%)	84.0	88.0	59.7
Total Solids (%)	91.0	91.0	92.9
Non-Tannins (%)	24.5	26.0	14.7
Tannins (%)	61.2	62.1	45.0
Insoluble Matter (%)	7.0	2.9	33.2

Table 9: Tannin content of Tara, after thermal extraction

It can be observed how the tara obtained has higher tannin content. The content of insoluble matter is almost negligible when compared with the commercially available tara powder. Nevertheless, non-tannin fraction has been increased considerably which means that tannin has been hydrolyzed.

As for the aqueous extraction process at 136°C, a slightly better result was obtained, although the difference with the process at 70°C is negligible, since the extracts obtained were with 62% and 61% of Tara, respectively. In these cases of such a small difference the energetic saving has to be considered.

3.1.2.2 Chemical extraction using acid and alkali

To carry out this chemical extraction, 2 solutions were prepared, the first one using 20 g of tara, 200 mL of water and 0.5 – 1.0 mL of NaOH 50% (basic process). The second one was prepared using 20 g of tara, 200 mL of water and 0.5 – 1.0 mL of HCl 33% (acid process). Each process was treated at 70°C and 136°C in autoclave for 6 and 3 hours, respectively. After that, the solutions were filtered by means of a fabric filter and finally the content of tannins was determined. The samples were prepared and treated as summarizes the next table.

	I	II	III	IV	V	VI	VII	VIII
Commercially available Tara (g)	2	2	2	2	2	2	2	2
H_2O (mL)	20	20	20	20	20	20	20	20
HCL 33% (mL)	0.10		0.05	0.05				
NaOH 50% (mL)		0.10			0.05	0.05		
Temperature (°C)	70	70	70	136	70	136	70	136
Time (h)	6	6	6	3	6	3	6	3

Table 10: Acid and alkali treatment of Tara powder

Tara tannins are notable for their high acidity and a mild acid hydrolysis; the tannin gives gallic acid, instead of the usual carbohydrate fragment, resultant of the alicyclic quinic acid. The acidity of the tannin is directly related to the presence of the free carboxyl group of quinic acid in its structure. Free gallic acid and other organic acids present in the extract are non-tannin compounds, as are carbohydrates. For this reason, the solutions shown in Table 10 of modified Tara were analyzed by HPLC to determine the gallic acid content (described in section 3.1.3). This will give an idea of the hydrolysis of the Tara tannins and whether this determination can be used to test the quality of the Tara products.

The following table shows the results of the analysis of the solutions of Tara concentrated at approximately 9% of water, after the acid and alkali processes of extraction. For a better reference, Figure 15 shows the composition of the resultant Tara extracts after the thermal, acid, and alkali extraction processes took place.

	Acid process		Basic process		Initial Tara powder
Determination	**70°C**	**136°C**	**70°C**	**136°C**	
Soluble Solids (%)	86.2	88.2	86.2	86.8	59.7
Total Solids (%)	91.0	91.0	91.0	91.0	92.9
Non-Tannins (%)	25.5	30.8	25.5	30.8	14.7
Tannins (%)	60.6	57.4	60.6	57.4	45.0
Insoluble Matter (%)	4.7	2.8	4.7	2.8	33.2

Table 11: Tannin content of Tara, after acid and alkali extraction processes

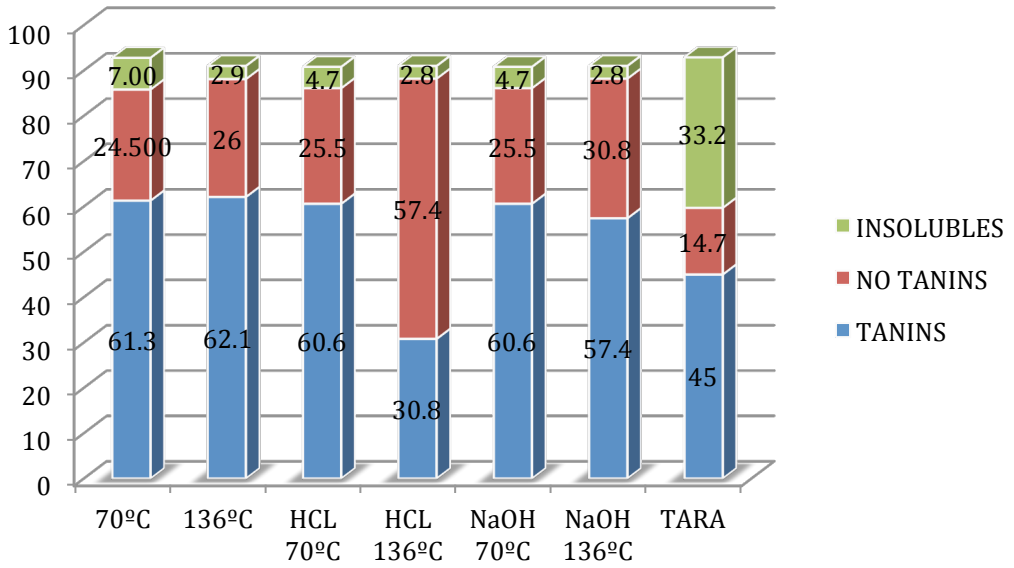


Figure 15: Composition of Tara extracts obtained

The extracts obtained, have high tannin content and very low concentration of insoluble matter.

The concentration of tannins increases considerably and the insoluble fraction shown is fairly low. The process at 70°C shows better results than at 136°C because of the increase in proportion of non-tannin due to tannin hydrolysis itself.

The chemical extraction process results in a greater concentration of tannins for the extracts obtained at 70°C. As can be seen in the results, no observable differences of basic or acid conditions have been obtained. At 136°C, the fraction of no tannins increases significantly, evidencing the hydrolysis process of the tannins.

3.1.2.3 Chemical modification process by sulphitation

To perform this chemical extraction, 3 solutions were settled, the first one using 10 g of Tara, 100 mL of water, 1 mL of NaOH 50% and 1 g of sodium metabisulphite ($Na_2S_2O_5$). The second one was prepared using 10 g of tara, 100 mL of water, 1 mL of HCl 33% and 1 g of sodium metabisulphite. The third one was prepared using 20 g of tara, 200 mL of water and 1 g of sodium metabisulphite. Each process was treated at 70°C and 136°C in autoclave for 6 and 3 hours, respectively. After that, the solutions were filtered by means of a fabric filter and finally the content of tannins was determined.

Table 12 shows the results of the analysis of the Tara solutions concentrated at approximately 9% of water after the sulphitation processes of extraction. Figure 16 shows the composition of Tara extracts obtained after the sulphitation treatment.

	I (NaOH+ Metabisulphite)		III (HCl+ Metabisulphite)		V (Metabisulphite)		Initial Tara powder
	70°C	**136°C**	**70°C**	**136°C**	**70°C**	**136°C**	
Soluble Solids (%)	81.1	91.0	85.2	87.2	91.0	87.2	59.7
Total Solids (%)	91.0	92.0	91.0	91.0	91.0	91.0	92.9
Non-Tannins (%)	29.8	56.4	37.6	43.6	27.8	34.1	14.7
Tannins (%)	52.9	36.4	47.7	42.3	63.2	53.1	45.0
Insoluble Matter (%)	8.3	1.0	5.8	3.8	1.0	3.8	33.2

Table 12: Tannin content of Tara, after sulphitation process

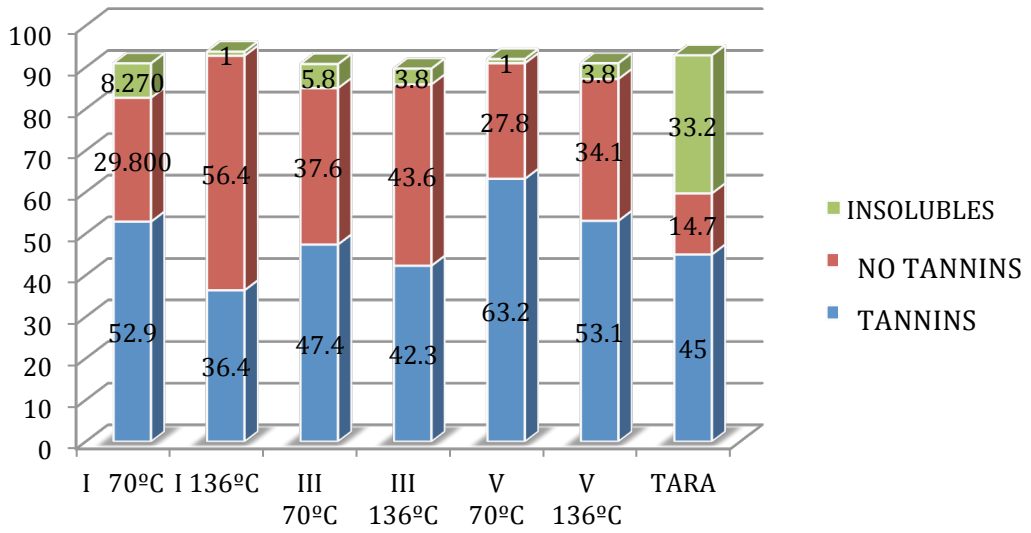


Figure 16: Composition of modified Tara by sulphitation

A modified tara with a high concentration of tannins was obtained. It was observed that the best process is developed in presence of metabisulphite. The addition of alkali and acid is a negative factor since it leads to the conditions for the chemical hydrolysis of tannins. We can observe an increase in non-tannin fraction and a decrease in tannic fraction. Also, the process is much more satisfactory at 70°C than it is at136°C since there is an increase in non-tannic fraction.

As with the previous process, this one was disesteemed, due to the high increase of non-tannin percentage.

3.1.3 Hydrolysis degree of Tara by HPLC analysis

As told, Tara powder is a hydrolysable tannin. From a chemical point of view, hydrolysable tannins generally consist of one molecule of a monosaccharide (glucose in most cases), which connects several units of polyphenolic acids. The simple polyphenolic acid is gallic acid. The ester linkages are formed between the alcohol groups-OH of the sugar molecule and the carboxylic groups-COOH of the molecules of phenol-carboxylic acids. The number of ester linkages in a molecule of tannin depends on the sugar molecules present in the core of the tannin molecule. The hydrolysis of hydrolysable tannins produces gallic acid.

Figure 17: Formation of free Gallic acid by hydrolysis of hydrolysable tannin

Where 'R' represents the glucose molecule.

The chemical extraction (acid and alkali treatment) has been analyzed.

Test	I	II	III	III'	IV	IV'	V	V'
Commercial Tara (g)	2	2	2	2	2	2	2	2
H_2O (mL)	20	20	20	20	20	20	20	20
HCL 33% (mL)	0.1		0.05	0.05				
NaOH 50% (mL)		0.1			0.05	0.05		
Temperature (°C)	70	70	70	136	70	136	70	136
Time (h)	6	6	6	3	6	3	6	3

Table 13: Acid and Alkali treatment of Tara powder

In order to obtain the best results, the following conditions were considered:

- Instrument : Agilent 1200 chromatograph
- Column : Zorbax eclipse XBC C-18 (Agilent)
- Gradient: A=80% H_2O / HCOOH (999 / 1 v/v) + B=20% Methanol / HCOOH (999 / 1 v/v), in 15 min 100% B
- Injection volume : 10 µL
- Flux : 1 mL/min
- Temperature: 25°C

Calibration curve of gallic acid (Panreac) is calculated to be able to proceed with the analytic determination of the tara powder samples.

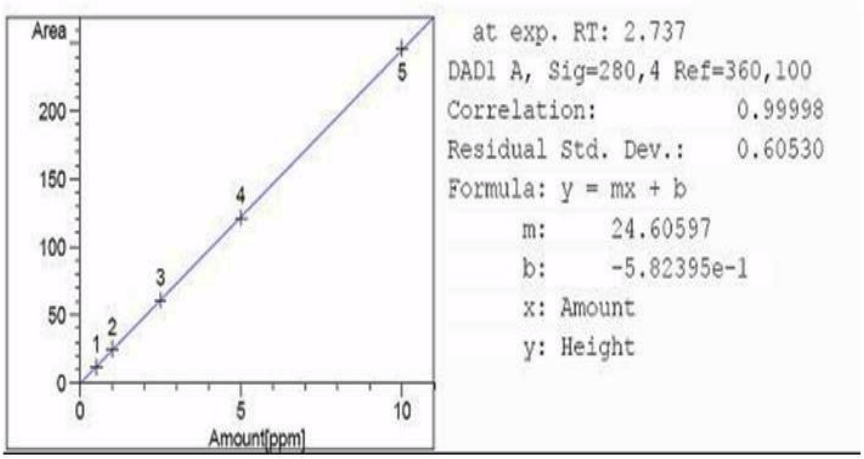


Figure 18: Calibration curve of Gallic acid (HPLC)

As for the calibration curve, 5 watery analytical solutions are acidified with 1% formic acid at the following concentrations: 0.5; 1; 2.5; 5 and 10 mg/L. Samples are analyzed by HPLC and calibration is calculated through the area graphic of the obtained pick of gallic acid against the concentration.

To quantify the gallic acid content for each sample, a 2% of tara solution was prepared and the analytical solution was diluted 1/20. The analysis was carried out according the described conditions.

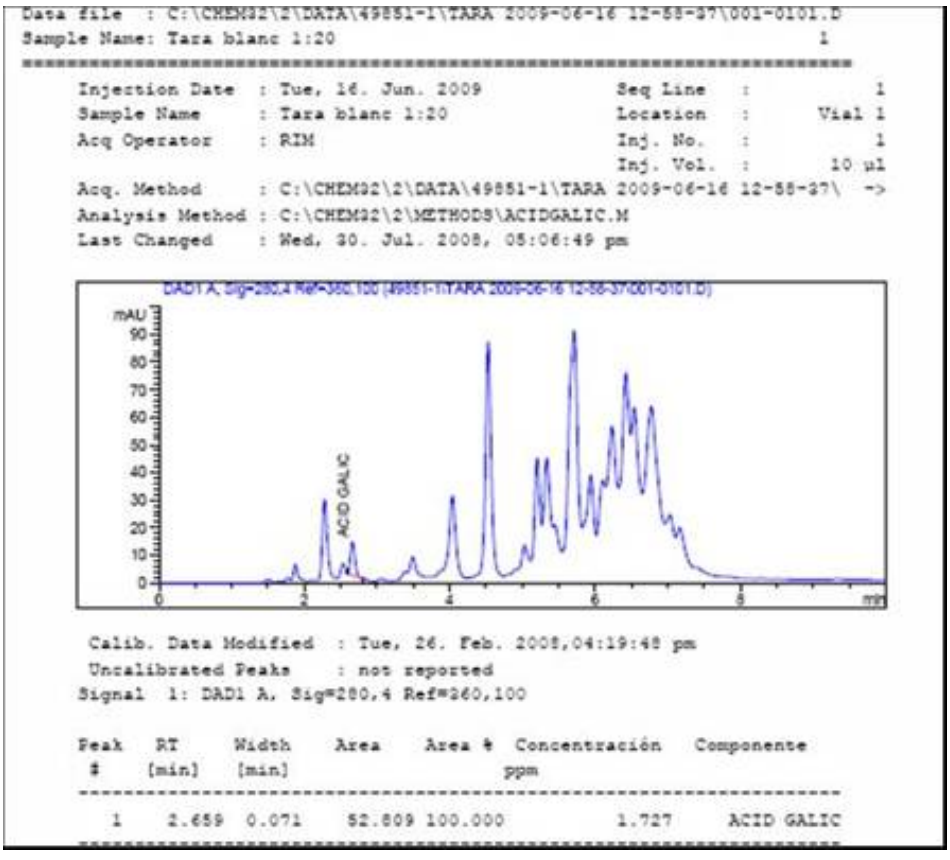


Figure 19: Determination of free gallic acid of commercially available Tara powder (HPLC)

The values of free gallic acid content of the modified tara solutions are described in Table 14.

Test	Gallic acid (ppm)	Gallic acid (%)
I HCl	3424	0.3
II NaOH	10322	1.0
III HCl 70°C	5232	0.5
III' HCl 136°C	15684	1.6
IV NaOH 70°C	6849	0.7
IV' NaOH 136°C	12032	1.2
V 70°C	2500	0.2
V' 136°C	16929	1.7
Commercially available tara 10%	1043	0.1

Table 14: Gallic acid obtained in the hydrolysis

It can be observed that the content of gallic acid released in the modification processes, increases considerably at 136°C. On the other hand, no significant differences are observed with the addition of acid or alkali.

Therefore, it can be concluded that all the modification process is based on thermal hydrolysis. The total hydrolysis of tannins is not produced due to the fact that the acid concentrations tested were very low (0.15%). However, at higher concentrations, much higher yield can be reached.

3.1.4 Optimization of the tannin extraction process

The values of free gallic acid in previous tests, showed an increase of hydrolysis when the temperature is higher. In order to optimize the process, aqueous extractions of tara were carried out at lower temperatures. By doing so, the energy costs of the process could be reduced.

In this process, solutions of tara at 10% content were prepared and treated at 40°C and 70°C for 6 and 3 hours, respectively. Next, the solutions were filtered with fabric and the tannin content was determined.

Table 15 shows the results of the analysis of the solutions of Tara concentrated at approximately 9% of water after the aqueous processes of extraction. To allow comparison, figure 20 shows the composition of Tara extracts obtained at lower temperatures.

Determination	40ºC/3h	40ºC/6h	70ºC/3h	70ºC/6h
Soluble Solids (%)	89.2	84.9	91.0	89.3
Total Solids (%)	91.0	91.0	91.0	91.0
Non-Tannins (%)	22.7	19.7	22.7	20.2
Tannins (%)	66.5	71.3	68.2	67.4
Insoluble Matter (%)	1.7	6.1	0.0	1.7

Table 15: Tannin content of Tara, after aqueous extraction

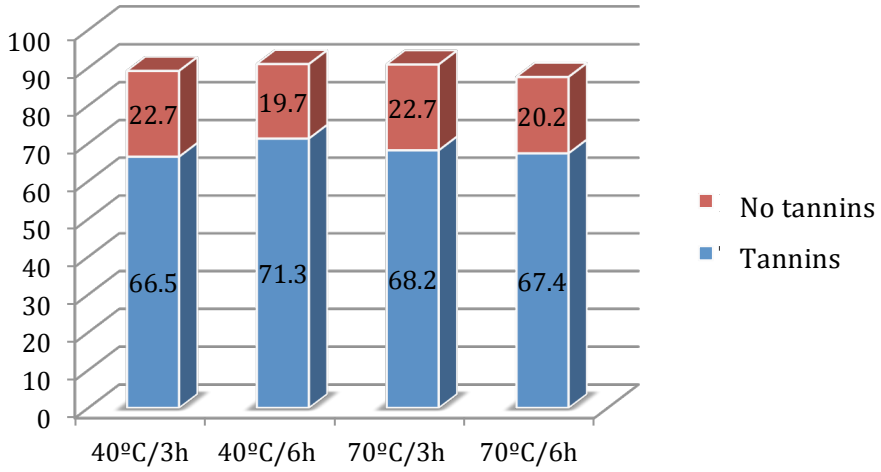


Figure 20: Composition of Tara extracts obtained at lower temperatures

It can be noticed that temperature is not a relevant factor to obtain a greater percentage of tannins. However, a higher content of tannins can be obtained with a longer extraction process. This means that the increase in the tanning content is proportional to the time spent on this process.

3.1.5 Application of Tara from thermo-chemical modification

Finally, the solutions of aqueous extractions resulting from the optimization process at low temperature, from the experimental part 3.1.4, were applied to hides samples.

The application of modified Tara in a pre-tanning process was performed. Also a test with original Tara was carried out, in order to assess a possible improvement. One of the aims is to reduce the amount of synthetic pre-tanning agents.

Bovine pickled hides (pH 3.5) were used to perform the experiment. The formulation of pre-tanning process is shown in next table.

STAGE	ºC	%	PRODUCT	Gr.	Time
Pre-tanning	20				
		84	**Tara Extract 40ºC / 70ºC**		
		7	Synthetic		
		2	Sulphite oil	Aut. night	Cross section testing
		0.8	Formic acid	2h	pH=3.59
					Drain
Washing	20	300	Water	20’	Drain
					Rest on horse
					Samming and air drying

Table 16: Pre-tanning formulation

Shrinkage temperature was determined to evaluate the thermal stability of the pieces of leather obtained from the application of modified Tara. The results are shown in table 17. The higher the shrinkage temperature applied, the better the skin is tanned.

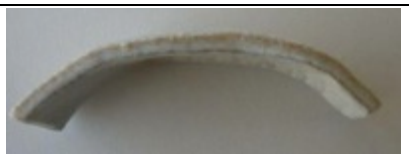
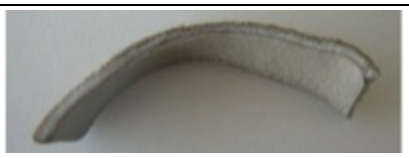
Sample	Ts (ºC)	Cross section
1. Aqueous tara extract 40ºC/6h	56	
2. Aqueous tara extract 70ºC/6h	58	
3. Original tara powder	61	

Table 17: Shrinkage temperature and leather cross-section

As the above table shows, the penetration of the extract into the leather cross section is poor and the shrinkage temperature is low, lower than the original Tara powder. Leather appearance of samples 1 and 2 is slightly worse; there is more shrunk grain and astringency, penetration is not sufficient.

3.1.6 Conclusions part 3.1.

The extraction processes tested were grouped into thermal processes and thermo-chemical processes. The best results are obtained with the thermal processes at low temperatures since the addition of acids or alkalis to the extraction solution and high temperatures, favors hydrolysis as proved, the fraction of non-tannins is therefore increased. This occurs because the tara tannins are hydrolysable tannins. In the hydrolysis process, gallic acid monomers are released, which increases the non-tannin fraction.

As for thermal processes no significant differences (in tannin fraction) were observed between extraction at 70 °C and at 136 °C. The tara extract obtained had a tannin concentration of 62%. Considering that the initial tara had a tannin concentration of 45%, the increase in tannic fraction is significant.

Another objective of this part of the thesis was to obtain a reduction in the insoluble matter fraction through the applied processes of extraction. This objective was achieved, since this fraction was reduced from 33% content, for the initial commercial Tara powder, to 1-7% for the Tara aqueous extracts.

Seeing that at a higher temperature the content of free gallic acid increased, the procedures of the aqueous extraction tests were carried out at lower temperatures, which is an advantage since it is energy saving.

There is another point to take into account, which is the fact that if a natural product is chemically modified automatically gets on the lists of the REACH, and that is something that we don’t pretend.

As to the use of the modified Tara (optimized aqueous extracts) in the pre-tanning process, the results were slightly worse than the ones obtained from the direct application the original Tara powder.

Considering this, it is necessary to broaden and deepen the study to improve the properties of the modified tara with respect to the size of the particle, which will be done in the following section 3.2.

3.2 Physical modifications

The activity focuses on making optimum physical changes for better product penetration. Commercial Tara has been milled with the methodology described below, and the particle size of the modified Tara and the original Tara is determined by sieving with different sieve sizes.

There has been a test for the application of the Tara products on skin at laboratory scale to determine its tanning power, as well as analysing the degree of penetration, the stabilization of the collagen structure, and the physical and organoleptic properties acquired.

The leather samples obtained were characterized and the results allow us to propose the optimization process and design of Wet White pre-tanning formulations.

This experimental part takes place in two stages:

- The first stage describes a test where the original Tara was milled and sieved with a mesh of 90 microns.

- The second stage consists of milling the original Tara, and then sieving it at various screen sizes, and analyse it.

Experimental Development

3.2.1 First stage (Separation by sieving the original tara)

The powder sample of commercial tara has been applied through a screening process. In the first experiment, 90 micron sieve was used.

Two fractions are separated:

- > 90 microns
- ≤ 90 microns

Initial Tara	100.17 gr
> 90 microns	13.56 gr
≤ 90 microns	82.68 gr

Table 18: Weight of tannins obtained by particle size

Tannins determination

The values obtained for the determination of tannins, using the method described in Annex 4. The results of the characterization of the samples are the following.

Determination	> 90	≤ 90 microns
Soluble solids	37.1	62.0
Total solids (%)	90.3	91.9
No tannins (%)	11.7	14.0
Tannins (%)	25.4	48.0
Insoluble (%)	53.2	30.0
Water (%)	9.7	8.1
pH	3.9	3.7

Table 19: Determination of tannins (Part I)

Below 90 microns, there is a great amount of powder and the % of tannins is also higher, it can also be seen that the amount of insoluble matter is considerably high in the particle size exceeding 90 microns.

3.2.2 Second stage (milling, sieving at different sizes)

During the second stage the commercial Tara was milled and sieved; only this time, it was done with different screen sizes.

Method of milling

A powder sample of commercial Tara goes through a milling process. According to the following methodology:

- A 1-litter canister is filled to a third of its capacity with the powder sample. (Photo 1)
- Introduction of bearing steel balls of different sizes.
- Let it roll for 50 hours in laboratory rotary shaker (speed 15 rev / min.).

Powder samples of Tara (commercial and milled) were treated for a sieving process to determine the grain size of the sample.

Mesh sieves stainless steel AISI 316 compliant UNE 7050-3, ISO 3310-1 and ASTM E11. They are used for test sieves of various sizes of light and 20 cm diameter (200µm, 160 µm, 125µm, 100µm, 80 µm, 63 µm, 50 µm, 45 µm s and 40 µm), mounted on a column from largest to smallest.

Photo 1: Filters and milling equipment used, Sieve UNE 7050-3

Determination of Tara granulometric parameters

Table 20 shows the weight distribution on the sieving process, of the Original Tara sample without milling.

Sieve	Aperture (µm)	% Partial retained	%Accumulated retained	% Pass through sieve
92	200	1	1	96,77
94	160	0,88	1,88	95,89
96	125	2,86	4,74	93,03
98	100	10,63	15,37	82,40
100	80	6,61	21,98	75,79
102	63	27,29	49,27	48,50
104	50	17,26	66,53	31,24
105	45	28,94	95,47	2,30
106	40	1,18	96,65	1,12
< 106	< 40	1,12	97,77	0

Table 20: Result Original Tara granulometric study

After the test sample a loss of 2.23 gr is caused (2.23%).

The following charts show the granulometric composition of the samples studied.

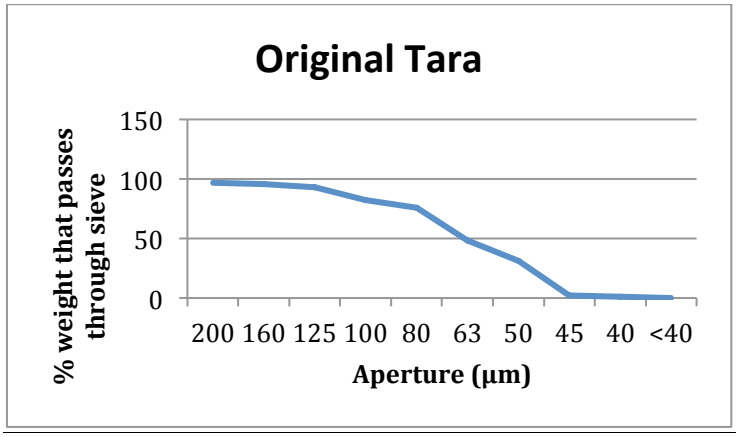


Figure 21: Graph Original Tara weight percent as it passes through various sieves

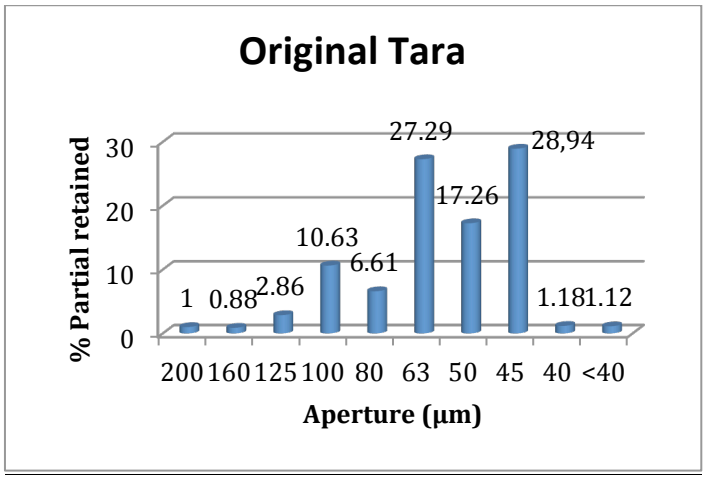


Figure 22: Distribution Tara weight percent retained on each sieve Original

The milled Tara and sieving results are:

Sieve	Aperture (µm)	%Partial retained	%Accumulated retained	% pass
92	200	1,74	1,74	95,54
94	160	1,32	3,06	94,22
96	125	4,14	7,20	90,08
98	100	2,25	9,45	87,83
100	80	5,89	15,34	81,94
102	63	10,67	26,01	71,27
104	50	8,31	34,32	62,96
105	45	58,57	92,89	4,39
106	40	4,39	97,28	0
< 106	< 40	0	97,28	0

Table 21: Outcome Study Tara sieve after grinding

After the test sample causes a loss of 2.71 gr. (2.71%)

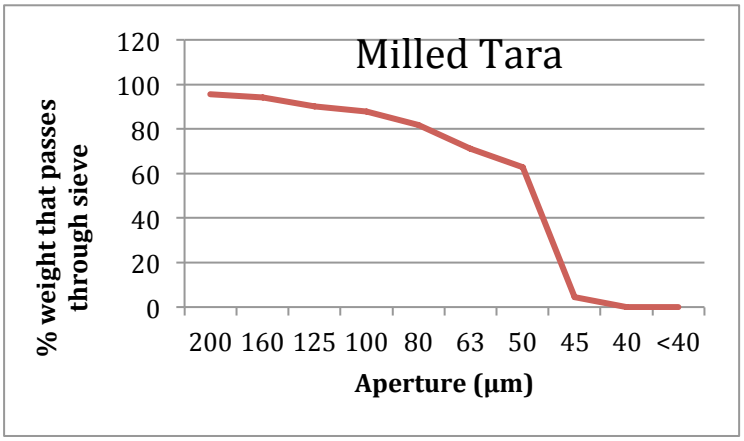


Figure 23: Graph of percentage by weight of milled Tara as it passes through various sieves

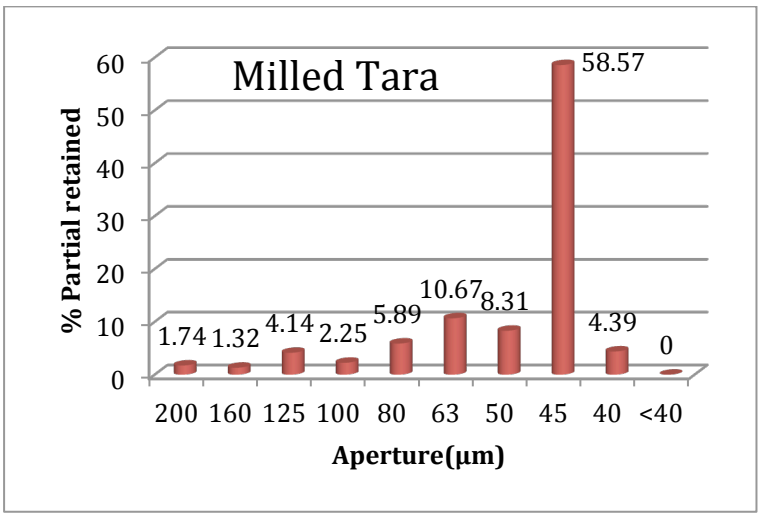


Figure 24: Distribution in weight percent after grinding Tara retained on each sieve

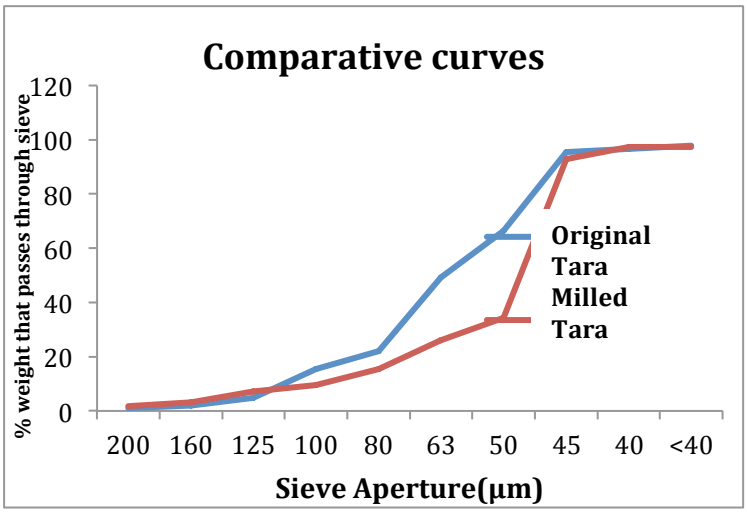


Figure 25: Graphical Comparison of the granulometric curve samples and milled Original Tara

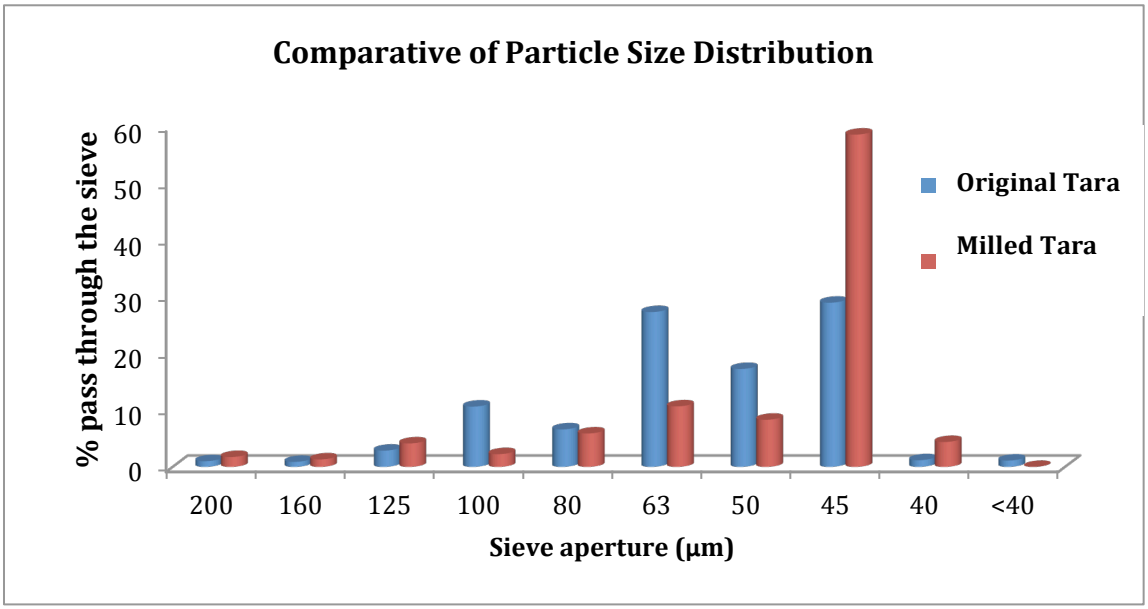


Figure 26: Comparison of particle size between original and milled Tara

It can be seen that by grinding the original Tara, the number of particles smaller than 63 microns have increased, homogenizing the particles to a size of 45 microns; whereas, one can see a wider range of sizes in the original Tara.

We conclude that the grinding process manages to reduce the particle size to values below 50 microns.

3.2.3 Tannins determination

Samples are analyzed according to the milled Tara at different particle size fractions. For this test, just two sieves were used (80 and 50 microns), because within these ranges, the size distribution is more concentrated.

- Milled Tara (total sample)
- Milled Fraction Tara 200-80 microns
- Milled fraction Tara <80-50 microns
- Milled fraction Tara <50-40 microns
- Original Tara

Once the original Tara is milled, a sample is sieved according to the previous screen sizes (> 80 microns; between 80-50 microns and <50 microns), and the percentage distribution remained as follows:

Fraction	%
>80µm	9,11%
Between 80-50µm	9,79%
<50µm	**81,10%**

Table 22: Fraction and percentage obtained after the milling and sieving process

The determination of the content of tannins of the samples is included in the following table.

Determination	Tara sieved	200 – 80 µm	80 – 50 µm	50 – 40 µm	Original Tara
Soluble solids (%)	59.6	40.2	57.9	64.0	59.7
Total solids (%)	86.0	76.0	95.4	93.6	92.9
No tannins (%)	13.1	12.5	11.4	14.7	14.7
Tannins (%)	46.4	27.7	46.5	49.3	45.0
Insoluble (%)	26.5	35.8	34.4	29.6	33.2
Water (%)	14.0	24.0	7.6	6.4	11.0
pH	3.7	3.7	3.7	3.7	3.8

Table 23: Determination of tannins (Part 2)

As can be seen in the above table, there is, once more, variability across the different samples. The Tara powder with particle sizes ranging between 200 and 80 micron, presents low values of soluble solids, total solids, and tannins; in contrast, it presents a high amount of insoluble matter. The Tara composed of smaller particles has a higher percentage of tannins and presents a low content of insoluble matter.

Therefore, we will continue with the application of three different samples of Tara on leather: i) original Tara, ii) milled Tara, and iii) milled Tara, whose particle size fraction is of 50-40 microns.

3.2.4 Application of the physical modified Tara to the leather

Finally, the application of modified tara in the pre-tanning process was studied. Bovine pickled hides (pH 3.5) were used to perform the experiment. The formulation of the pre-tanning process is shown in the following table.

STAGE	ºC	%	PRODUCT	Time	
Pre-tanning	20	50	Water with salt	15’	10 ºBé
		11	**Modified tara**		
		7	Synthetic S-3		
		2	Sulphite oil	Aut. night	Cross section testing
		0.8	Formic acid	2h	pH=3.59
					Drain
Washing	20	300	Water	20’	Drain
					Rest on horse
					Samming
					Drying

Table 24: Pre-tanning formulation

Shrinkage temperature was determined to evaluate the thermal stability of the pieces of leather obtained from the application of the three samples of Tara: i) original Tara, ii) milled Tara, and iii) milled Tara and sieved, whose particle size fraction is of 50-40 microns.

The better the hide is tanned, the higher the shrinkage temperature. Also hides are evaluated regarding color and organoleptic parameters of hardness, using the "Softness Test". Also the penetration of pre-tanning agents into the hide is also valued by cut observation thereof and softness values.

Test	Ts	Cut	Softness
Original tara	**69,5**		1.1
Milled tara	**69,0**		1.0
Milled and sieved tara (50-40 microns)	**70,5**		1.1

Table 25: Shrinkage temperature, leather cross-section and softness

Table 26 shows the chemical analysis of residual floats in each of the test.

Test	Suspended matter (mg/L)	Chemical oxygen demand decanted 2H (mg/L)	Chlorides (mg/L)
1. Original tara	22772	63700	33038
2. Milled tara	19773	44400	32385
3. Milled and sieved tara	11996	40600	33779

Table 26: Analysis of residual floats

As can be observed, the cuts are very similar. Despite not being clearly visible from the photographs included in table 25, there seems to be thorough penetration throughout the cross section. The extract penetration into the leather cross section was correct and the shrinkage temperature is similar in the three tests.

The decrease of suspended matter and the chemical oxygen demand is especially noticeable (almost 50% less in sample 3). Both the suspended matter and the chemical oxygen demand decreased with the smaller particle size, which is something to take into account for the objective of this thesis. However, the softness obtained is not desirable; all the test leather samples were significantly hard.

3.2.5 Conclusions part 3.2

Obtaining an extract with a high tanning content could not be accomplish through the physical modification process, as it happened with the aqueous extraction (see Section 3.1: Chemical modifications), although neither one of these decreases, and it also improves the penetration of the extract into the leather and reduces the suspended matter and the chemical oxygen demand of the residual floats.

Milling and sieving the particles to a size fraction of 50-40 microns, resulted in the best physical modification when applied on skin, the residual floats also show a great reduction on suspended matter and COD. This is why, based on the results, and taking into account the organoleptic properties of the samples, it is decided that the Milled and sieved Tara gives better results.

We believe that in order to overturn the negative aspect of softness, some improvements need to be made. This thesis will be further broadened and developed by studying different mixtures of milled and sieved tara, in the next part, using other products: quebracho, mimosa, dispersants and synthetic tannins.

3.3 Mixtures of modified Tara with different products

Given that the conclusions of section 3.2 proved that the milled and sieved Tara with particle sizes around 40-50 microns gives better results in terms of organoleptic properties and reduction of the pollutant loads of final baths; from now on, this product will be used as the basis for different applications and optimizations, and it will be referred to as Modified Tara.

In this section, different combinations of modified Tara with other products; such as vegetable tannins (quebracho and mimosa), dispersants, and synthetic tannins, have been studied with the aim of finding the best auxiliary to help reducing the astringency of the Tara, and therefore improving the penetration within the leather structure and enhancing the tanning power.

A series of trials have been developed for the application of the Milled and sieved Tara products on skin at laboratory scale to determine their tanning power, and analysing the degree of penetration, the stabilization on the skin structure, as well as the physical and organoleptic properties acquired.

The obtained pieces of leather were characterized and the result obtained allows reaching the optimization process and designing formulations of pre-tanning.

The products to be analysed correspond to different mixtures of modified Tara and vegetable extracts, synthetic tanning agents and auxiliaries, using a ratio of 2:1in all cases.

In the first place, the characterization was performed to different mixtures in terms of their theoretical tannin content. The values of said theoretical tannin content are the ones with which these products are marketed. The following table describes their composition:

Sample	Composition	% Theoretical tannins		% Theoretical tannins, mixture
		Tara	Product	
1	Modified Tara/Mimosa	47	70	52.8
2	M. Tara/Quebracho	47	70	52.8
3	M. Tara/Naphthalene sulphonic	47	49	47.6
4	M. Tara/phenolic	47	50	48.0
5	M. Tara/ Dihidroxidiphenilsulphone	47	41	44.8
6	M. Tara/sodium Pyrophosphate acid	47	-	36.1
0	Original Tara	47	-	47.0

Table 27: Theoretical tannins of the different mixtures of Milled Tara

3.3.1 Characterization of mixtures of Tara

The method used for determining the tannin content of the samples of tara or changes is the Extraction procedure of tannins in a vegetable extract, by the method of the hood, described in Annex 4.

A determination of tannins for each mixture has been conducted, so we can establish with certainty their real content of tannin. This is done to know the actual quantities, and to apply the same amount of tannins in each test, in order to perform comparable tests. The results of the characterization of the samples are the following.

Determination	1	2	3	4	5	6	0
Soluble solids (%)	66.0	67.1	72.1	72.3	87.3	57.4	57.5
Total Solids (%)	92.0	90.7	92.6	89.0	85.1	73.9	87.7
No tannins (%)	15.9	14.2	31.7	26.7	43.0	21.3	13.6
Tannins (%)	50.1	53.0	40.4	45.7	44.3	36.1	43.9
Insoluble matter (%)	25.9	23.5	20.4	16.6	0.0	16.4	30.2
Water (%)	8.0	9.3	7.4	11.0	12.7	26.2	12.3
pH	3.7	3.8	3.8	3.7	3.7	3.9	3.7

Table 28: Characterization of different mixtures of Tara

The results of theoretical and real tannic content are described in Table 29. This is a comparative study to know if there is a big difference between the two of them.

Samples	Composition	% Theoretical tannins, mixture	% Real tannins, mixture
1	Modified Tara/Mimosa	52.8	50.1
2	M. Tara/Quebracho	52.8	53.0
3	M. Tara/Naphthalene sulphonic	47.6	40.4
4	S. Tara/phenolic	48.0	45.7
5	M. Tara/Dihidroxidiphenilsulphone	44.8	44.3
6	M. Tara/Sodium Pyrophosphate acid	36.1	36.1
0	Original Tara	47.0	43.9

Table 29: Analysis of theoretical and real tannin content

There are some differences between theoretical and real tannin content. Due to the fact that the theoretical content is given by the brand, it is better to use the real figures that were obtained.

It is observed that the content of tannins in the commercial Tara is 44%.The vegetable extracts, quebracho and mimosa, increase their tannin content considerably, followed by the synthetic products like naphthalene sulphonic and phenolic.

Regarding the Dihidroxidiphenilsulphone, more than a synthetic tanning, it is considered a dispersant; this means that it favours the penetration of the tannins without reacting with the collagen in the skin.

Such is the case of the sodium pyrophosphate acid, which possesses the qualities of a dispersant, and can also act as sequestering iron.

3.3.2 Applications of mixtures on leather

We start by pickling cowhide at pH 3.5, and by weighing and measuring its thickness (2.2 / 2.5 mm). The process begins by neutralizing the pH at around 5.0, in DD Simplex Drum (10 rpm). Once neutralized, the skin is divided into several pieces of about 250 g each, which undergo pre-tannage tests.

This process is performed in Drum SIMPLEX-4 (12rpm). The process and formulation applied are described in the following table:

OPERATION	ºC	%	PRODUCT	TIME	Observation
Pre-tannage	20				
		X	**Modified Tara mixture with product**		
		7	Synthetic S-3		
		2	Sulphited oil	night	
		0.8	Formic acid	2h	pH=3.59, drain
Wash	20	300	Water	20’	drain
					repose
					Samming
					Dry on air

Table 30: Base formulation mixtures Tara

The ‘**X**’ value in table 30 is referred to the % of mixes with modified tara and the different products mentioned.

The different mixed products applied on hides in each tests, are described in the following table.

Test	Composition	%Real tannins	% Applied respect to commercial Tara
1	Modified Tara/Mimosa	50.1	7.90
2	M. Tara/Quebracho	53.0	7.45
3	M. Tara/Naphthalene sulphonic	40.4	9.80
4	M. Tara/phenolic	45.7	8.60
5	M. Tara/Dihidroxidiphenilsulphone	44.3	8.90
6	M. Tara/sodium Pyrophosphate acid	36.1	11.0
0	Original Tara	43.9	9.00

Table 31: Products and quantities applied to the test on hides

The different products are compared with the application of the original Tara (test 0). This means that a 9% of commercial tara, with 43.9% of real tannins, is applied; therefore, for each test the amount of mixture to be applied is calculated to obtain comparable results.

The shrinkage temperature of the hides is determined to evaluate their stability at the temperature. The better the hide is tanned, the higher its shrinkage temperature.

3.3.3 Results

The hides are assessed to determine the penetration values of the pre-tanning agents by observing the cuts.

The following table shows the results obtained from the tests of shrinkage temperature, hardness (softness) and appearance of the cuts of hides (penetration rating products):

Test	Composition	Ts (ºC)	Softness (mm)	Cuts photos
1	Modified Tara/Mimosa	60	1.1	
2	Modified Tara/Quebracho	59	1.0	
3	Modified Tara/ Naphthalene sulphonic	64	0.7	
4	Modified Tara/ phenolic	64	0.6	
5	Modified Tara/ Dihidroxidiphenilsulphone	62	1.1	
6	Modified Tara/ sodium Pyrophosphate acid	62	0.9	
0	Original Tara	61	0.6	

Table 32: Results of hide tests Ts, softness and cut-penetration

With respect to the penetration of the products, it did not go very well. The best shrinkage temperature observed in mixtures is with synthetics. An increase in the tanning properties could not be observed in mixtures with Sieved Tara and vegetable extracts.

The best results regarding the shrinkage temperature were observed with the naphthalene sulphonic mixture and with the phenolic syntan mixture, followed by the pyrophosphate and Dihidroxidiphenilsulphone ones.

The following table shows the results in terms of assessing the color of the hide samples:

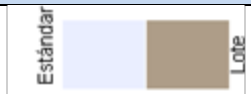
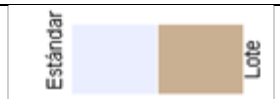
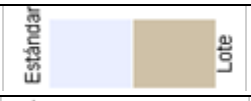
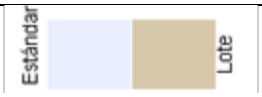
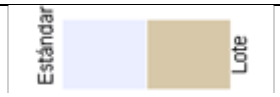
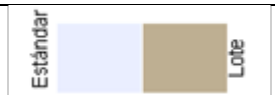
Test	Composition	Data Color				
			DL	Da	Db	Strength (%)
1	Modified Tara/Mimosa		-23.09	2.59	17.99	9108
2	M. Tara/Quebracho		-16.76	4.42	22.16	6505
3	M. Tara/ Naphthalene sulphonic		-12.61	0.39	19.39	4077
4	M. Tara/ phenolic syntan		-19.65	0.95	20.65	8092
5	M. Tara/ Dihidroxidiphenilsulphone		-10.53	0.03	20.51	3585
6	M. Tara/ sodium Pyrophosphate acid		-10.53	0.25	21.17	3749
0	Tara		-18.00	0.69	21.16	7361

Table 33: Results of skin tests Data Color

Differences in Color with respect to the Original Tara correspond to the mixtures of Tara with vegetable extracts, due to their intrinsic characteristics (brown or reddish color) and ease of oxidation. Among vegetable extracts, Tara is characterized for contributing with little coloration to the skin.

The data color test shows good results for the modified Tara and Naphthalene sulphonic mixutre, as well as with the Dihidroxidiphenilsulphone and sodium Pyrophosphate acid one.

3.3.4 Conclusions

In general, the skins obtained are rigid, and the level of penetration achieved is not the most adequate. Tests will be developed, in order to increase the mechanical effect, thus promoting penetration.

As a conclusion, the auxiliary product Naphthalene sulphonic acid has been chosen to use in the optimization of a pre-tanning process, due the results obtained in Shrinkage temperature, data color and organoleptic properties.

Sodium acid pyrophosphate also possesses dispersant qualities, and also acts as an iron sequestrate. Because good organoleptic properties of the pyrophosphate and Tara mixture have been observed, further tests will be developed using this product. And it will be evaluated, for its ability to improve the behaviour of Tara against contamination of iron

particles generated from the shaving processes of leather. Furthermore, the possibility of removing salts by decreasing the amount of sodium chloride in the tanning process will be considered.

Here is a sample of the iron sequestering power of pyrophosphate, by applying a drop of ferric chloride in the wetted surface of the leather, and by observing the color change compared with a sample of leathers without pyrophosphate.

The following photographs, shows the change of color after two hours and two weeks for trial 6 (Tara with pyrophosphate) and trial 0 (Tara alone).

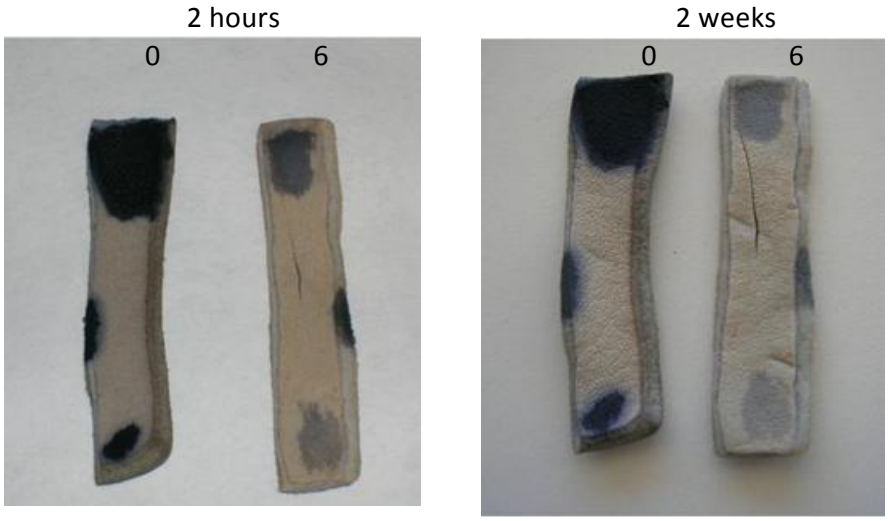


Photo 2: Ferric chloride reaction after 2 hours and after 2 weeks

Obviously, when you add iron pyrophosphate, the stain fades over time; unlike the sample alone with Tara where the stain remains and is very noticeable. This is a clear proof of the iron sequestering power of pyrophosphate, and the big importance to use it in terms of reducing the possibility of stains resulting from iron in shaving process.

3.4 Use of modified Tara as Pre-tanning agent

Considering the goals of the thesis of using Tara as sustainable tanning agent, we observe that the test with Tara alone (test 0, in 3.3) has the best results regarding light fastness. Good results were also obtained with the combinations of modified Tara tannin with the naphthalene sulphonic syntan acting as tanning auxiliary.

As concluded, naphthalene sulphonic is the most adequate based on reaching the goal of improving the penetration into the hide and the organoleptic assess.

It is assumed that the combination of: Modified Tara + naphthalene sulphonic syntan + pyrophosphate will enhance the performance of the Tara tannins, which is the aim of this thesis.

In this case, a new experimental design will be developed. By using the new modified product (Milled and sieved Tara) and a product based on the naphthalene sulphonic powder but with a higher purity and the use of oil with better penetrating power, to help the powders having a better distribution within skin. Another product to consider is the sodium acid pyrophosphate that, besides of being a good sequestering iron, it helps in the distribution of materials.

The experimental design will analyse as variables the different percentages of the two products (Modified Tara + naphthalene sulphonic syntan), in order to define the most appropriate recipe for a sustainable wet white formulation. The Pyrophosphate will remain in 4% for all tests.

This experimental design is performed with the aim of improving the formulation, using natural products (Tara) as much as possible and minimizing the use of synthetic tanning auxiliaries.

Products:

- Milled and sieved Tara (50 – 40 µm)
- Naphthalene Sulphonic syntan
- Sodium acid Pyrophosphate
- Oil (sulphited oil, used to enhance the penetration)

3.4.1 Factors to consider:

- Improved mechanical effect to enhance the penetration on skin (in pilot scale the mechanical effect is reduced by the characteristics of the drums).

- Using sodium pyrophosphate (4%) and decreasing the amount of sodium chloride to achieve 6 °Be in the pre-tanning process.
- Experimental design will be further described below
- This products has been applied together as a mix (M) as follows:

  - **X_1% Milled and sieved Tara (50 – 40 µm)**
  - **X_2% Naphthalene Sulphonic syntan**
  - **4% Pyrophosphate**

For this selection, the shrinkage temperature, the measurement of tensile strength and percentage elongation (EN ISO 3376 – IUP6) and the Measurement of tear load (EN ISO 3377-2, IUP8) were evaluated.

As discussed previously, Tara is well appreciated in the leather industry as vegetable tanning agent because its light fastness. Therefore, the influences of the components of the different mixtures on this property will be considered.

This test starts with hides pieces neutralized at pH=5, following the base formulation as follows:

OPERATION	ºC	%	PRODUCT	Gr.	TIME	OBSERVATIONS
PRETANNING	20	50	WATER + SALT			6 ºBe
		X	**MIX M_x**			
		2	Sulphited oil		Over night	Cut
		0.8	Formic acid		2h	pH=3.75
						Drain

Table 34: Base formulation for pre-tanning optimization process

The technical description of products used in this experimental design is described in annex 8.

3.4.2 Pre-tanning experimental design

The study of wet white formulations is centralized in the factorial experimental design, where two levels are defined for each factor. Two variables with two levels each (2^2) were studied, adding four central points. The variables to consider are the concentration of both Tara and synthetic naphthalene sulphonic. This design has 12 different trials.

To optimize a magnitude that depends from on one or more variables X = (x, y, …z), it is necessary to determine the values of the parameters, whose function obtains the absolute optimal, maximal or minimal values.

There are several techniques to optimize a function, but in order to simplify and better understand the behaviour of the blend; the experiments will be based on a design with a response surface.

The mathematical model of a Surface graph of a quadratic equation, centralized design, orthogonal and rotatable (Fig. 27) is described in Annex 7.

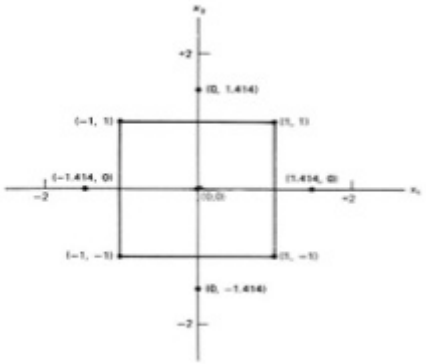


Figure 27: Surface graph of a quadratic equation, centralized design, orthogonal and rotatable

The experimental design ratios are described in this table:

Level	-1.414	-1	0	1	1.414
Milled and sieved Tara	7	7.6	9	10.4	11
Syntan	2	2.9	5	7.2	8

Table 35: Variables, levels for experimental design

Experimental factors: % of sieved tara powder and % Naphthalene sulphonic syntan added to the pre-tanning process according to the application recipe of table 35:

Test	x_1	x_2	% Tara	% Syntan
1	-1	-1	7.6	2.9
2	-1	1	7.6	7.2
3	1	-1	10.4	2.9
4	1	1	10.4	7.2
5	0	-1.414	9	2
6	0	1.414	9	8
7	-1.414	0	7	5
8	1.414	0	11	5
9	0	0	9	5
10	0	0	9	5
11	0	0	9	5
12	0	0	9	5

Table 36: % of Tara and syntans for each trial

3.4.3 Laboratory scale tests at hide samples.

This process is conducted on hide samples of 2370 g pickled (3550 g pelt weight) in a Simplex-4 Drum. The pH of these skin samples is first neutralized to = 5. Then the wash and pre-tanning assays are performed.

A bath with salt is prepared, and adjusted to reach 6°Be. Hides are introduced in the drum, after 15 minutes the pre-tannage starts with the percentages according to each of the 12 trials scheduled.

The product penetration is controlled into the skin, the shrinkage temperature is determined, and its organoleptic characteristics are measured after the drying operations conclude, and the skin samples were softened.

3.4.4 Results and Experimental Design

Results from this experimental part are summarized in table 37, as follows:

Test	**x_1**	**x_2**	**% Tara**	**% Syntan**	**Ts (ºC)**	**DSC (ºC)**	Thickness (mm)	Tear Load (Strength, N/mm)	Tensile Strength (N/mm2)	Softness Test (mm)
1	-1	-1	7.6	2.9	67,5	98,4	2,33	85,2	28,5	1,5
2	-1	1	7.6	7.2	67,5	98,2	2,32	84,6	28,2	1,5
3	1	-1	10.4	2.9	69,0	99,4	2,59	102,6	30,4	1,7
4	1	1	10.4	7.2	68,0	98,4	2,50	90,9	29,1	1,6
5	0	-1.414	9	2	71,0	100,7	2,35	111,8	37,6	1,9
6	0	1.414	9	8	67,5	98,8	2,60	80,0	24,4	1,4
7	-1.414	0	7	5	67,0	98,6	2,72	77,5	18,9	1,2
8	1.414	0	11	5	68,5	99	2,73	80,5	25,5	1,4
9	0	0	9	5	70,0	99,7	2,24	108,1	33,2	1,8
10	0	0	9	5	69,5	99,9	2,13	108,4	33,5	1,8
11	0	0	9	5	69,5	100,1	2,08	108,7	32,7	1,8
12	0	0	9	5	70,0	100	2,26	108,3	32,9	1,8

Table 37: Analysis results of Experimental part 4.2.

In this case, as can be seen for the Shrinkage Temperature, no significant differences were found, so a DSC (Differential Scanning Calorimeter) analysis was performed on dry leather to see if it yielded better results.

DSC is an instrument for measuring the dry temperature at which the leather undergoes a state change. In this case, it can be said that the leather shows a denaturalized structure.

All results were submitted to the Statgraphics Plus version 5.1, using the Simplex method.

To analyse the results of this design, it is first necessary to look at the ANOVA table, which tells us if these variables (%Tara and % synthetic) are statistically influenced by the Shrinkage Temperature (Ts), the Tear Resistance, the Tensile Strength, and the Softness test.

Tables and figures from Statgraphics of this Experimental Design are described next.

3.4.4.1 Statistical analysis of Experimental Design for Shrinkage Temperature (Ts)

The following Anova table shows each of the estimated effects and interactions. It also shows the standard error of each of the effects, which measures their sampling error. It then evaluates the statistical significance of each effect by comparing the mean square with an estimate of the experimental error.

Analysis of Variance for Ts

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	2,12316	1	2,12316	4,71	0,0729
B: Syntan	4,42493	1	4,42493	9,83	0,0202
AA	8,10001	1	8,10001	17,99	0,0054
AB	0,25	1	0,25	0,56	0,4844
BB	0,899998	1	0,899998	2,00	0,2072
Total error	2,7019	6	0,450316		
Total (corr.)	17,75	11			

Table 38: Analysis of variance for Ts

R-squared = 84,7781 percent
R-squared (adjusted for d.f.) = 72,0931 percent
Standard Error of Est. = 0,671056
Mean absolute error = 0,405943
Durbin-Watson statistic = 2,37398 (P=0,2319)
Lag 1 residual autocorrelation = -0,296779

In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. These effects are B: Syntan and the interaction AA.

The R-Squared statistic indicates that the model as fitted explains 84,7781% of the variability in Ts. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 72,0931%. The standard error of the estimate shows the standard deviation of the residuals to be 0,671056. The mean

absolute error (MAE) of 0,405943 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart, shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Ts.

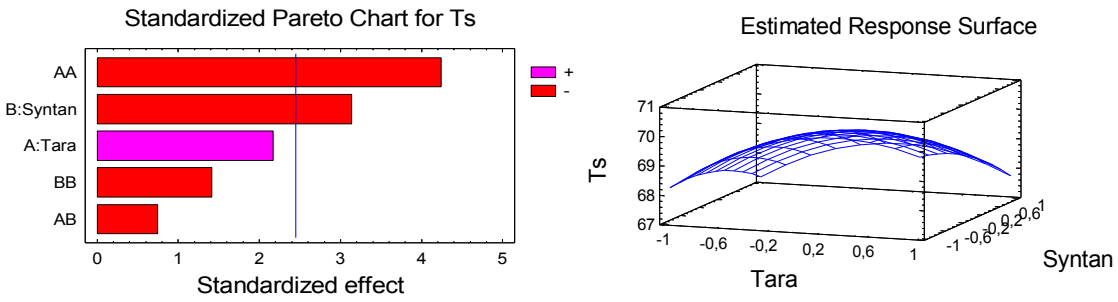


Figure 28: Standardized Pareto Chart and Response surface for Ts.

The values AA and B: syntan are statistically significant, but in this case in a negative way, which means that the higher the amount of synthetic and Tara the lower the Ts is.

Excluding the values that are not statistically significant (P-value >0.05), the optimization tables and the Regression equation comes like this:

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is:

Ts = 69,45 - 0,743719*Syntan - 1,05001*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Ts
Goal: maximize Ts
Optimum value = 70,5018

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 39: Optimize response for Ts.

This table shows the combination of factor levels, which maximizes Ts over the indicated region.

For a better understanding of the previous table, it is important to remember that the value 0,0 for Tara factor is the central point, representing 9%; and that the value -1,41421 represents the minor value for Syntan, which is 2%.

3.4.4.2 Statistical analysis of Experimental Design for DSC (Differential Scanning Calorimeter)

The following Anova table shows each of the estimated effects and interactions. Also shown is the standard error of each of these effects, which measures their sampling error. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error.

Analysis of Variance for DSC

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	0,389706	1	0,389706	1,76	0,2324
B: Syntan	1,8886	1	1,8886	8,55	0,0265
AA	3,42226	1	3,42226	15,49	0,0077
AB	0,16	1	0,16	0,72	0,4274
BB	0,420251	1	0,420251	1,90	0,2170
Total error	1,32543	6	0,220905		
Total (corr.)	7,26667	11			

Table 40: Analysis of variance for DSC

R-squared = 81,7601 percent
R-squared (adjusted for d.f.) = 66,5602 percent
Standard Error of Est. = 0,470005
Mean absolute error = 0,266665
Durbin-Watson statistic = 1,15775 (P=0,0541)
Lag 1 residual autocorrelation = 0,28199

In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. These effects are B: Syntan and the interaction AA.

The R-Squared statistic indicates that the model as fitted explains 81,7601% of the variability in DSC. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 66,5602%. The standard error of the estimate shows the standard deviation of the residuals to be 0,470005. The mean absolute error (MAE) of 0,266665 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in the data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the DSC.

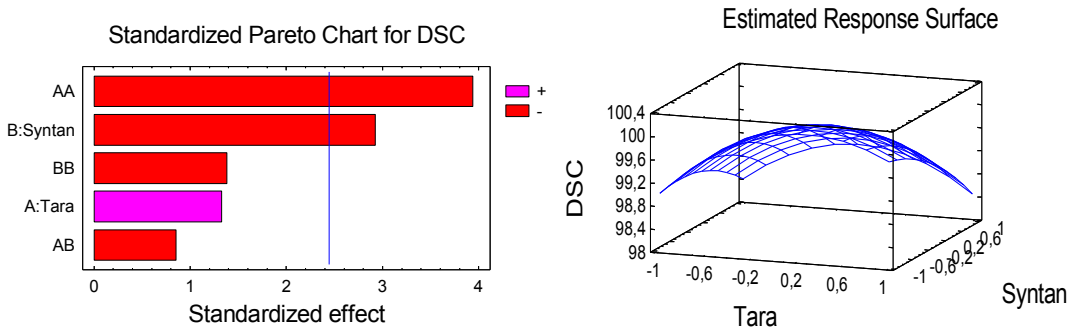


Figure 29: Standardized Pareto Chart and Response surface for DSC.

The values AA and B: syntan are statistically significant, but in this case in a negative way, which means that the higher the amount of synthetic and Tara the lower the DSC is.

By excluding the values that are not statistically significant the optimization tables and the Regression Coefficients come like this:

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is:

DSC = 99,72 - 0,485876*Syntan - 0,680004*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response

Goal: maximize DSC

Optimum value = 100,407

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 41: Optimize response for DSC.

This table shows the combination of factor levels, which maximizes DSC over the indicated region.

For a better understanding of the previous table, is important to remember that the value 0,0 for Tara factor is the central point representing 9%; and the value -1,41421 represents the minor value for Syntan, which is 2%.

3.4.4.3 Statistical analysis of Experimental Design for Tensile Strength

The following Anova table shows each of the estimated effects and interactions. Also shown is the standard error of each of these effects, which measures their sampling error. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error.

Analysis of Variance for Tensile strength

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	18,4036	1	18,4036	2,04	0,2031
B: Syntan	51,3469	1	51,3469	5,69	0,0543
AA	148,996	1	148,996	16,52	0,0066
AB	0,25	1	0,25	0,03	0,8732
BB	1,15594	1	1,15594	0,13	0,7326
Total error	54,1222	6	9,02036		
Total (corr.)	275,063	11			

Table 42: Analysis of variance for Tensile Strength

R-squared = 80,3237 percent
R-squared (adjusted for d.f.) = 63,9267 percent
Standard Error of Est. = 3,00339
Mean absolute error = 1,50985
Durbin-Watson statistic = 2,17682 (P=0,3492)
Lag 1 residual autocorrelation = -0,0887702

In this case, 1 effect has P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. That effect is the interaction AA.

The R-Squared statistic indicates that the model as fitted explains 80,3237% of the variability in Tensile strength. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 63,9267%. The standard error of the estimate shows the standard deviation of the residuals to be 3,00339. The mean absolute error (MAE) of 1,50985 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Tensile Strength.

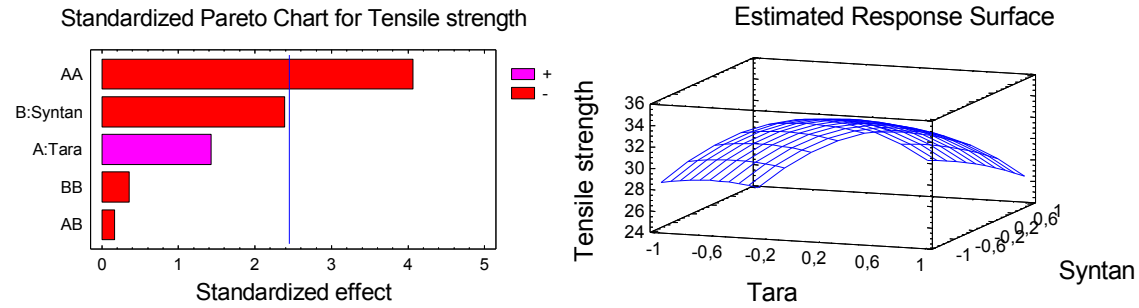


Figure 30: Standardized Pareto Chart and Response surface for Tensile Strength.

The value AA is statistically significant, but in a negative way, which means that the higher the amount of Tara the lower the Tensile Strength. For the next step we decided not to exclude the value B: Syntan, because the p-value is too close to 0.05.

By excluding the values that are not statistically significant the optimization tables and the Regression Coefficients come like this:

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is:

Tensile strength = 32,735 - 2,53345*Syntan - 4,74002*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Tensile Strength
Goal: maximize Tensile strength
Optimum value = 36,3178

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 43: Optimize response for Tensile Strength.

This table shows the combination of factor levels, which maximizes Tensile strength over the indicated region.

For a better understanding of the previous table, it is important to remind that the value 0,0 for Tara factor is the central point representing 9%; and the value -1,41421 represents the minor value for Syntan, which is 2%.

3.4.4.4 Statistical analysis of Experimental Design for Tear Load

The following Anova table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error.

Analysis of Variance for Tear load

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	97,7388	1	97,7388	2,87	0,1414
B: Syntan	411,141	1	411,141	12,06	0,0133
AA	1227,11	1	1227,11	35,98	0,0010
AB	30,6916	1	30,6916	0,90	0,3794
BB	185,2	1	185,2	5,43	0,0586
Total error	204,629	6	34,1048		
Total (corr.)	2016,72	11			

Table 44: Analysis of variance for Tear Load.

R-squared = 89,8534 percent
R-squared (adjusted for d.f.) = 81,3979 percent
Standard Error of Est. = 5,83994
Mean absolute error = 2,96745
Durbin-Watson statistic = 2,21547 (P=0,3247)
Lag 1 residual autocorrelation = -0,165279

In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. These effects are B: Syntan and the interaction AA.

The R-Squared statistic indicates that the model as fitted explains 89,8534% of the variability in Tear load. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 81,3979%. The standard error of the estimate shows the standard deviation of the residuals to be 5,83994. The mean absolute error (MAE) of 2,96745 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based in the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart, shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Tear Load.

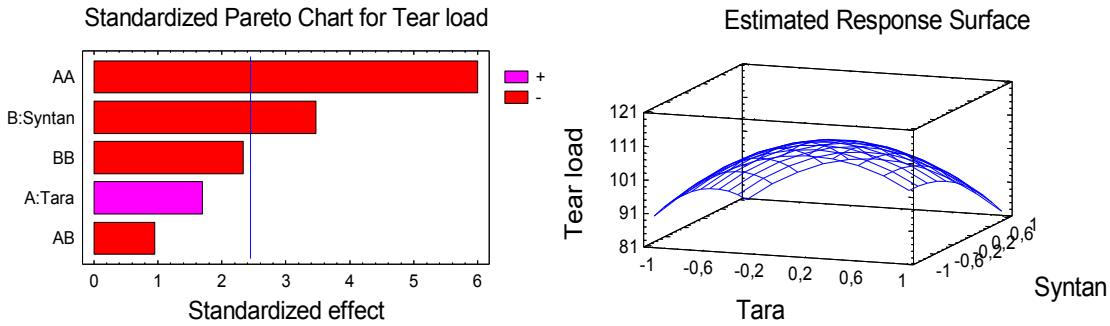


Figure 31: Standardized Pareto Chart and Response surface for Tear Load.

The values AA and B: syntan are statistically significant, but in this case in a negative way, which means that the higher the amount of synthetic and Tara the lower the Tear Load is.

By excluding the values that are not statistically significant the optimization tables and the Regression Coefficients come like this:

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is:

Tear load = 104,072 - 7,16888*Syntan - 12,7711*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Tear Load
Goal: maximize Tear load
Optimum value = 114.21

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 45: Optimize response for Tear Load.

This table shows the combination of factor levels, which maximizes Tear load over the indicated region.

For a better understanding of the previous table, it is important to remember that the value 0,0 for Tara factor is the central point representing 9%; and the value -1,41421 represent the minor value for Syntan, which is 2%.

3.4.4.5 Statistical analysis of Experimental Design for Softness test

The following Anova table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error. It

then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error.

Analysis of Variance for Softness

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	0,0424632	1	0,0424632	3,85	0,0973
B: Syntan	0,0814275	1	0,0814275	7,39	0,0347
AA	0,323999	1	0,323999	29,41	0,0016
AB	0,0025	1	0,0025	0,23	0,6507
BB	0,0159997	1	0,0159997	1,45	0,2736
Total error	0,0661098	6	0,0110183		

Table 46: Analysis of variance for Softness Test

R-squared = 87,2045 percent
R-squared (adjusted for d.f.) = 76,5417 percent
Standard Error of Est. = 0,104968
Mean absolute error = 0,0515168
Durbin-Watson statistic = 2,0258 (P=0,4496)
Lag 1 residual autocorrelation = -0,0188444

In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. These effects are B: Syntan and the interaction AA.

The R-Squared statistic indicates that the model as fitted explains 7,2045% of the variability in Softness. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 76,5417%. The standard error of the estimate shows the standard deviation of the residuals to be 0,104968. The mean absolute error (MAE) of 0,0515168 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in the data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Softness.

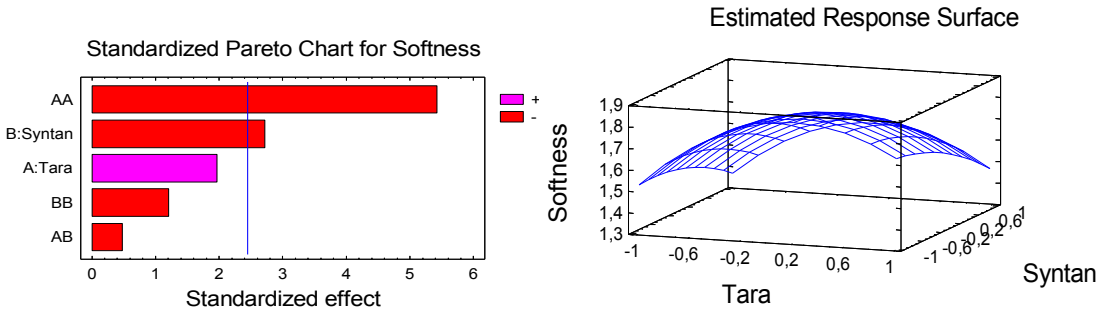


Figure 32: Standardized Pareto Chart and Response surface for Softness Test.

The values AA and B: syntan are statistically significant, but in this case in a negative way, which means that the higher the amount of synthetic and Tara the lower the Softness is.

By excluding the values that are not statistically significant the optimization tables and the Regression Coefficients come like this:

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is:

Softness = 1,76 - 0,100888*Syntan - 0,215001*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Softness Test
Goal: maximize Softness
Optimum value = 1,90268

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 47: Optimize response for Softness Test.

This table shows the combination of factor levels, which maximizes Softness over the indicated region.

For a better understanding of the previous table, it is important to remind that the value 0,0 for Tara factor is the central point representing 9%; and the value -1,41421 represents the minor value for Syntan, which is 2%.

Light fastness is another analysis done for this experimental design.

6 5 4 3 2 1 1 2 3 4 5 6

Photo 3: Light Fastness for experimental part 4.2(samples 1-6)

12 11 10 9 8 7 7 8 9 10 11 12

Photo 4: Light Fastness for experimental part 4.2, (samples 7-12)

As can be seen, there is a change of color in all processes; nevertheless, they are too similar to each other, which makes it too difficult to assess and make a conclusion in light fastness basis. However, even when changes can be observed, there are not final colors that are too dark.

Three different technicians assessed all pieces of leathers; they are members of the European project party, and their impressions about organoleptic Fullness, Smooth feel and Tightness are described in Table 48. Taking into account that the symbols '+' means that the leather has a better behaviour against each analysis. There is a scale for this analysis, each technician simply asked to put more or less symbols '+' to each sample.

Test	x_1	x_2	% Tara	% Syntan	Fullness	Smooth feel	Tightness
1	-1	-1	7.6	2.9			
2	-1	1	7.6	7.2	++	+++	++
3	1	-1	10.4	2.9	++		
4	1	1	10.4	7.2			
5	0	-1.414	9	2	+++ +++	+++, +++, +++	+++, +++
6	0	1.414	9	8			
7	-1.414	0	7	5			
8	1.414	0	11	5			
9	0	0	9	5	+++	+++	
10	0	0	9	5			
11	0	0	9	5	+++	+++	
12	0	0	9	5			

Table 48: Assessment of three different technicians, in order to obtain organoleptic

The Optimization tables from Experimental design (Statgraphics) represent the best-fitted value and these are summarized as follows:

- **Optimize Response for Ts**

Goal: maximize Ts

Optimum value = 70,5018

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 40: Optimize response for Ts.

- **Optimize Response for DSC**

Goal: maximize DSC

Optimum value = 100,407

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 44: Optimize response for DSC.

- **Optimize Response for Tensile Strength**

Goal: maximize Tensile strength

Optimum value = 36,3178

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 48: Optimize response for Tensile Strength.

- **Optimize Response for Tear Load**

Goal: maximize Tear load

Optimum value = 114,21

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 52: Optimize response for Tear Load.

- **Optimize Response for Softness Test**

Goal: maximize Softness

Optimum value = 1,90268

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 56: Optimize response for Softness Test.

The values 0,0 for Milled and sieved Tara means 9%; and the values -1.414 for syntan naphthalene sulphonic means 2% in the Mix.

As a conclusion, it can be said that the optimal values obtained in the statistical program represent the trial number 5, which is also presented along with a SEM (Scanning electronic microscope) photo of the sample.

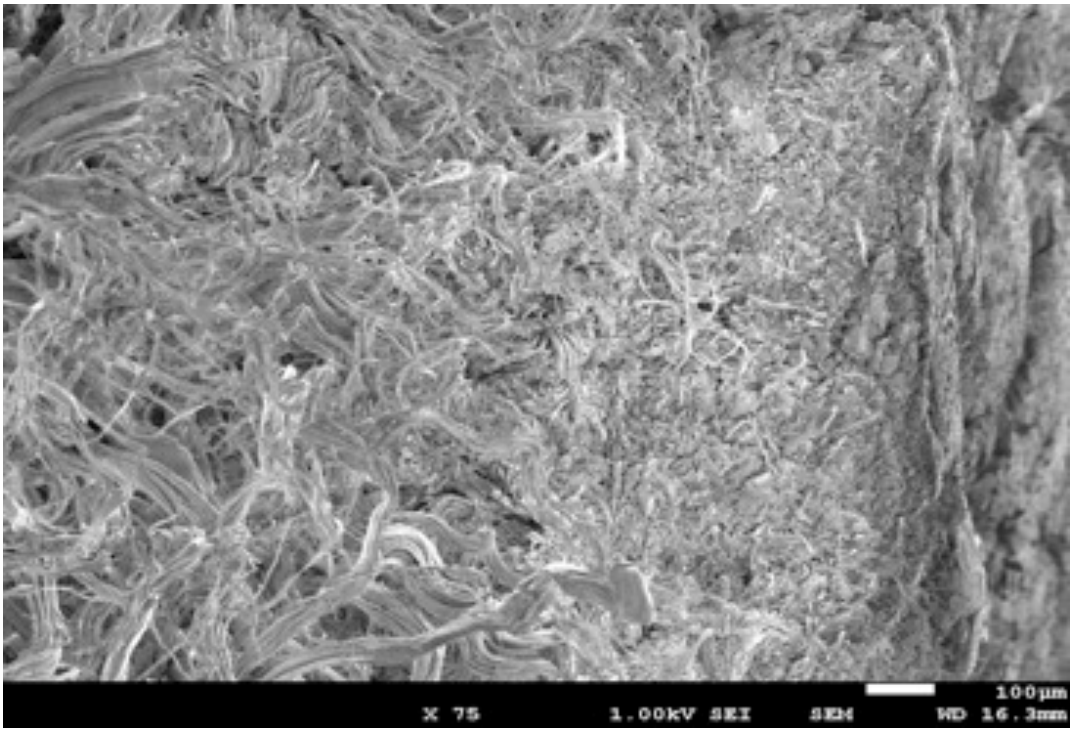


Photo 5: SEM photo of the optimal trial number 5 (right side is the grain side) (75x)

The compactness of the fibrils can be noticed, as and it can be seen that the products used in the pre-tanning process penetrated uniformly.

In a general way, you can see a difference between fibers as the right side of the photo (grain) is the most compact and closed while the left side is more open fibers, which is completely normal within the structure of skin.

3.4.5 Conclusions

Upon analysing the statistical results from Statgraphics, and the organoleptic evaluations performed by three different tanning technicians; and bearing in mind that the goal is to reduce the volume of material, it can be concluded that the optimum percentage for Milled and sieved Tara (50 – 40 µm) and naphthalene sulphonic synthetic, is the following:

9% Milled and Sieved Tara (50 – 40 µm)
2% Naphthalene sulphonic Syntan

These values correspond to the test number 5. In terms of all Mix, this percentage means the following:

81.81% Milled and sieved Tara
18.18% of Naphthalene sulphonic Syntan

Based on the objectives of this thesis, which are the use of sustainable products and the reduction in the use of synthetic auxiliary products; it can be said that the goal was accomplished, and therefore the use of natural products increased, in this case the Tara. It shall be noted that the changes made in the Tara powder are physical ones, and do not need extra chemicals to be manufacture, such as synthetic products so they will not be subject to revision, as defined by Reach.

Due to the optimal values achieved , which, compared to those obtained in previous studies (64% Original Tara and 36% of syntan), we can say that there is a decrease of around 20% in the use of synthetic products.

3.5 Characterization of pre-tanning process

The results obtained from the experimental design of section 3.4, which were made with mixtures of modified Tara, Synthetic naphthalene sulphonic and sodium acid pyrophosphate, it can be concluded that the following percentages can be applied (Mix M_1):

9% Modified Tara
2% Naphthalene sulphonic Synthetic
4% Sodium acid pyrophosphate

Then a test was done with the optimal formulation found, using hide sides in a pilot scale drums. The aim is to check the repeatability of the experimental design on a scale larger than laboratory scale.

A comparison was also made with a conventional WW process, using glutaraldehyde as a pre-tanning agent. The idea is to compare the appearance of leather and, most importantly, the final pre-tanning baths and a possible environmental improvement.

3.5.1 Procedure

The hides were collected in pelt, then a de-liming, bating and pickle process were performed in laboratory, following a standard formulation.

A standard neutralization is performed with all hides (including the one with enzymatic pre-treatment) in the same drum to homogenize them and to obtain a pH value of around 5.0, which has proven to be the optimum value to work with Tara.

		WET PHASE				
		Nº:		Date:		13/12/12
		Enterprise:	I+D Lowest	Hides:		3 Bovine sides
		Article:	**Neutralizing**	Status:		Pickled
		Technician:	JDM	% (Weight):		Hide
		Drum	Simplex - 4	Weight (gr):		21.71 kg
OPERATION	**ºC**	**%**	**PRODUCT**	**Gr.**	**TIME**	**OBSERVATIONS**
NEUTRALIZING	20	50	Water	3400		
		4	Salt	272	10’	ºBé= 6
		0.7	Sodium Formate	47.6		
		0.5	Sodium bicarbonate	34	2H	
		0.4	Sodium bicarbonate	27.2	Night	pH=5.05
						Drain
Rinse	20	300	Water		20’	Drain

Table 49: Neutralizing process

The formula of pretanning was performed as found in the previous experimental design and showed next:

		WET PHASE				
		Nº:		Date:		13/12/12
		Enterprise:	I+D Lowest	Hides:		3 Bovine sides
		Article:	**Pre-tanning**	Status:		Neutralized
		Technician:	JDM	% (Weight):		Hide
		Drum	Simplex - 4	Weight (gr):		21.71 kg
OPERACIÓN	**ºC**	**%**	**PRODUCTO**	**Gr.**	**TIEMPO**	**OBSERVACIONES**
PRE-TANNING	20	50	Water + salt			
					15’	ºBé= 10
		9%Tara- 2%Naphthalene 4% Pyrophosphate	Mix M_1	3.906 k		
		2	Phosphoric ester		Night	pH= 4.32
		0.8	Formic Acid		2h	pH=3,69
						Drain
Wash	20	300	Water		20’	Drain
						Horse up
						Sammy
						Air dry

Table 50: Base formulation for pre-tanning

The pre-tanning was performed with all the hides together in the same drum, subsequently, these were sent to a tannery to undergo the Sammy and shaving process.

A final tanning bath was taken and a chemical analysis was performed. The pre-tanning formulation was strictly followed, according to the latest experimental design.

At the end of the pre-tanning process, a check was made, and it could be confirmed that the penetration of the product was very good and showed the characteristic color of Tara; however, insoluble matter appeared over the leather.

One of the biggest concerns in this research project is the fact that the Tara tannin forms complex with iron, represented by black spots on the leather. The iron particles generally come from the blades of the shaving or samming machines; hence the importance of using sodium pyrophosphate acid as an iron sequestering.

After the shaving process the flesh-side was monitored to check for iron stains. Although a couple of spots were seen, after a couple of days when these underwent re-tanning, the iron stains had disappeared. Pictured below are the photographs of the final product.

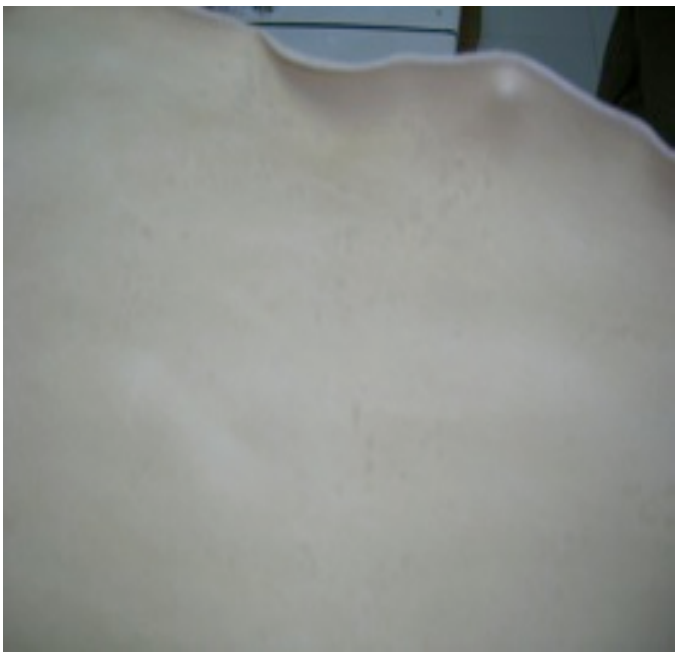


Photo 6: Light iron spots after shaving.

Here is the importance of sodium pyrophosphate acid, in terms of reducing the possible stains from iron particles, is once again emphasized. After a while the little spots were gone.

To make the comparison with a conventional wet-white process with glutaraldehyde as the main pre-tanning agent, it is necessary to perform the process in the same pilot scale.

This is said to be a conventional process, because it is a process that is actually performed in the tanneries that gave us this formulation. This process may slightly vary from one tannery to another; however, we decided to carry out a process that is currently used. A bovine hide on pickle was taken and the following process was performed.

	Conventional pre-tanning process			
	Nº:		Date:	19/03/2012
	Enterprise:	I+D Lowest	Hides:	1 hide
	Article:	Pre-tanning	Status:	Pickle pH 3,2
	Technician:		% (Weight):	Pelt (pickle x 1,5)
	Drum	Italprogetti nº 2	Weight (gr):	

OPERACIÓN	ºC	%	Product	Kg	Time	Observations
Pre-tanning	20	50	Agua			
		5	Sal		15'	ºBé=6
						pH=3.2
		2.5	**Glutaraldehyde 50%, exempt from free formaldehyde**		3,5h	pH= 4,2-4,4
		5	Synthetic sulfone type		5h	pH= 4,0-4,2
Rinse	20	300	Water		20’	Drain
						Horse up
						Sammy

Table 51: Base formulation for a conventional pre-tanning process with glutaraldehyde

The pre-tanned leather seemed to be very good, with good appearance. The leather was sent to Sammy and shaved process to a tannery. A final bath was taken and assessed to compare it with the new process.

The shaved leathers returned to the laboratory for the re-tanning, dying and fatliquoring processes, following the formulations gave by a Chemical supplier. These processes are presented in the following chapter 4.

3.5.2 Results of pre-tanning

The comparison of results is important because it provides us with a general overview of where we are heading. It is not just about proving that the modified product works on the skin, but is also important to check if the resulting leather and the process to create it are competitive against one that is completely demonstrated and currently used.

The next table shows the results of the chemical analysis, of a final bath taken from the pre-tanning process. If we compare the results of this bath with those results from pre-tanning process made in section 3.2 with original Tara, it can be seen a huge difference, by reducing the values of the new process on suspended matter, COD, tannins, etc. However, the following table shows a comparison with a conventional process. The results are noticeable in the next table.

Determination	**Tara WW**	**Conventional WW**	Units	Intern method
pH	3.8	4.3		
Suspended matter (M.E.S.)	7976	9097	mg/L	UNE-EN 872:2006
Chemical Oxygen Demands Kit. Decanted	25560	32550	mgO_2/L	Kit Merck
Organic Nitrogen Ammonia Kit	390	362	mgN/L	Kit Merck
Conductivity	69855	78315	µS/cm	UNE-EN 27888:1994

Table 52: Results from Chemical determination of final floats comparing one process with modified Tara and the conventional one.

The values for the new pre-tanning process with modified Tara show a clear decrease in almost every determination. In the case of COD there is a reduction of about 21%, which highlights the improvements obtained from using a natural product, as opposed to the use of a chemically synthesized product.

It has been said that glutaraldehyde products pose a risk to workers' health if not handled properly, and now we can see that the wastewater from the conventional pre-tanning processes has a higher amount of COD.

The values of suspended matter have also decreased; this could be due to the fact that the synthetic tannin used in the conventional process presents high insoluble matter. It is important to say, that 5% of the syntans used (Synthetic sulfone type) in the conventional process, is the minimal measure that can be used, because technicians recommend a 5-7% range, which could increase the suspended matter.

The organic nitrogen gives slightly higher values for the new process; though regarding conductivity, we achieve opposite results as these latter decreases with the new process, but the difference is negligible.

Also a determination of tannins has been made for the new process with modified tara, in order to determine the tannin exhaustion on final baths.

Determination	Tara WW	Units	Intern method
Solids	16.6	%	
Ashes a 500º	7.5		
pH Analytic Solution	4.0	%	Hood method
Soluble solids	9.1	%	
Total solids	9.3	%	
No tannins	8.3	%	
Tannins	0.8	%	
Insoluble	0.7	%	
Water	90.2	%	
pH Solution 100%	3.8		
Density	9.7	ºBe	

Table 53: Results from tannins determination of new pre-tanning final floats

As can be see, there is a small value on tannin (0.8%), which makes us notice the great penetration of the tannins into the leather structure.

This tannin determination has been made to determine the penetration improvement of Tara. For the conventional process with glutaraldehyde, there is no need to determine the tannin content in final baths.

3.5.3 Conclusions

It was important to carry out this comparison, because not only did we have to determine what the optimal mix between the modified tara and synthetic agents was for the formulation, but we also had to determine whether we'd be able to perform this process at a higher scale and place it on the market.

It is also important to determine that the optimum process found with the experimental design, can be brought to a pilot scale and may even give better values than the ones obtained from laboratory scale in final floats determinations. This may be due to volume increase and the mechanical effect.

The comparative between the conventional and new pre-tanning process showed an environmental improvement for the new one. As told, there is a decrement in COD and suspended matter in the new process with modified Tara.

These differences between processes are analysed more deeply in chapter four where a quality, economic and life cycle assessment is performed.

CHAPTER 4- QUALITY, ECONOMIC AND ENVIRONMENTAL ASSESMENTS

4.1 Manufacture of automotive leather

Since the use of the modified Tara as pre-tanning agent has been proven, the pre tanned leather needs to be finished, and then manufacture final articles with the aim to determine whether these meet the parameters set by different regulations. At the end, this will tell us, if the use of modified Tara, can really be marketed and used in the industry as a replacement for some of the less sustainable products currently used.

The aim of this section is to use the modified Tara obtained from chapter 3 for the manufacture of automotive upholstery leather articles.

Currently, the Tara powder is greatly used in the re-tanning of automotive upholstery leather all over the world, and the demand of this kind of leather is increasing. This is why we have focused on this type of leather, even if it could also be perfectly applied to all kinds of leather articles and footwear.

Once the leathers are pre-tanned, continues with the process of re-tanning, dyeing and fatliquoring. Applying recipes gave by a member of the project.

The leather obtained from the conventional pre-tanning, is also prepared for the re-tanning, dyeing and fatliquoring processes; following a real formulation provided by a tannery like in the pre-tanning process. Both formulas are different and described below.

4.1.1 Re-tanning, dyeing and fatliquoring process of WW leather with modified Tara

The following formulation is applied taking into account the characteristics needed for automotive leather upholstery, such as good fullness and compactness in all areas of the leather as well as a uniform dye and a good smoothness.

It shall be noted that we need to use materials with excellent physical performance, with high light fastness, low fog oils, stitch resistance, etc. considering that the conditions undergone by automotive leather upholstery are extreme, like high temperatures, friction and general use.

Thinking of a possible use of the optimal mixture achieved in section 3.4 (9% modified Tara, 2% naphthalene sulphonic syntan and, 4% pyrophosphate), as one product in a pack, it has been used as part of the re-tanning in the new process.

Pre-tanned leathers are shaved at 1.2 mm. The percentages on next recipe are in shaved leather weight based. Leathers are re-tanned according to next formulation.

		RE-TANNING, DYEING AND FATLIQUORING FOR AUTOMOTIVE LEATHER				
		Nº:		Date:		13/01/13
		Enterprise:	I+D Lowest	Hides:		Bovine side
		Article:	**Automotive**	Status:		WW
		Technical:	JDM	% (weight):		Shaved
		Drum	Simplex - 4	Peso (gr):		
OPERATION	**°C**	**%**	**PRODUCT**	**Gr.**	**TIME**	**OBSERVATIONS**
Wash	20	200	Water			
		0,5	Oxalic Acid		**20'**	
						Drain and wash
Neutralizing	25	60	Water			
		1	Sodium Formate		**60'**	pH= 4,2/4,4
		0.5	Sodium Bicarbonate		**60'**	pH final= 4.7
Re-tanning		5	**Compact Product ***			
		2	Naphthalene sulphonic syntan		**30'**	
		3	Sulphited synthetic oil			
		3	Lecithin		**30'**	
Main Re-tanning	30	50	Water		**5'**	
		3	Naphthalene sulphonic syntan			
		5	Modified Tara		**60'**	
		1	Dye			
		4	Naphthalene sulphonic syntan			
		6	Modified Tara		**2 hr**	
	50	50	Water		**5'**	
Fatliquoring		2	Sulphited synthetic oil			
		2	Lecithin			
		2	Sulphated oil		**2 hr**	
						Over night
						R-10' stop 45'
		1	Formic Acid		**60'**	pH = 3,6/3,8-
						Drain
	45	150	Water At 45 ºC			
		2	Sulphited synthetic oil			
		2	Lecithin			
		4	Sulphated oil		**60'**	
		1	Formic Acid		**30'**	pH final = 3.50
	30	200	Water At 30			Drain and wash

Table 54: Re-tanning, dyeing and fatliquoring process for a new automotive leather article

* The compact product refers to the combination of 9% modified tara, 2% Synthetic naphthalene sulphonic and 4% Sodium Acid Pyrophosphate. The wet leather is submitted to a series of processes till dry, like horse up, samming, toggling for 3 hours and stacking.

4.1.2 Re-tanning, dyeing and fatliquoring process of WW leather with glutaraldehyde (Conventional process)

	RE-TANNING, DYEING AND FATLIQUORING FOR AUTOMOTIVE LEATHER					
	Nº :		12_001020	Date:		22/03/2012
	Enterprise:		I + D Lowest	Hides:		1 bovine hide
	Article:		**WW Automotive**	Status:		WW Shaved
	Technician:		JDM	% (weight):		WW Shaved
	Drum:		Italprogetti nº 2	Weight (Kg):		5,0
OPERATION	**ºC**	**%**	**PRODUCT**	**Kg**	**TIME**	**OBSERVATIONS**
WASH	30	200	Water	10,00	10'	Drain
NEUTRALIZING	30	200	Water	10,00		
		1	Sodium formate	0,020		
		0,5	Sodium bicarbonate	0,020	20'	pH= 5,0
RE-TANNING		10	Phenol syntan	0,500	30'	
		5	Tara	0,250	30'	
		2	Resin syntan	0,100	40'	
		10	Phenol syntan	0,500	30'	
		5	Tara	0,250	30'	
		1	Dye	0,050	3h	
					Night	Cut trough
		1	Formic acid (1:10)	0,050	60'	pH= 3,8, DRAIN
WASHING	50	200	Water	10,00		
FATLIQUORING	50	200	Water	10,00		
		4	Combination of Synthetic and natural oil	0,200		
		8	Low fog oil	0,400	60'	
		1,5	Formic acid (1:10)	0,075	30'	pH= 3,8
						Drain
WASH	40	200	Water	10,00	10'	Drain
						Rest horse-up
						Samming machine, air dry

Table 55: Re-tanning, dyeing and fatliquoring process for a conventional automotive leather article

The wet leather is submitted to a series of processes till dry, like horse up, samming, toggling for 3 hours and stacking.

4.1.3 Observations

As can be seen, there are some changes between the two processes; however, they both aim at obtaining the same final leather article. *

These kinds of differences are a good example of what happens in real life, each tannery performs different processes, and there are different ways of doing things.

The new process formulation to re-tan WW leather with tara, has been developed by the project team and this, in turn, was reevaluated by a couple of technical experts in the tanning sector.

We took into consideration the fact that this pre-tanned leather is treated with modified Tara, given that the objective is to use the least amount of synthetic and as much as possible natural products.

In this case, Tara is the main re-tanning agent and the synthetic naphthalene sulphonic acid was used as an auxiliary, following the path of the new pre-tanning process.

During the conventional process, the re-tanning process is a real formulation commonly used. So we can compare a new process that uses Tara as a main re-tanning agent with a conventional process.

For the recipes there are some technical sheets in Annex 8, for most of the products used in these tables.

Once re-tanned and fatliquoring the automotive upholstery leathers were machined in tannery, where they made the Sammy process and the toggling process till dry. Later they were staked in Machine.

When they were collected seemed rigid so they were sent to tannery for conditioning and later stake, which was a big improvement.

The organoleptic assessment was done, and the conclusion that both processes are similar in terms of appearance, fulfilment, and softness. This makes us notice that the chemical and physical tests, presented below, will mark the differences.

* From now on we will refer to the complete process of re-tanning, dyeing and fatliquoring only as “re-tanning”.

4.1.4 Results of re-tanning processes

The following table shows the results of the chemical analysis, of a final float taken from the re-tanning processes. There are chemical analysis done for the conventional process, and the comparative are showed next.

Determination	**Tara WW**	**Conventional WW**	Units	Intern method
pH	3.7	3.5		
Suspended matter (M.E.S.)	2245	2641	mg/L	UNE-EN 872:2006
Chemical Oxygen Demands Kit. Decanted	29852	35120	mgO_2/L	Kit Merck
Cr total	<3.0	<3.0	mgO_2/L	Kit Merck
Organic Nitrogen Ammonia Kit	314.5	370	mgN/L	Kit Merck
Conductivity	15667	14702	µS/cm	UNE-EN 27888:1994

Table 56: Results from Chemical determination of final floats comparing one process with modified Tara and the conventional one.

We could determine, once again, that there is a big difference among these processes in almost every determination. The increase of suspended matter and COD in the conventional process took place because of the great quantity of phenol syntan used.

The use of naphthalene sulphonic syntan as an auxiliary in the new re-tanning process is a difference maker in terms of better penetration of the products into the leather and therefore a decrease in COD and Suspended matter in the wastewater.

Determinations of total chromium are commonly conducted in the analysis of the re-tanning baths; however, as expected in this case, chromium was not detected.

Physical tests were carried out and compared. Results are presented in following table.

Determination	**Tara WW**	**Conventional WW**	Minimum	Unit	Intern method
Thickness	1,46	1,35		mm	IUP-4 / EN ISO 2589
Tensile Strength					IUP-6 / ISO 3376
Strength	259,90	249.90	100	N	
Elongation at break	46,70	44,40	35-60	%	
Tear Resistance	107,10	61,90	40	N/mm	IUP -8/ ISO3377
Softness test	3	3		mm	IUP -36/ EN ISO 17235
Shrinkage Temperature (Ts)	74	79		ºC	IUP -16 / ISO 3380
DSC (dry leather)	118	120		ºC	

Table 57: Automotive Upholstery physical tests

As can be seen, all results are within the parameters (minimum); so it is evident that the leather articles meet the standards and could be marketed.

Both processes show little differences in terms of Tensile Strength (strength and elongation at break), Shrinkage temperature, DSC, and softness test. However, Tear resistance shows a huge difference, of about 40% more for the new process.

It remains unclear what provokes the increase in tear strength, because any product used in the re-tanning process could inflict it. However, we believe that high percentages of vegetable tannin in the WW process with modified Tara, increase the resistance considerably, as it is well known in vegetable tanning.

4.1.5 SEM photos of automotive upholstery leather

There are some SEM photos of the leather articles. The following pictures are from the new process of automotive upholstery leather (75x and 40x), showing a cross section of the leather.

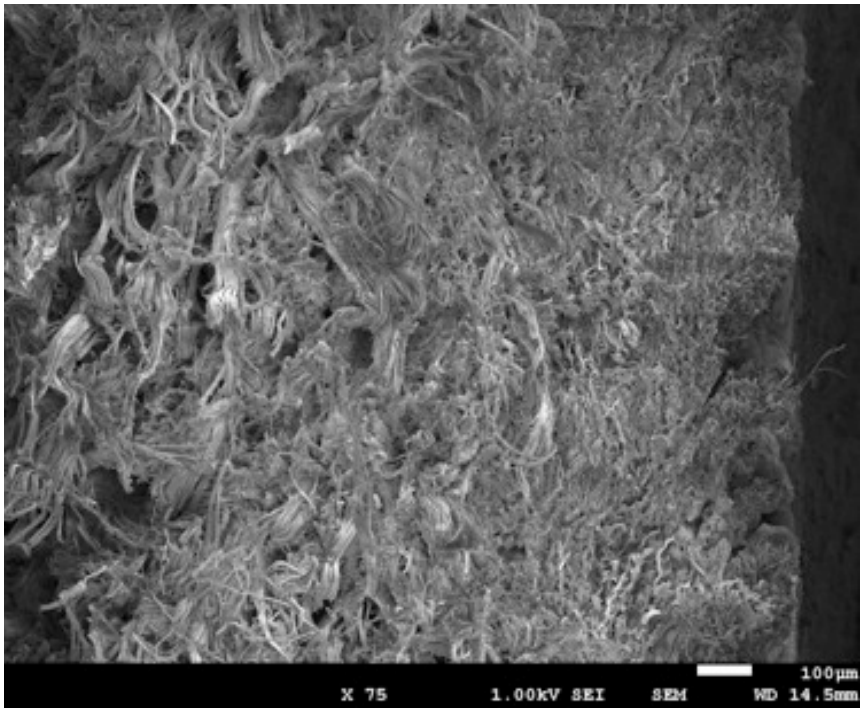


Photo 7: SEM of automotive upholstery leather with new process (75x)

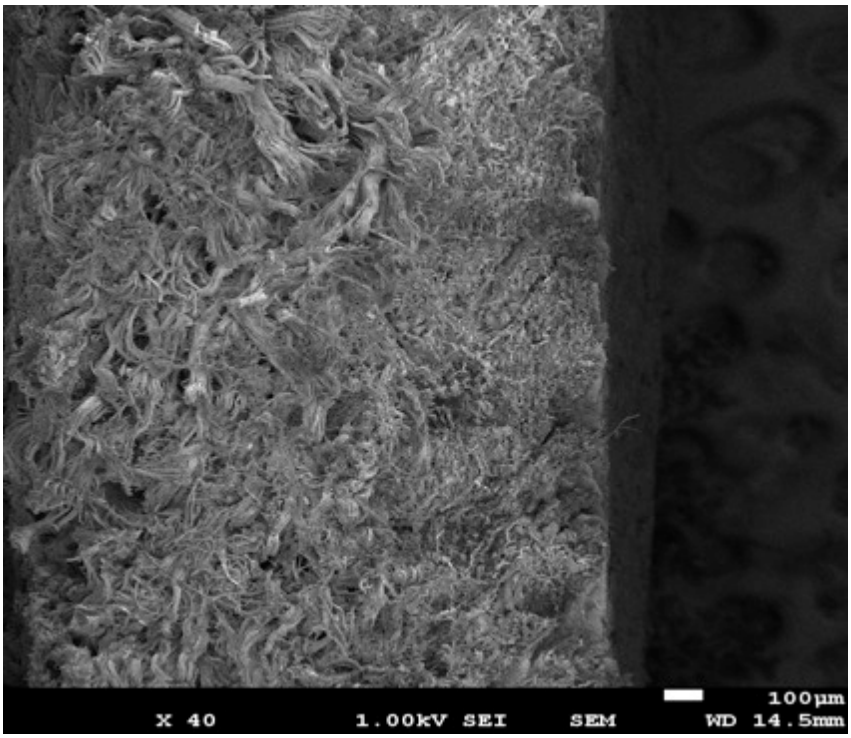


Photo 8: SEM of automotive upholstery leather with new process (40x)

As can be seen, there is a good compactness in both photos. The right side of the pictures is the grain side, were all leathers show tighter.

The following images represent the SEM photos for the conventional re-tanning process at 40x and 75x.

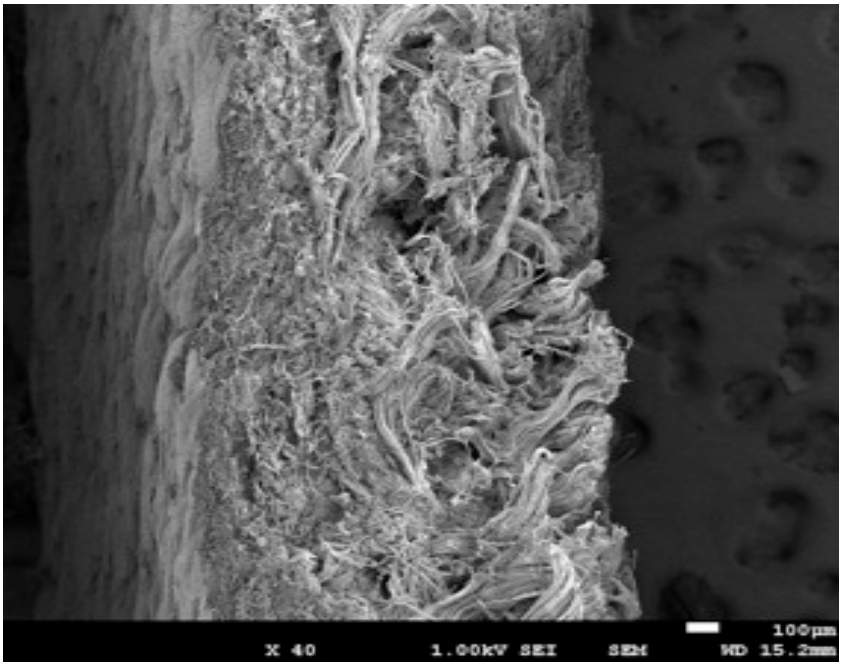


Photo 9: SEM of conventional automotive upholstery leather (40x)

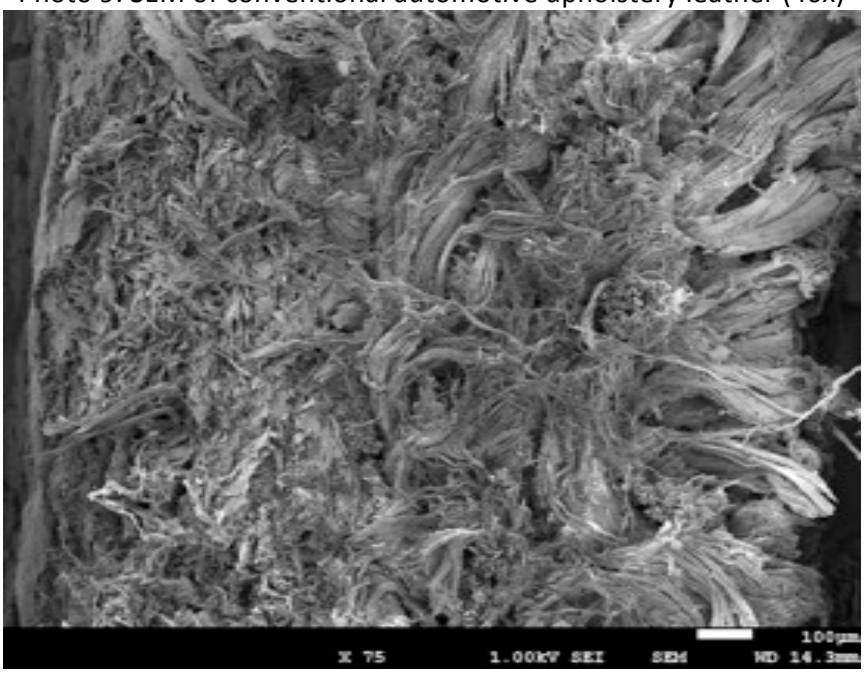


Photo 10: SEM of conventional automotive upholstery leather (75x)

The fibers are not as compact as in the previous case, but it can be seen the products penetration through all the leather structure, because there is no color change. SEM photos of the conventional process show the grain side on the left.

By comparing the pictures of the conventional process with the new process, you can see a clear difference in the compactness of fibers. Both are acceptable, but it is evident that the use of Tara tannins gives greater compactness and filling throughout the leather structure.

4.1.6 Conclusions

The leathers have a very good appearance, with a uniform dye and acceptable smoothness; also the results from physical tests are within the parameters established for each item.

At first, we expected to have a better softness in the final products, but resulted a bit stiff, so they were stricken in drum on dry leather, like is commonly developed in the industry for automotive leather, and they achieved a great softness.

Some specialized technicians in the tanning sector, made an organoleptic assessment of the final articles. All of them agreed that the articles are quite good, with good appearance and commented that these items could be commercialized in the current market.

We can conclude that the optimal combination achieved in Section 3.4 (9% of modified Tara, 2% of naphthalene sulphonic acid and 4% of pyrophosphate), is a reliable product to be used in a pre-tanning process. This is because the final leather developed in this thesis has the appropriate values of resistance, as well as very good organoleptic properties, which might suggest the feasibility of using this product as a pre-tanning product for any leather article in the tanning industry.

Upon chemical analysis of the baths processes, we saw, once again, that the new process shows environmental advantages as it significantly decreases the levels of COD and suspended matter.

Nevertheless, the physical tests show a more equal, since the new leather process marks a clear improvement in tear strength compared to the conventional process.

The conventional process was developed many years ago, as an alternative to chrome-free processes, and has since shown excellent results ever since. Now, we propose an alternative using a natural product that does not require a chemical process for extraction and gives a remarkably higher environmental advantage than the traditional processes.

4.2 Quality assessment (Physical tests parameters)

It is important to carry out a series of quality assessments in any process, in order to determine if a final product meets the established parameters, when the process is repeated.

In the case of leather, there are very specific controls for each item, depending on the type of leather and the end use that it will be given.

As mentioned above, the demands for leather automotive upholstery have indeed increased considerably; being the largest car companies and the people the cause for this increase. It is now very common that cars have leather seats, even if they are not luxury ones. That is why in this thesis we have been focused on this type of leather article.

Automotive leathers were manufactured in the past section (4.1), in order to check if they met the quality parameters mentioned in previous tables. As to meet the minimum parameters, there are other common parameters that must be fulfilled for some types of items and procedures.

Although there is an international agency that regulates chemical and physical test, each automotive company sets the values to meet in each test.

Listed below are the parameters for some leather articles, for us to determine if the articles manufactured in this thesis are within the established parameters.

4.2.1 Test Methods

As can be seen in this thesis, we take the physical parameters on dry leather as a main reference; such as the Tear load, Tensile strength, Elongation at break, Shrinkage Temperature, and Light fastness.

The following tables show those methods established by IULTCS to regulate the tests. IULTCS is the international standardizing body that regulates the leather standards.

There are many more methods for the leather industry; however, these are the most common in crust leather and the ones this work is based upon. Also, if the values of these parameters are exceeded, most likely all the other tests will overcome.

There are other regulatory bodies that set standards on the methods of the physical and chemical tests; such as the UNE standards that apply to the European Union, or DIN standards from Germany.

It is important to take into account that before starting any physical test, the leather needs to be conditioned according to certain parameters described next.

IULTCS - PHYSICAL TEST METHODS			
IU No.	Method name	ISO Standard	EN Standard
IUP 1 & IUP 3	Sample preparation and conditioning	**ISO 2419:2006	**EN ISO 2419
IUP 6	Measurement of tensile strength and percentage elongation	**ISO 3376:2002	**EN ISO 3376
IUP 8	Measurement of tear load - Double edge tear	ISO 3377-2: 2002	EN ISO 3377-2
IUP 36	Measurement of leather softness	**ISO 17235:2002	**EN ISO 17235

Table 58: Physical test methods from IULTCS.[65]

IULTCS - FASTNESS TEST METHODS			
IU No.	Method name	ISO Standard	EN Standard
IUF 120 (1966)	General principles of colour fastness testing of leather	***ISO 105-A01:2010	***EN ISO 105-A01
IUF 412	Change of colour with accelerated ageing.	**ISO 17728:2005	**EN ISO 17228

Table 59: Fastness test methods from IULTCS

The IUP-6 is a method to determine the tensile strength, elongation at a specified load and elongation at break of leather. It is applicable to all types of leather. The principle of this method is applied to a test piece, which is extended at a specified rate until the forces reach a predetermined value or until the test piece breaks.

The test piece is placed on a tensile testing machine, which have jaws, minimum length 45 mm in the direction of the applied load, designed to apply constant clamping by mechanical or pneumatic means. The modern machines stop when the sample is cracked, and the values appear in a screen.

The test sample has a standard shape and the dimensions of the sample are as follows.

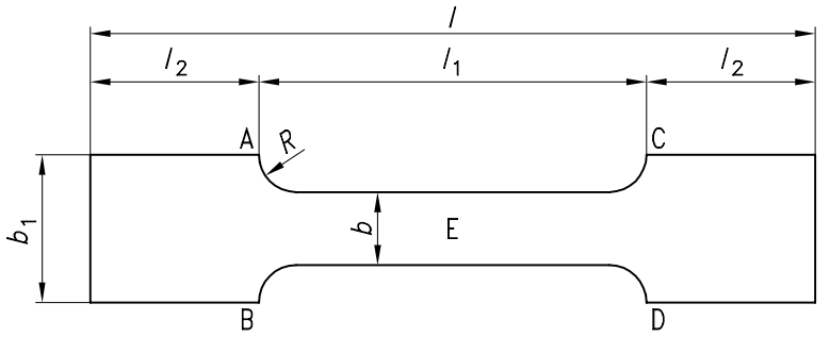


Figure 33: IUP-6 shape of test sample[66]

Designation	l	l_1	l_2	B	B_1	R
Standard	110	50	30	10	25	5
Large	190	100	45	20	40	10

Table 60: Dimensions of IUP-6 test samples

To calculate the tensile strength is necessary the next formula.

The tensile strength, Tn, in Newton per square millimeter is calculated using the equation:[66]

$$Tn = \frac{F}{w \times t}$$

Where:

F is the highest force recorded in Newton;
w is the mean width of the test piece in millimeters;
t is the mean thickness of the test piece in millimeters.

The percentage of elongation at break is calculated following the next equation.[66]

$$Eb = \frac{L2 - L0}{L0} \times 100$$

Where:

L_2 is the separation of the jaws or sensors at break;
L_0 is the initial separation of the jaws or sensors.

The method IUP-8, follows the same principles as the method IUP-6, however, the shape of the sample piece is very different and has other dimensions.

The machine is also the same, but a kind of hooks are placed, where the piece is settled and the machine stops when the piece breaks. The shape and dimensions are as follows.[67]

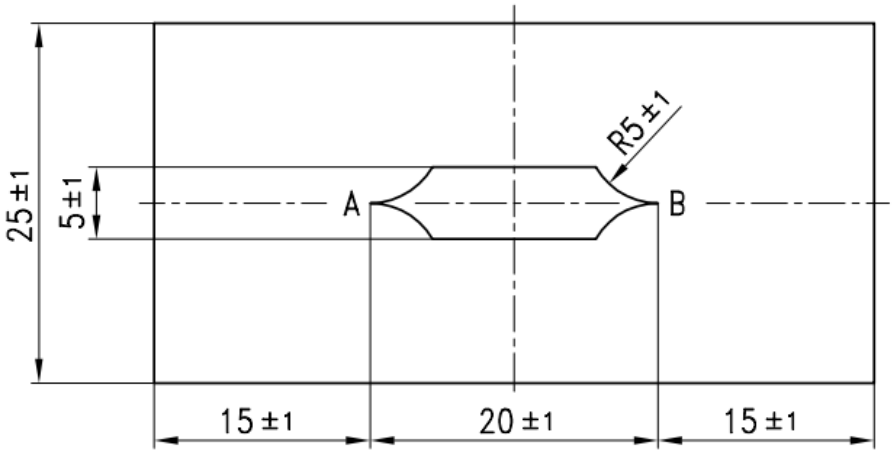


Figure 34: Test piece for double edge tear (all dimensions in millimeters ± 1mm, R=radius)

All physical tests have been carried out testing three pieces in parallel to the spine of leather and three perpendiculars. Then the mean is obtained.

4.2.2 Companies Testing Leather

Every Company presents a series of Standard Requirements before accepting any batch from the suppliers; here are some of the requirements demanded by almost every Company.

- **Conditioning**

Prior to testing, the samples must had been accustomed to local weather conditions for at least 24 hours, according to DIN EN ISO 2419 at (23 ± 2) °C and (50 ± 5)%relative humidity (RT).

- **Sampling point**

Chemical, Physical, mechanical tests must be carried-out, as well as an authenticity test according to DIN ES ISO 2418.

- **Appearance**

The color, grain, visual aesthetics hands and finish shall match the master sample approved by the Design Centre, or shall be specified on the engineering drawing.

- **Grade**

The leather must be thoroughly dyed to prevent undyed fibers from showing after sewing or perforation. Besides, the color of the dye must be compatible in appearance with the surface coating.

- **Finish**

No hides shall show paint defects or surface blemishes that could affect the appearance of the material, such as brush marks or stop and bad flows.

- **Samples Selection**

Samples for testing shall be selected no closer than 80mm from de edge of the hide. Sampling according to IUC/2 and IUP/2: Sampling location for leathers, whole hides and sides.[68]

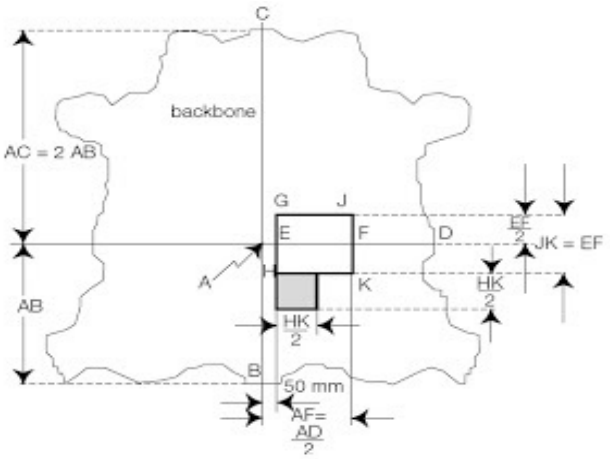


Figure 35: Sampling location for leathers, whole hides and sides

In a full bovine hide or side, there is the location where the samples have to be taken to determine the physical fastness or chemical analysis. The following figure, shows where the samples have to be taken in bovine shoulders.

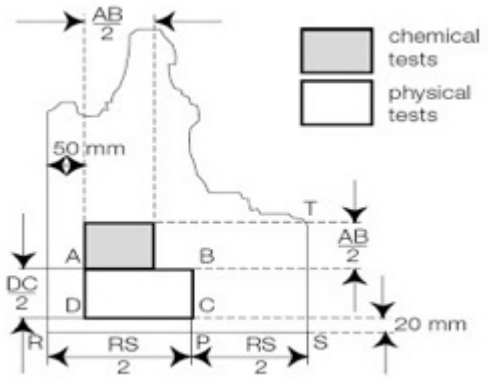


Figure 36: Sampling location for shoulders

The following table is an extract of Testing Leather from Volkswagen TL 52064 (issue 2009-12), and presents the required material properties of automotive upholstery leather.

5.2 Required material properties

Table 2

No.	Properties	Unit	Types, requirements
1	Maximum tensile strength acc. To DIN EN ISO 3376 standard specimen	N	Average value, determined on the basis of 6 specimens (3 longitudinal, 3 transverse): ≥130 All individual values ≥ 80
2	Maximum elongation at break acc. To DIN EN ISO 3376 standard specimen	%	35 - 60
3	Load displacement curve (see Section 6.3) acc. To DIN EN ISO 3376 standard specimen		The result is to be provided
4	Stitch tears resistance acc. To DIN EN ISO 23910	N	≥ 60 (indication of min. And max. Values)
5	Tear propagation force acc. To DIN EN ISO 3377-1	N	All individual values ≥ 25 (indication of all measured values required)
6	Elongation behaviour and return behaviour acc. To PV 3909, see section 6.4		
6.1	Static Elongation	%	The result is to be provided
6.2	Permanent elongation (measured after 30 min.)	%	The result is to be provided
7	Bending force acc. To VDA 230-209-209 parameter set A	N	The values must be recorded and provided
8	Water resistance (see section 6.5)		no color changes, no formation of rings on the grain side

Table 61: Leather specification for automotive upholstery by Volkswagen Company[69]

The following table shows an extract of the same parameters on leather from Ford Company.

ENGINEERING MATERIAL SPECIFICATION

WSS-M1F26-A

3.6	THICKNESS, mm, range (ASTM D 1813)	1.0 - 1.4
3.7	BREAKING STRENGTH, min (ASTM D 2209) Any direction	125 N
3.8	ELONGATION AT BREAK (ASTM D 2211)	30 - 70 %
3.9	ELONGATION AT 100 N LOAD, min (ASTM D 5733	15 - 40%
3.10	TEAR STRENGTH, min. (ASTM D 5733) Any direction	70 N
3.11	SEAM FATIGUE RESISTANCE (FLTM BN 106-02, average of 3 samples, any direction) Needle hole elongation after test, max.	1 mm
3.12	COLOR PROPERTIES	
	General Acceptance criteria:	
	The material shall no exhibit any change in appearance, such as color, tone change, fading or gloss change in excess of the require AATCC rating. In addition, the material shall not exhibit staining, blistering, loss of coating adhesion, flaking, chipping, checking, chalking, cracking, splits, sinks, bulges, peeling, tackiness or delamination.	
3.12.1	Resistance to Fade (SAE J 1885, ISO 105-A02/ AATCC Evaluation procedure 1)	
	225.6 kJ/m2	Rating 4
	488.8 kJ/m2	Rating 3
	In addition, the material must remain flexible and exhibit no cracking when bent around a 2.5 mm	
3.12.2	Resistance to Heat ageing. Min (7 days at 100 +/- 2°C, ISO 105-A02/ AATCC Evaluation procedure 1)	Rating 4
	The heat-aged sample shall not exhibit color tone change in excess of the above rating or excessive gloss change greater than the sample originally approved by Materials Engineering.	

Table 62: Leather specification for automotive upholstery by Ford Company[70]

Each automotive company sets these values; however, these are very similar to each other as they follow the same guidelines, which the regulatory agency proposes. This is why we only mentioned two of the most important automotive companies worldwide.

4.2.3 Conclusions

If the previous mentioned values are compared with those obtained in the production of the automotive leather of chapter 4.1, it can be concluded that the leathers products, produced in this thesis meet the specifications and are within the parameters.

The average value requested by the companies for the Tear strength ranges from 125 to 130 N, and the leather obtained from the new process with modified tara reached almost 260 N, which doubles the resistance required.

The elongation at break must range between 35-70% being an average value the most suitable, and the new leather article got a value of 46.7%.

Tear resistance or tear strength standard, requires values of above 70N, during this new process a value of 107.1 N was achieved, which way above the minimum. The conventional process leather meets the standards, except for tear strength, which obtained a value of 61 N, a little below the minimum. Which again indicates advantages in quality obtained from the process in which the modified Tara is applied.

This indicates that the viability of placing this project on the market is quite high, in terms of quality of the final article.

There are a lot of parameters to achieve for the case of automotive leather, but most of them are parameters to be applied in the finishing coats of the leather, which is not a part of this thesis. However, a following proposed work could be the application of finishing coatings on leather articles with modified Tara and the physical assessment.

4.3 Economical Assessment

Unfortunately, nowadays the industry is mainly focused on economic gains; this means that any product or process used has to offset the cost incurred by it.

This project is no exception; we must make a brief analysis of the costs that represents the new process and get a final estimate cost, in order to compare it with a conventional process currently used in the industry.

For the economical assessment, only the pre-tanning process has been compared with a conventional one, because this is just an indicative of the differences in the final costs.

The aim is to economically compare the new process proposed in this thesis with a conventional process of this tannery; the results obtained are the following:

The next table includes the new recipe using the modified Tara, with its optimal percentages, which were found in this thesis.

		New pre-tanning process with modified Tara				
		Nº:		Date:		13/12/12
		Enterprise:	I+D Lowest	Hides:		Bovine sides
		Article:	**Pre-tanning**	Status:		Pickle ph=5
		Technician:	JDM	% (weight):		Pelt (pickle x 1,5)
		Drum	Italprogetti nº 2	Weight (gr):		
Operation	**ºC**	**%**	**Product**	**Gr.**	**Time**	**Observations**
Pre-tanning	20	50	Water + salt			
					15’	ºBé= 6
		9%Modified Tara 2%Naphthalene 4% Pyrophosphate	Mix M_1			
		2	Leatheroil EFA		Night	pH= 4.32
		0.8	Formic Acid		2h	pH=3,69
						Drain
Rinse	20	300	Water		20’	Drain
						Horse up
						Sammy
						Air dry

Table 63: Base formulation for pre-tanning process using modified Tara

The following formulation is for a conventional pre-tanning process, using glutaraldehyde as pre-tanning agent. It is important to know that in the conventional processes it is necessary to add a synthetic auxiliary, in most of the cases the use of this synthetic is around 5-7%, We´ll take into account 5%, which is the amount that the tannery uses.

	Conventional pre-tanning process			
	Nº:		Date:	19/03/2012
	Enterprise:	I+D Lowest	Hides:	1 hide
	Article:	Pre-tanning	Status:	Pickle pH 3,2
	Technician:		% (weight):	Pelt (pickle x 1,5)
	Drum	Italprogetti nº 2	Weight (gr):	

OPERACIÓN	ºC	%	Product	Kg	Time	Observations
Pre-tanning	20	50	Agua			
		5	Sal		15'	ºBé=6
						pH=3.2
		2.5	Glutaraldehyde 50%, exempt from free formaldehyde		3,5h	pH= 4,2-4,4
		5	Synthetic sulfone type		5h	pH= 4,0-4,2
Rinse	20	300	Water		20’	Drain
						Horse up
						Sammy
						Air dry

Table 64: Base formulation for a conventional pre-tanning process with glutaraldehyde

This formulation could be different depending on the tannery that uses, however, this one in particular is a formulation given by a tannery, and member of the project. This tannery gives also all the costs of the processes.

4.3.1 Costs in chemical products

- **Pre-tanning process**

Furthermore, there are different prices for the various products used in both recipes, and these products are measured with respect to the total amount needed to be applied on 100 kg of pelt hides. Later, the amount of material is converted to the equivalent of 100 kg of fresh hides; because, in pelt the hides are divided in flesh side and grain side and for the

pre-tanning process only the grain side is processes, and it represents the 65% of the fresh hides.

Conventional pre-tanning process				**New pre-tanning process with modified Tara**			
Product	Price (€)	Weight (kg)	Amount (€/kg)	Product	Price (€)	Weight (kg)	Amount (€/kg)
Glutaraldehyde 50%, exempt of free formaldehyde	5,84	2,50	14,60	Modified Tara	1,91	9,00	17,19
Synthetic sulfone type	4,10	5,00	20,50	Naphthalene Sulphonic Syntan	3,20	2,00	6,40
				Sodium Pyrophosphate acid	1,61	4,00	6,44
			35,10 (€/kg)				**30,03 (€/kg)**

Table 65: Total price and comparative between conventional and new pre-tanning process

Is important to notice that the price of the modified tara, indicated in previous table, includes the modification cost.

There is a difference between the total pre-tanning prices, in terms of percentages, it can be said that there is a difference of around:

(35,10) - (30,03)= **5,07 €/kg**

$$\frac{5.07}{35.10} = \mathbf{14.4}\%$$

Up to **14,4%** of the total costs incurred in chemical products could be saved.

- **Re-tanning, dyeing and fatliquoring process**

The following table includes the prices and quantities of chemicals used for the re-tanning processes. These prices have been obtained from the various business houses that make them, so they are real prices.

The chemicals listed in this table are those described in the re-tanning formulations of Section 4.1, some of which are repeated in the formula, but in this table the full value of the product is shown.

The weight basis is 100 kg of shaved leather, and later becomes the cost, relative to the total kilograms of fresh skin.

New re-tanning process			
Product	**%**	**Price (€)**	**Cost (€)**
Oxalic Acid	0.5	0.90	0.450
Sodium Formate	1	0.75	0.750
Sodium Bicarbonate	0.5	0.38	0.188
Compact Product	5	2.00	10.000
Naphthalene sulphonic syntan	9	1.90	17.100
Dye	1	6.00	6.000
Sulphited synthetic oil	7	1.20	8.400
Lecithin	7	1.30	9.100
Tara	11	1.85	20.350
Sulphated oil	6	1.26	7.560
Formic acid	2	0.92	1.840
Total			**81.738**
Conventional re-tanning process			
Product	**%**	**Price (€)**	**Cost (€)**
Sodium Formate	1	0.75	0.750
Sodium Bicarbonate	0.5	0.38	0.188
Phenol syntan	20	1.85	37.000
Tara	10	1.85	18.500
Resin syntan	2	2.10	4.200
Dye	1	6.00	6.000
Combined oil (natural – synthetic)	4	2.90	11.600
Low fog oil	8	3.10	24.800
Formic acid	2.5	0.92	2.300
Total			**105.338**

Table 66: Total price and comparative between conventional and new re-tanning process

The compact product on the new re-tanning process, refers to the combination of 9% modified tara, 2% Synthetic naphthalene sulphonic and 4% Sodium Acid Pyrophosphate; and the cost is calculated from there.

There is a difference of total pre-tanning prices, in terms of percentages, it can be said that there is a difference about:

(105.338) - (81.738)= **23.6 €/kg**

$$\frac{23.6}{105.338} = \mathbf{22.4}\%$$

Up to **22.4%** of the total costs incurred in chemical products for re-tanning, dyeing and fatliquoring process could be saved.

4.3.2 Entire Process cost

In a more general way, costs of the whole process are calculated, from the soaking process till the finished leather.

In the first part, it is deemed that the processes that go from the soaking to the tanning, represent around 0,68 €/kg; but the tanning process represents 0.22€/kg, which means that the cost incurred from the soaking to the pickle process are:

0,68 €/kg - 0.22€/kg = **0.46 €/kg** (from soaking to pickle)

To determine the price of the pre-tanning process, it is necessary to remember that only the 65% of the total of fresh hides are used for the tanning process in pelt. This means:

100 kg of fresh hides is: 100/65 x 100= **154 kg on pelt.**

- **For the conventional pre-tanning process:**

$$\frac{35.10€/\text{kg}}{154} = \mathbf{0,23}\ €/\mathbf{kg}$$

- **For the new pre-tanning process with modified Tara:**

$$\frac{30.03€/\text{kg}}{154} = \mathbf{0,19}\ €/\mathbf{kg}$$

To determine the price of re-tanning process, it is necessary to remember that only the 26.2% of the total of fresh hides are used for re-tanning process (shaved leather). This means:

100 kg of fresh hides is: 100/26.2 x 100= **381.6 kg on shaved leather weight.**

- **For the conventional re-tanning process:**

$$\frac{105.33€/\text{kg}}{381.6} = \mathbf{0,276}\ €/\mathbf{kg}$$

Adding costs of the other processes: 0.46 + 0.276 + 0.23 **= <u>0.966 €/kg</u>**

- **For the new re-tanning process with modified Tara:**

$$\frac{81.738€/\text{kg}}{381.6} = \mathbf{0.2141}\ €/\mathbf{kg}$$

Adding up the costs of the other processes: 0.46 + 0.2141 + 0.19 **= <u>0.864 €/kg</u>**

In percentage terms, it represents a savings of about:

0.966 – 0.864 = <u>0.102 €/kg</u> 0.102/0.966= **<u>10.55%</u>**

4.3.3 Costs for wastewater treatment

The value 2.3%, represents the savings process only, but now we have to add up the costs incurred in the waste water treatment.

The following table shows the values obtained by the chemical analysis on the final baths. The values of conventional pre-tanning processes are those obtained in section 3.5, and the following prices of the chemical products and the costs of the processes were provided by a tannery; the values of the new pre-tanning processes with modified Tara are also extracted from section 3.5. As those values are given in mg/L, it is necessary to convert them in kg/L, as follows.

	Pre-tanning process			
	Conventional		**New with modified Tara**	
Determination	**mg/L**	**kg/L**	**mg/L**	**kg/L**
DQO	32550	0,032550	25560	0,025560
Suspended Matter	9097	0,009097	7976	0,007976
Organic Nitrogen Ammonia kit	362	0,000362	390	0,000390
Conductivity (µS/cm)	78315		69855	

Table 67: Values of chemical assessment in final baths

The waste water treatment represents a cost, depending on how polluted the water is, the next table shows a comparative between the conventional pre-tanning processes and the new pre-tanning process were the modified Tara is applied, and the costs that those treatments represent.

	Pre-tanning process					
	Conventional			New with modified Tara		
Determination	**Value**	**Price**	**Amount (€/L)**	**Value**	**Price**	**Amount (€/L)**
DQO (kg/L)	0,032550	0,294 €/kg	0,0095697	0,025560	0,294 €/kg	0,00751464
Suspended Matter (kg/L)	0,009097	0,769 €/kg	0,006995593	0,007976	0,769 €/kg	0,00613354
Organic Nitrogen Ammonia kit (kg N/L)	0,000362	0,606 €/kg	0,0002193	0,000390	0,606 €/kg	0,00023634
Free Formaldehyde (ppm)	Not found	-	-	Not found	-	-
		Total	0,016784665€/L = 16,78466 €/m^3		Total	0,0138845 €/L = 13,8845 €/m^3
Conductivity (µS/cm)	78315	0,00008 €cond./m^3	6,2652 €/m^3	69855	0,00008 €cond./m^3	5,5884 €/m^3

Table 68: Values for some water determinations and treatment prices

Conventional process:

6,2652 €/m^3 + 16,78466 €/m^3= **23,049865€/m^3**

New process:

5,5884 €/m^3 + 13,8845 €/m^3 = **19,4729 €/m^3**

Free formaldehyde does not represent a direct expense for wastewater treatment; but this value could be included because if the wastewater contains free formaldehyde, then, the product cannot be commercialized.

Since aldehyde is not used in this new process at any time, there is no trace of free formaldehyde in wastewater. In contrast to the conventional process, that could contain aldehyde because of the glutaraldehyde is used as a pre-tanning agent.

As can be seen, expenses decrease when the new modified Tara is used. Achieving savings of about 3,57 €/m^3 for the wastewater treatment, this latter translates to costs savings of about 15%.

It is important to clarify that costs process, not includes machining processes costs or the cost of the leather itself, is just chemicals products.

Summarizing, the cost of the chemical products used in new processes and the cost of water treatment, the results present savings of about:

10.55% in chemical products and
15.51% in waste water treatment

4.4 Life Cycle Assessment (LCA)

4.4.1 Environmental balance of the process

From an environmental point of view, the ratio cost/benefit of this proposal is that the new product has less environmental impact than the products currently used.

In the case of the pre-tanning, the idea is to reduce the use of products of synthetically origin as well as the controversial tanning agents like the chrome and the aldehydes. As to the vegetable tannin process, the aim is to substitute the vegetable extracts with the greatest environmental impact.

It is well known that deforestation is not environmentally friendly, if we compare the current source of tanning agents like mimosa, quebracho and chestnut with the new proposal in this thesis, where deforestation is not needed, the advantages are much higher.

Even though, in some cases there is a system to reforest and renew the trees cut, the natural renewal capacity of a tree is rather slow. A clear example being quebracho, which needs about 80-100 years to mature; or chestnut and mimosa, which need 40 years and 10 years respectively.

The new process proposed in this thesis, doesn't need any extra treatment, or additional chemical processes, nor the application of chemical products to obtain it, which is another energy saver that lessens the environmental impact, which is one of the main objectives of this project.

Different parts of the species are used to extract tannins. This way, and taking into consideration the most common commercial extracts, quebracho and chestnut wood is used to extract tannins and, therefore, almost the whole tree is used. On its part, only the bark of mimosa is used to obtain tannins.

The annual production obtained from the Tara tree in its mature stage ranges from 25-70 kg per tree, its most productive stage begins from 5-7 years to 60-70 years. Its production also depends if it's a tree planted, then the harvesting occurs twice a year; or if it is a wild tree only does it once a year.[71] Another source says that the tree of Tara, has an average production of 25-46 kg of pods per plant at each harvest and can be harvested twice a year.[72] We take the aforementioned as an average value 45 kg a year.

However, just about 62% of the Tara fruit is the pod, while 38% are the seeds. This means that around 28 kg per tree are used for the tanning industry each year.

In a recent study, in order to determine the feasibility of using grape seed as a source of tannin for the tanning industry,[73] a determination of the years of maturity of each tree used for the extraction of tannins was carried out, as well as the amount of tannin extracted powder each.

In the following table, there is a comparative of the commercial production of each tree, their extracts are estimated and compared with the Tara tannin as a source of tannin extracts.

Tannin source	Time of growth to be mature	Tree weight (kg)	Part used from each source	Matter used (kg/tree)	Output extraction (%)	Solubilised matter (kg)
Quebracho	80-100 years	2000	≈ total	1200	30	360
Chestnut	40 years	1000	≈ total	800	12	96
Mimosa	10 years	200	Bark	20	12	2.4
Tara	Renewal	-	Fruit pod	28/year	62	

Table 69: Values obtained of Technical final report of Life-Grape project.[71]

In the same study, the amount of trees required to annually produce 1000 tons of commercial extract was estimated.

Tannin source	Trees required
Quebracho	2.778
Chestnut	10.417
Mimosa	416.667

Table 70: Trees need to cut down to produce 1000 tons of each tree.

In Peru, over 17000 tons of Tara products were exported in 2012,, of which 10 500 tons is Tara powder for the tanning industry.

In the ecological side, there is a clear improvement. The calculations may not be 100% accurate because this depends on many factors like harvests year after year, but are approximate and very punctual about the improved sustainability achieved from using Tara products.

The following table shows the main Peruvian exporters of Tara, and the total amount of Tara exported in 2012.

PERUVIAN SUPPLIERS	Kg
Agrifood sociedad comercial de responsabilidad limitada	746,227.43
Agrotara S.A.C.	1,018,092.42
Exandal S.A.	11,421,428.57
Exportadora el sol S.A.C.	6,997,780.00
Gomas y taninos S.A.C.	933,279.06
Molinos Asociados S.A.C.	6,915,138.09
Productos del Pais S.A.	1,355,536.86
R. Muelle S.A.	115,866.70
RG Induagro S.A.C.	302,308.57
Silvateam Perú S.A.C.	10,090,976.59
Sociedad mercantil (exportación) S.A.	1,689,659.04
Tecnacorp S.A.C.	2,817,230.57

Table 71: Peruvian Tara exporters and FOB 2012[74]

The following are the environmental savings obtained from using new processes to extract tannins:

1. Reducing the use of synthetic products and other not sustainable products.
2. Besides the replacement of derivatives of aldehydes that are considered sensitive or potentially dangerous use for operators.
3. The use of external chemicals is not necessary, and the possibility of pollution produced by the chemicals released in such obtaining process.
4. The replacement of chrome, which can cause allergies to the users or, under special conditions, the possible formation of chromium (VI) considered carcinogen.
5. Deforestation is the major problem that could be reduced using the renewable sources of tannin from Tara tree for the leather industry. This could reduce the cutting down of quebracho, mimosa and chestnut trees, as well as for other less common species.
6. The obtaining and extraction processes of the new tannins are considerably more energy saving, and contributed to the reduction in heat and CO_2 emissions; as compared to the actual vegetable extract production.

As a conclusion, the new process developed in the project is environmentally friendly because it reduces deforestation and minimizes the use of non-sustainable products.

4.4.2 Possible complementary uses of remaining waste

In section 3.2, a test of milling and sieving process is carried out and decided to use the smaller particle size because better results were obtained in terms of penetration and reduction in pollutant loads.

It was also said that in the sieving process would be obtained about 82% of tara powder for use as modified product; in an investigation to carry on an industrial scale this milling and sieving process, we were told that this percentage could rise to about 90%. Whatever the percentage is, this means that we have an amount not used in the tanning process, so we propose some actions to give added value to this sub-product.

Some possible proposals on complementary uses are:

1. Gallic acid extraction
2. Tannic acid extraction.
3. Compost use
4. Thermal use: combustion, pyrolysis (source of activated carbon)
5. Fibre in animal feeding stuffs

The following table from chapter 3 shows that the Tara of particle sizes bigger than 50µm, presents good values for tannins, which means that there is a great quantity of Gallic acid and tannic acid able to be extracted.

Determination	Tara sieved	200 – 80 µm	80 – 50 µm	50 – 40 µm	Original Tara
Soluble solids (%)	59.6	40.2	57.9	64.0	59.7
Total solids (%)	86.0	76.0	95.4	93.6	92.9
No tannins (%)	13.1	12.5	11.4	14.7	14.7
Tannins (%)	46.4	27.7	46.5	49.3	45.0
Insoluble (%)	26.5	35.8	34.4	29.6	33.2
Water (%)	14.0	24.0	7.6	6.4	11.0
pH	3.7	3.7	3.7	3.7	3.8

Table 72: Tannins determination by different particle size

As it has been widely discussed, the Tara is a plant product; this means that the by-product with a larger particle size is completely natural and can be traditionally used as compost because it contains the proper nutrients.

During this project, it was also concluded that it is not needed to make any kind of chemical process to improve the tara tannin, which leads us to the conclusion most important of all, tara wastes can be used same as traditionally given, as in the field of food and medicine extracting tannic acid or gallic acid.

4.4.3 Life Cycle Assessment (LCA)

Currently the life cycle assessment is widely used because it shows an overview of the costs and environmental savings between two processes.

Subsequently, a life cycle assessment is presented for the entire process from this thesis in which the modified Tara product is applied. For the LCA, a process to obtain automotive upholstery leather has been assessed, starting from raw hides (1000 kg of wet salted hides) and finishing with dry leather.

This LCA it does not take into account the slaughterhouse neither the finishing process nor final disposal; because we want to compare the process sections where no difference between each other. The entire life cycle assessment from cradle to grave could be a following proposing work.

To carry out this analysis a computer program designed by the Engineering School of Igualada (UPC) has been used. This program has been programmed to submit the inputs and outputs of the entire process, and it then summarizes and compares them between the conventional and the new process.

Inputs refer to mechanical processes, chemical products used, hours on drums, heat and electric needs, etc. Whereas, outputs refer to wastewater disposal, Chemical Oxygen demand, Suspended Matter, etc.

It is important to start with some of the units used among the LCA. Those are values obtained from real average tanneries. If 1000 kg of wet salted hides are used, then it is assumed that the following weights are average weights to be used as reference in each of the steps undertaken in an actual process.

Quantity	Unit	Hide
1.100	Tn	Fresh hides
1.000	Tn	Wet salted hides
1.100	Tn	Limed hides
0.715	Tn	Split hides
0.262	Tn	WW Shaved hides
0.195	Tn	Finished leather

Table 73: Weight units of hides on different parts of the process

- 1 kg of wet salted hide is equivalent to 4 m^2

It must be stressed that, for this study, both processes took the same steps from soaking to deliming-bathing; but for the pickling, pre-tanning and wet-end finishing the steps were different. Every step of the process can is described in the annex 10, where the aforementioned differences can be noticed.

The assessment starts with the soaking process; the following tables depict inputs and outputs submitted into the aforementioned computer program.

Process: **New process with modified Tara**
Step: **Soaking process**.
Base unit: **1 tone of wet salted hides.**

INPUTS								
Type	I/O	Type name	Description	Reference		Quantity		
W	I	Water	H_2O (20ºC)	8000	*kg/tn*	8000	kg	
C5	I	Ch: Surfactant	Anionic surfactant	0.5	%	5	kg	
C6	I	Ch: Sodium Carbonate	Na_2CO_3	0.2	%	2	kg	
D1	I	Drum 1 (beamhouse proc.)	Run	19.5	h	19.5	h	
EE	I	Electrical energy	Drum 1 (beamhouse)	1014	MJ/tn	1014	MJ	

Table 74: Inputs of soaking process

OUTPUTS							
Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from soaking	8	m3/tn	8	m3
LW_DQO	O	LiqWaste: CDO	COD content	28[75]	kg/tn	28	kg
LW_DBO5	O	LiqWaste: BOD5	BOD_5 content	12[73]	kg/tn	12	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	13[73]	kg/tn	13	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	1.5[73]	kg/tn	1.5	kg
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	150[76]	kg/tn	150	kg

Table 75: Outputs of soaking process

The table above is an example of how is the program used to carry out the LCA.

Following this process, the unhairing and liming processes take place; subsequently, the mechanical treatment of Fleshing and Splitting; then comes the De-liming, bating, pickling and the Pre-tanning process, being this latter, the one that we are interested in. Once the

leather is pre-tanned and rested, the Samming and shaving process are performed, followed by the Neutralization, Re-tanning and fatliquoring processes, and finally, the drying process.

In the inputs part, water is referred in kilograms per tone of rawhide; the chemical products used are referred in % of raw hides. The electrical energy used as inputs is referred in MJ per tones of rawhides; and it is taking into account the working hours of the drums.

Another important thing to note, is the fact that the Drums used are different; this means that the mentioned Drum 1 is bigger than Drum 2 and Drum 3, this is because the Drum 1 is used for the beamhouse process with whole hides; drum 2 is used for split hides to de-liming, bating, pickling and pre-tanning processes, and finally drum 3 (smaller than drum 2), is used for shaved leather in wet-end phase. This is mentioned because the bigger the drum, the more energetic input is necessary.

For outputs, the water is given in m3 per ton of rawhide, and parameters as COD, BOD5, etc. are given in kg per ton of rawhide. These expressions, both inputs and outputs, are expressed in such units because in most of the bibliography consulted, these are the units used and it is important to homogenize them.

Furthermore, the new pre-tanning process of this assessment is presented and compared with the conventional one. This process and the re-tanning one included below are the same processes described in section 3.5 for pre-tanning and in section 4.1 for re-tanning.

Step: **Pre-tanning process**.
Base unit: **0.715 tons of split hides (pelt)**

INPUTS New process with modified Tara							
Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water (20ºC)	500	*kg/tn*	357.5	kg
C14	I	Ch: Modified Tara	Modified Tara as pre-tanning	9	*%*	64.35	kg
C11	I	Ch: Naphthalene sulphonic syntan, pretanning	Pretanning Precursor	2	*%*	14.3	kg
C16	I	Sodium, Pyrophosphate acid	Pretanning Precursor	4	*%*	28.6	kg
C12	I	Ch: Formic Acid	Fixing agent	0.8	*%*	5.72	kg
W	I	Water	Rinsing Water (20ºC)	3000	*kg/tn*	2145	kg
D2	I	Drum 2 (tanning proc.)	Run	12	*h*	12	h
EE	I	Electrical energy	Drum 2 (pickling-tanning)	834	MJ/tn	596.31	MJ

Table 76: Inputs of New Pre-tanning process

OUTPUTS New process with modified Tara							
Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from tanning	4	m3/tn	2.86	m3
LW_DQO	O	LiqWaste: COD	COD content	102.24	kg/tn	73.1016	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	31.9	kg/tn	22.8085	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total Nitrogen Content	1.5	kg/tn	1.0725	kg

Table 77: Outputs of New Pre-tanning process

Furthermore, the conventional pre-tanning process is assessed using Glutaraldehyde as the main pre-tanning agent. Following the formulation showed in the economical assessment.

Step: **Pre-tanning process**.

Base unit: **0.715 tones of split hides (pelt)**

INPUTS Conventional process							
Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water (20ºC)	500	*kg/tn*	357.5	kg
C17	I	Glutaraldehyde	Glutaraldehyde 50%	2.5	*%*	17.875	kg
C18	I	Syntan sulphone type	Synthetic sulphone type	5	*%*	35.75	kg
W	I	Water	Rinsing Water (20ºC)	3000	*kg/tn*	2145	kg
D2	I	Drum 2 (tanning proc.)	Run	10	*h*	10	h
EE	I	Electrical energy	Drum 2 (pickling-tanning)	695	*MJ/tn*	496.925	MJ

Table 78: Inputs of conventional Pre-tanning process

OUTPUTS Conventional process							
Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from pickling-tanning	4.5	m3/tn	3.217	m3
LW_DQO	O	LiqWaste: DQO	DQO content	146.5	kg/tn	104.747	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	40.94	kg/tn	29.272	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total Nitrogen Content	1.6	kg/tn	1.144	kg

Table 79: Outputs of conventional Pre-tanning process

To summarize these inputs and outputs there is a comparative table to find important savings or wastes presented in the new process.

CONVENTIONAL					COMPARATIVE		NEW PROCESS WITH MODIFIED TARA				
Type name	**I**	**O**	**O-I**		% input	% output	**Type name**	**I**	**O**	**O-I**	
				-							-
Water	2502.5		-2502.5	kg			Water	2502.5		-2502.5	kg
Electrical energy	496.92		-496.925	MJ	20.0%		Electrical energy	596.31		-596.31	MJ
Drum 2 (tanning proc.)	10		-10	h	20.0%		Drum 2 (tanning proc.)	12		-12	h
Glutaraldehyde	17.875		-17.875	kg	-100.0%		Glutaraldehyde				kg
Syntan sulphone type	35.75		-35.75	kg	-100.0%		Syntan sulphone type				kg
Waste: Water		3.2175	3.2175	m3		-11.1%	Waste: Water		2.86	2.86	m3
LiqWaste: DQO		104.7475	104.747	kg		-30.2%	LiqWaste: DQO		73.1016	73.1016	kg
Susp. Matter		29.272	29.272	kg		-22.1%	LiqWaste: Susp. Matter		22.8085	22.808	kg
Nitrogen		1.144	1.144	kg		-6.2%	LiqWaste: Nitrogen		1.0725	1.0725	kg
pH		3.9	3.9	-		-2.6%	pH		3.8	3.8	-
Conductivity		78315	78315			-10.8%	Conductivity		69855	69855	

Table 80: Summarize conventional and new Pre-tanning process with their inputs and outputs

In the middle columns (% Inputs - % Outputs), the differences of percentages between each process are described. As mentioned in the economical assessment section, it was presented the savings in wastewater disposals as can be proved in previous table.

Regarding energy consumption, there is 20% more consumption in the new process due the higher amount of hours of running drum. It is important to remind that this is only for the pre-tanning process and the entire process will be summarized below.

Now, the new re-tanning process of this assessment is presented and compared with the conventional one. The inputs are presented separately in the neutralizing, re-tanning and fatliquoring processes. Firstly, the inputs and outputs of the new process where the modified tara has been applied are shown.

Operation: **Neutralization**

Base unit: **0.262 tones of wet-white shaved hides**

INPUTS		New process with modified Tara			
Type	I/O	Type name	Description	Reference	Quantity
W	I	Water	Water	600 kg/tn	157.212 kg
C19	I	Oxalic Acid	Oxalic Acid	0.5 %	1.3101 kg
C20	I	Sodium formate	Sodium formate	1 %	2.6202 kg
C21	I	Sodium bicarbonate	Sodium bicarbonate	0.5 %	1.3101 kg
D3	I	Drum 3 (wet-end proc.)	Run	2.2 h	2.2 h
EE	I	Electrical energy	Drum 3	149.6 MJ/tn	39.198192 MJ
W	I	Water	Washing Water	2000 kg/tn	524.04 kg

Table 81: Inputs of new Neutralization process with modified Tara

Operation: **Re-tanning**

Base unit: **0.262 tones of wet-white shaved hides**

INPUTS		New process with modified Tara			
Type	I/O	Type name	Description	Reference	Quantity
C22	I	Compact product	Pre-tanning mixed product	5 %	13.101 kg
C23	I	Syntan (substitution)	Substitution syntan	2 %	5.2404 kg
C24	I	Oil	Sulphited synthetic oil	3 %	7.8606 kg
C24	I	Oil	Lecithin	3 %	7.8606 kg
W	I	Water	Water 30º	500 kg/tn	131.01 kg
C23	I	Syntan (substitution)	Substitution syntan	3 %	7.8606 kg
C25	I	Original Tara	Tara	5 %	13.101 kg
C23	I	Syntan (substitution)	Substitution syntan	4 %	10.4808 kg
C25	I	Original Tara	Tara	6 %	15.7212 kg
W	I	Water	Water 50 ºC	500 kg/tn	131.01 kg
D3	I	Drum 3 (wet-end proc.)	Run	4.2 h	4.2 h
EE	I	Electrical energy	Drum 3	285.6 MJ/tn	74.832912 MJ

Table 82: Inputs of new re-tanning process with modified Tara

Operation: **Fatliquoring**

Base unit: **0.262 tones of wet-white shaved hides**

INPUTS New process with modified Tara					
Type	I/O	Type name	Description	Reference	Quantity
W	I	Water	Water 45 ºC	1500 kg/tn	393.03 kg
C24	I	Oil	Sulphited synthetic oil	2 %	5.2404 kg
C24	I	Oil	Lecithin	2 %	5.2404 kg
C24	I	Oil	Sulphated (semi-synthetic) oil	2 %	5.2404 kg
C12	I	Ch: Formic Acid	Formic acid. Fixing	1 %	2.6202 kg
C24	I	Oil	Sulphited synthetic oil	2 %	5.2404 kg
C24	I	Oil	Lecithin	2 %	5.2404 kg
C24	I	Oil	Sulphated (semi-synthetic) oil	4 %	10.4808 kg
C12	I	Ch: Formic Acid	Formic acid. Fixing	1 %	2.6202 kg
W	I	Water	Water to wash (30ºC)	2000 kg/tn	524.04 kg
D3	I	Drum 3 (wet-end proc.)	Run	4.5 h	4.5 h
EE	I	Electrical energy	Drum 3	306 MJ/tn	80.17812 MJ
TE	I	Thermal energy	Water heating (45-50ºC)	3840 MJ/tn	1006.1568 MJ

Table 83: Inputs of new fatliquoring process with modified Tara

OUTPUTS New process with modified Tara					
Type	I/O	Type name	Description	Reference	Quantity
WW_H2O	O	LiqWaste: Water	Wastewater from post-tanning operations	5.101 *m3/tn*	1.33656402 m3
LW_Cr	O	LiqWaste: Chromium (III)	Chromium (III) content	0.0006 *kg/tn*	0.000157212 kg
LW_DQO	O	LiqWaste: DQO	DQO content	211 kg/tn	55.28622 kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	16 kg/tn	4.19232 kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen Content	2.2 kg/tn	0.576444 kg

Table 84: Outputs of general re-tanning process with modified Tara

Conventional process

Operation: **Neutralization**
Base unit: **0.262 tones of wet-white shaved hides**

INPUTS Conventional process							
Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water 30ºC	2000	kg/tn	524.04	kg
C20	I	Sodium formate	Sodium formate	1	%	2.6202	kg
C21	I	Sodium bicarbonate	Sodium bicarbonate	0.8	%	2.09616	kg
W	I	Water	Washing Water	2000	kg/tn	524.04	kg
EE	I	Electrical energy	Drum 3	149.6	MJ/tn	39.198192	MJ
D3	I	Drum 3 (wet-end proc.)	Run	2.2	h	2.2	h

Table 85: Inputs of conventional Neutralization process

Operation: **Re-tanning**
Base unit: **0.262 tones of wet-white shaved hides**

INPUTS Conventional process							
Type	I/O	Type name	Description	Reference		Quantity	
C23	I	Synthan (substitution)	Phenol condensation syntan	10	%	26.202	kg
C25	I	Original Tara	Original tara	5	%	13.101	kg
C23	I	Synthan (substitution)	Copolimer syntan	2	%	5.2404	kg
C23	I	Synthan (substitution)	Phenol condensation syntan	10	%	26.202	kg
C25	I	Original Tara	Original tara	5	%	13.101	kg
C26	I	Dye	Dye	1	%	2.6202	kg
C12	I	Ch: Formic Acid	Formic acid (1:10) to fix	1	%	2.6202	kg
W	I	Water	Washing water (50ºC)	2000	kg/tn	524.04	kg
D3	I	Drum 3 (wet-end proc.)	Run	8	h	8	h
EE	I	Electrical energy	Drum 3	544	MJ/tn	142.53888	MJ

Table 86: Inputs of conventional re-tanning process

Operation: **Fatliquoring**
Base unit: **0.262 tones of wet-white shaved hides**

INPUTS Conventional process							
Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water 50ºC	2000	kg/tn	524.04	kg
C24	I	Oil	Comb. synthetic and natura	4	%	10.4808	kg
C24	I	Oil	Sulphited fish oil	8	%	20.9616	kg
C12	I	Ch: Formic Acid	Formic acid. Fixing	1.5	%	3.9303	kg
W	I	Water	Rinsing water 40ºC	2000	kg/tn	524.04	kg
D3	I	Drum 3 (wet-end proc.)	Run	2	h	2	h
EE	I	Electrical energy	Drum 3	136	MJ/tn	35.63472	MJ
TE	I	Thermal energy	Water heating (45-50ºC)	3840	MJ/tn	1006.1568	MJ
TE	I	Thermal energy	Drying	3840	MJ/tn	1006.1568	MJ

Table 87: Inputs of conventional fatliquoring process

OUTPUTS Conventional process							
Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from post-tanning operations	8.001	*m3/tn*	2.09642202	m3
LW_Cr	O	LiqWaste: Chromium (III)	Chromium (III) content	0.001	*kg/tn*	0.00026202	kg
LW_DQO	O	LiqWaste: DQO	DQO content	351.2	kg/tn	92.021424	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	26.41	kg/tn	6.9199482	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen Content	3.7	kg/tn	0.969474	kg

Table 88: Outputs of general re-tanning conventional process

These tables show the actual data of the processes and later the final comparative table is shown, which summarizes all inputs and outputs including the ones from the first steps of the process that is not shown in this section.

It must be understood that the values shown in the previous tables and the increased and decreased percentages in the comparisons, may vary in many ways. Different values can be obtained from different tanneries, every tanner can use different processes or different products, those values can also change if there is a wastewater treatment prior to discharge, or can vary depending the type of water used in other regions. For this thesis

processes we have been using water, materials, chemicals and energetic values that have been obtained from our own process and with real data from actual tanneries.

The column named ‘Comparison Input and output’ shows the difference between each process; positive numbers are shown if the percentages have increased, and negative numbers are shown for the decreased percentages. This means, for example, that there is a saving of about 5.2% the water input from the new pre-tanning process with modified Tara.

The ‘Increase – Reduction’ columns show the actual increasing, most of which is measured in kilograms per ton of raw hide, or Mega-Joules for energy values, unlike the column explained above, which was expressed in percentage terms.

Finally, on the right of the table, there are two columns named ‘Input variation’ and ‘Out variation’. These columns are not a repetition of the center columns, the values shown in these columns are reduced or increased values expressed in kg per 1 m2 of final leather, and not for tons of raw hides like every other values.

The following table shows a summary of the whole process.

	CONVENTIONAL			COMPARISON INPUT & OUTPUT		NEW PROCESS			Increase - Reduction					Input variation	Output variation	
									Inc./red.		Inc./red.			1	m^2	
Type name	**I -Input**	**O-Output**	Units	**% Input**	**% Output**	**I- Input**	**O-Output**	Units	**Input value**	% Input	**Output value**	% Output		**Total value**	**Total Value**	**Units**
			-					-								-
Water	21355.20		kg	-5.2%		20237.84		kg	-1117.36	-0.05				-279.340		kg
Electrical energy	4775.26		MJ	1.6%		4851.49		MJ	76.22	0.02				19.056		MJ
Thermal energy	2012.31		MJ	-50.0%		1006.16		MJ	-1006.16	-0.50				-251.539		MJ
Processing time	0.00		h			0.00		h	0.00	0.00				0.000		h
Drum 1 (beamhouse proc.)	48.00		h			48.00		h	0.00	0.00				0.000		h
Drum 2 (tanning proc.)	13.75		h	14.5%		15.75		h	2.00	0.15				0.500		h
Drum 3 (wet-end proc.)	12.20		h	-10.7%		10.90		h	-1.30	-0.11				-0.325		h
Chemical (unclassified)	0.00		kg			0.00		kg	0.00	0.00				0.000		kg
Sodium chloride	50.05		kg	-42.9%		28.60		kg	-21.45	-0.43				-5.363		kg
Chromium (III) Salts	0.00		kg			0.00		kg	0.00	0.00				0.000		kg
Sodium sulphide	20.00		kg			20.00		kg	0.00	0.00				0.000		kg
Sodium hydroxide	0.00		kg			0.00		kg	0.00	0.00				0.000		kg
Surfactant	5.00		kg			5.00		kg	0.00	0.00				0.000		kg
Sodium Carbonate	2.00		kg			2.00		kg	0.00	0.00				0.000		kg
Calcium hydroxide	50.00		kg			50.00		kg	0.00	0.00				0.000		kg

Magnesium Oxide	0.00		kg			0.00		kg	0.00	0.00			0.000		kg
Amino compound	5.00		kg			5.00		kg	0.00	0.00			0.000		kg
Enzyme	5.01		kg			5.01		kg	0.00	0.00			0.000		kg
Naphthalene sulphonic syntan, pretanning	0.00		kg	100%		14.30		kg	14.30	No			3.575		kg
Formic Acid	10.13		kg	78.9%		18.11		kg	7.98	0.79			1.996		kg
Di-carboxylic Acid	10.73		kg			10.73		kg	0.00	0.00			0.000		kg
Modified Tara	0.00		kg	100%		64.35		kg	64.35	No			16.088		kg
Sulphuric Acid	5.01		kg	-100.0%		0.00		kg	-5.01	-1.00			-1.251		kg
Sodium, Pyrophosphate acid	0.00		kg	100%		28.60		kg	28.60	No			7.150		kg
Glutaraldehyde	17.88		kg	-100.0%		0.00		kg	-17.88	-1.00			-4.469		kg
Syntan sulphone type	35.75		kg	-100.0%		0.00		kg	-35.75	-1.00			-8.938		kg
Oxalic Acid	0.00		kg	100%		1.31		kg	1.31	No			0.328		kg
Sodium Formate	2.62		kg			2.62		kg	0.00	0.00			0.000		kg
Sodium bicarbonate	2.10		kg	-37.5%		1.31		kg	-0.79	-0.38			-0.197		kg
Compact product	0.00		kg	100%		13.10		kg	13.10	No			3.275		kg
Syntan (substitution)	57.64		kg	-59.1%		23.58		kg	-34.06	-0.59			-8.516		kg

Oil	31.44	0.00	kg	66.7%		52.40		kg	20.96	0.67				5.240		kg
Original Tara	26.20	0.00	kg	10.0%		28.82		kg	2.62	0.10				0.655		kg
Solid Waste		570.90	kg				570.90	kg								kg
Intermediates		107.00	kg				107.00	kg								kg
LiqWaste: Water		19.33	m3		-5.8%		18.21	m3			-1.11735	5.78%			-0.27933	m3
LiqWaste: Chlorides		166.00	kg				166.00	kg								kg
LiqWaste: COD		290.77	kg		-23.5%		222.39	kg			-68.3811	23.52%			-17.0952	kg
LiqWaste: BOD5		39.00	kg				39.00	kg								kg
LiqWaste: Suspended Matter		74.19	kg		-12.4%		65.00	kg			-9.19122	12.39%			-2.297807	kg
LiqWaste: Nitrogen		8.51	kg		-5.5%		8.05	kg			-0.46453	5.46%			-0.116132	kg
LiqWaste: Sulphides		2.82	kg				2.82	kg								kg
LiqWaste: Sulphates		1.50	kg				1.50	kg								kg

Table 89: Summarize the entire conventional and new process with their inputs and outputs

As said before, some savings are generated from the new processes, among which the use of water of about 5.2%, are included thermal energy savings represents about 50%, compared with the conventional process. In a study made by the European Commission, it is stated in a table, which about 32% of the total energy consumed comes from the thermal energy used to heat water. This means that in this process there is a decrease of about 16% of the total energy consumed only by saving energy from the water heating process.

An energy consumption increase of around 20% had been measured for the new process in the pre-tanning stage, however, in this table where the whole process is measured, an increase of only 1.6% is shown, which is not very significant.

Also for wastewater assessment, there is a decrease in the Chemical oxygen demand of about 23% and total nitrogen of 5.5%. In the economical assessment section, a decrement of these values is shown; however, that analysis just includes the pre-tanning process, while this table shows the total amount of the entire process including wet-end finish.

There are still a few things to consider for the Life Cycle Assessment, like including the prior slaughter process, transportation, finishing, packing, final use and final disposal as some studies recommend. However, the intention of this thesis is to show the steps of the life cycle where there are actually differences as opposed to the conventional process.

According an environmental magazine,[77] the energy consumed by a 100 W bulb, running for 10 hours, corresponds to 3.6 MJ, and the production of this energy produces an emission to the atmosphere of approximately 0.5 kg of CO2.

Conventional process generates an amount of energy equivalent to 930 MJ. According to the magazine, this would translate into 129 kg of CO_2 per tone of rawhide processed more than the new process with modified Tara.

A following suggested work could be an entire LCA as mentioned, and also it could be interesting to asses the entire life cycle of other processes like Pre-tanning for Leather goods and shoe upper leather, vegetable tanning for leather goods or re-tanning of the chrome tanned leather process for automotive, or shoe upper using the new modified tara.

General Conclusions

The first part, consisted of a series of chemical and thermo-chemical treatments intended to modify the tara by aqueous extractions; starting with an aqueous extraction at high temperatures (70 and 136 ° C); and then, aqueous extractions at high temperatures and adding an acid or alkali; followed by high temperature aqueous extractions with sodium metabisulphite, where acid or alkali were also added with metabisulphite. When determining the percentage of tannins in these extractions, it was found that while increasing the percentage of tannins the percentage of non-tannin also increased, by determining free gallic acid by chromatography (HPLC). This only confirms the fact that the Tara tannin is hydrolysable tannin, and loses its tannin with different treatments.

For this reason, an aqueous extraction at a lower temperature (40 ° C) was conducted, and it was compared to the extractions performed at 70 ° C, the percentage of tannin showed that at lower temperature, tannins of Tara are less hydrolyzed. On seeing this, in the experimental part 3.1.5 this tanning was applied to hides and comparisons were made with the original Tara. The result was conclusive since the original Tara behaves way better in terms of skin penetration and shrinkage temperature. For all these reasons thermo-chemical modifications were discarded.

As to the physical modification, a milling process was performed, followed by a sieving process at different sizes. The determination of tannins was performed to see which particle size had the maximum tannin content. An application on hides and physical analysis were performed. Based on the results, it could be concluded that the milled and sieved Tara with particle sizes of 40-50µm, has the better physical modifications

After this, the milled and sieved Tara at 40-50 µm was combined with some products, such as some vegetable tannins agents or synthetic and other auxiliaries; these mixtures were tested on skin, and it was confirmed and concluded that the synthetic auxiliaries show the best results. Based on the results of this analysis, we found that the synthetic naphthalene sulphonic is the best auxiliary that can combine with modified Tara.

It shall be noted that during the experimental design 3.4, a naphthalene sulphonic synthetic powder with high purity was used, as well as a small amount of sulphited oil, with the aim of helping the penetration and distribution of the powders.

We decided to use modified Tara combined with synthetic naphthalene sulphonic as a experimental design, but also using sodium acid pyrophosphate, as sequestering iron and other properties mentioned above.

The experimental design was a surface graphic with a central design, orthogonal and rotable. The percentages of modified Tara and synthetic naphthalene sulphonic were the variables. The results are very promising and show that there are not many differences

relative to Shrinkage temperatures, however taking into account the results of the physical tests and organoleptic properties performed, it can be concluded that the optimal rates for this case are:

9% Milled and sieved Tara (50 – 40 µm)
2% Naphthalene sulphonic syntan
4% Sodium pyrophosphate acid

Given that, an increase of the use of a natural sustainable product, such as Tara took place, added to the fact that a reduction of 20% in the use of synthetic auxiliaries was also obtained; we could say that a more ecological article could be obtained. Additionally, possible iron stains were reduced thanks to the sodium pyrophosphate acid.

Other technical concept that has been tested is the avoidance of the possible complex of Fe (III) with the polyphenolic molecules of vegetable tannins. Pyrophosphate sequestering power was tested at the end of section 3.3 and 3.5; it was concluded that it has an excellent behavior as an iron sequestering.

Once the Tara modifications are selected new tailored formulations for leather articles have been designed.

The new optimized pre-tanning formulation using modified Tara, has been compare with a conventional pre-tanning process. It can be seen that the organoleptic properties are pretty much the same with good appearance and good behavior on the shaving process.

The determination of final baths showed an environmental improvement of the new process against the conventional one. This could be reflected in savings in the economical and environmental assessments.

Once the leather was pre-tanned and shaved, the re-tanning processes were carried out and compared.

The proposed formulations have been developed for upholstery leather articles at pilot scale. The leather articles were submitted to physical determinations and they fulfilled the technical specifications while accomplishing the environmental regulations involved.

The results were as expected, because new formulations were obtained by using the modified Tara to obtain end leather articles that meet the quality regulations, this can be corroborated in section 4.2, where some testing leather specification from some International car Companies are listed. This suggests the firm possibility of its marketing in the tanning industry.

As to the environment assessment in the final chapter, it can be said that the Tara tannins created are a sustainable product; because its obtaining does not require deforestation; its possible wastes can be reused to serve many fields; and the final waste water is less pollutant that the one resulting from some existing processes.

The life cycle assessment, besides showing a summarize of all inputs and outputs used in a whole tanning process, also found that there is a saving of approximately 129 kg of CO2 using the new process with modified tara.

In the economical side, we can say that the application of modified tara on the pre-tanning process, represents a lower cost in the chemical products and in the waste water treatment. This is a breakthrough, because in this case expenses have decreased while the sustainability of the end product has increased.

At the end of this thesis, very promising results can be seen. The conclusions of this thesis can support further experiments to develop technologies for a new range of leather articles. The objective of these is to satisfy the increasing consumer demand for sustainable and safe material used for manufacturing goods like shoes, apparel or upholstery leather.

Proposal for a new research work

This thesis has achieved some very promising results in the development of sustainable tannins with low carbon footprint and their optimum application in several steps of the tanning process.

Economic, environmental, and quality assessments were developed to determine its viability, which got pretty good results and led us to propose a product application on an industrial scale.

Therefore, a proposal to continue the research work would be to bring the modified tara to an industrial application, and to develop high quality leather.

There are many types of leather and many processes where the modified Tara could be applied; however, the following processes and the items proposed are those with the greatest application and demand.

- Pre-tanning: Automotive upholstery, footwear and leather goods.
- Vegetable tanning: Leather goods (belts, bag straps).
- Re-tanning: Automotive upholstery, footwear and leather goods.

For the vegetable tanning process, we propose to undertake a process to obtain a leather goods article, using a mixture of vegetable extracts as is commonly done, but in the mixture using the modified tara and find with an experimental design the optimal mix.

Once these applications take place, it would be important to conduct a broader life cycle assessment for each item, starting from the slaughter house, packing and transportation to the tannery; also taking into account the chemicals used and their production; and furthermore, the tanning and leather finishing processes, the treatment of tanning wastes (skin cuts, trimmings, shavings, waste water, etc.), distribution of leather, manufacture of leather article, distribution, product use and final disposal.

This life cycle analysis will allow to calculate the final carbon footprint and to compare it with a conventional process in order to give it a competitive advantage in the market.

Dissemination of results

Publications

Complementary to this thesis, there are two articles published in the Journal of the American Leather Chemists Association (JALCA), named:

- ***Low carbon products for the design of innovative leather processes. Part I: determination of the optimal chemical modification of tara. . (JALCA, Vol. 108, pag. 386-391, 2013)***

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- ***Low carbon products for the design of innovative leather processes. Part II: determination of the optimal physical modification of tara. (JALCA, Vol. 109, pag. 25-31, 2014)***

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One article pending to be published in the Journal of AQEIC (Asociación de Químicos Españoles de la Industria del Cuero).

- **Aplicación de taninos sostenibles con baja huella de carbono**

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Congresses

62nd Congress of AQEIC (Spanish Leather Chemists Association), Lorca (Murcia), May 10th and 11th, 2013

Presentation: **'APLICACIÓN DE TANINOS SOSTENIBLES CON BAJA HUELLA DE CARBONO'**
Author: **Jorge Gerardo Díaz Muñoz**

Glossary

Term	Definition
Auxiliary syntan	A synthetic tannin not suitable to be used alone as a tanning agent, but designed to be used with vegetable tannins to assist tannage, e.g. to accelerate penetration, or to enhance the characteristics of leather.
Beamhouse	The section of the tannery where hide and skins are prepared for tanning.
Caesalpinia spinosa	Scientific denomination for tara tree
Chrome tanned leather	Any leather article tanned mainly with chromium salts. Near 80% of commercialized leather is chrome leather.
Collagen	The protein composing the white fibers of vertebrate connective tissue, e.g. dermis of skin.
Corium	A kind of connective tissue forming the inner or the two layers of the skin of vertebrates, which is isolated for conversion into leather. Built-up essentially of collagen fibers, interspersed with small amounts of elastin and reticulum fibers, and with various kinds of cells.
Eco-friendly	Refers to any product or service that is not harmful to the atmosphere or surroundings. It also implies that the same precautions were taken in the manufacturing of the product.
Elongation (stretch) resistance	A measure of the stress needed to produce a certain increase in le length of a body
Grain	The surface of a hide or skin exposed by removal of the hair or wool and epidermis.
Greenhouse Gases (GHG)	It is a gas in an atmosphere that absorbs and emits radiation within the thermal infrared range
Grain tightening	The increase of the tightness or firmness of the grain of a leather, e.g. by application of a high molecular compound.
Hide	The outer covering of a mature, or fully-grown, animal of the larger kind.
Horse up, to	To place a hide or skin in process over the bar of a special stand, or horse, to drain or/and age
International	Any organization whose primary activities are developing, coordinating,

standardization body	promulgating, revising, amending, reissuing, interpreting, or otherwise maintaining standards that address the interests of a wide base of users outside the standard-developing organization.
Light fastness	Ability to endure long exposure to normal light conditions without serious deterioration of properties especially color.
Lining	A layer of leather, fabric or other material applied to the inside of a shoe upper, garment, glove, handbag, etc.
Tannin	A type of biomolecule. It is an astringent, bitter plant polyphenolic compound that either binds and precipitates or shrinks proteins and various other organic compounds including amino acids and alkaloids.
Tear resistance	Ability of a sheet of material, e.g. leather, to resist a shearing, or tearing, force applied merely by shearing one area across a second adjacent, firmly-held, area as in the tongue-tear test.
Tensile strength	The tensile force required breaking, or rupturing, a material, expressed as kilograms force per sq. mm. or cm of cross section.
Replacement syntan	A synthetic tanning agent that can largely, or entirely, replace the vegetable tannins without fundamentally altering the tannin process or the character of the finished leather.
Samming	Bringing leather to uniformly partly- dry state necessary for certain finishing operations, e.g. by partially drying-out, by passing it through the Samming machine or by pressing.
Shrinking temperature	The temperature at which a skin or leather decreases in dimensions when heated under special conditions, e.g. when heated in water.
Skin	The more or less thick, tough, flexible covering of human and other animal bodies
Syntan	An abbreviation of the term synthetic tannin.
Vegetable tannin	A tanning agent contained in, and obtained by extraction of, the barks, fruits, galls, leaves, roots or wood of certain plants
Wet blue	Term for a hide, or skin, which has been subjected to the usual beamhouse processes, chrome-tanned and left wet; may be stored or exported in this state.
Wet white	Term for a hide, or skin, which has been subjected to the usual beamhouse processes, chrome free and left wet, may be stored or exported in this state.

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"DEVELOPMENT OF SUSTAINABLE TANNIN WITH LOW CARBON FOOTPRINT TO OBTAIN HIGH QUALITY LEATHER"

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ANNEX

Annex 1: Tannin process (General overview)

Beamhouse:

- *Sorting:* On receipt, hides and skins may be sorted into several grades by size, weight, or quality. Hides are also sorted by sex.

- *Trimming:* Some o the edges (legs, tails, face, udders, etc.) of the raw hides and skins can be cut off.

- *Curing & storing:* Curing is a process that prevents de degradation of hides and skins from the time they are flayed in the abattoir until the process is the beamhouse are started. When the raw material cannot be processed immediately ("green") it must be cured. The methods for curing for long-term preservation are: salting, brining, drying and salt drying. Methods for short-term preservation are cooling, using crushed ice or refrigerated storage and biocides. Hides and skins are generally stored as they are received by the tannery on pallets in ventilated or air conditioned and/or cooled areas, depending on the method of curing chosen. From storage the hides and skins are taken to the beamhouse.

- *Soaking:* Soaking is carried out to allow hides and skins re-absorb water, to clean and to remove inter-fibrillar material from them. The soaking methods depend on the state of the hides. This process is carried out in two steps: a dirt soak to remove the salt and dirt and a main soak. The process is carried out in processing vessels, such as mixers, drums, paddles or pits. The duration of soaking may range from several hours to a few days. Depending on the type of raw materials, soaking additives can be used such a surfactants, enzyme preparations and bactericides.

- *Unhairing & liming of bovine hides:* The function of liming and unhearing is to remove hair, interfibrillar components and epidermis and to open up the fiber structure. Hair removal is performed by chemical and mechanical means. The keratinous materials (hair, hair roots, epidermis) and fat are eliminated from the pelts mainly with sulphides (NaHS or Na_2S) and lime. Enzymatic preparations are sometimes added to improve the performance of the process. The process of liming and unhearing can be carried out in process vessels such as drums, paddles, mixers or pits.

- *Pinting & liming of sheepskins:* The aim of painting is to bring about the breakdown of the wool root within the skin so that as much undamaged wool fiber as possible can be pulled easily from the pelt. Paint, generally, consisting of a mixture of sodium sulphide and lime, is applied to the flesh side of the skin and left for several hours. Application of the paint can be through a spraying machine or manually. After several hours the wool can be "pulled" from the skin, either manually or mechanically. After pulling, the skins are limed in process vessels, with the same purpose as the liming of bovine hides. Wool-on skins are not painted, unhaired or limed.

- *Fleshing:* Is a mechanical scraping off of the excessive organic material from the hide (connective tissue, fat, etc). The pelts are carried through rollers and across rotating spiral blades by the fleshing machine. Flashing can be carried out prior to soaking, after soaking or after pickling.

- *Splitting:* By mechanical splitting the thickness of hides and skins is regulated and they are split horizontally into a grain layer and, if the hide is thick enough, a flesh layer. Splitting is carried out on splitting machines, fitted with a band knife. Splitting can be done in limed condition or in the tanned condition.

Tanning operations:

- *Deliming:* To remove residual lime from the pelts and to take them to the optimum condition for bating. This involve a gradual lowering of the pH (by means of washing and addition of deliming chemicals), an increase in temperature and the removal of residual chemicals and degraded skin components. Generally, deliming is performed in a processing vessel such as a drum, mixer or paddle.

- *Bating:* Is a partial degradation of non- collagenic protein achieved by enzymes to improve grain of hide and the subsequent run and stretch of leather. In this process the rest of the unwanted hair roots and scud can be removed.

- *Degreasing:* Excess grease must be eliminated from fatty skins (sheep, pig) to prevent the formation of insoluble chrome-soaps or prevent the formation of fat spots at later stage. Degreasing is most relevant in processing sheep skins, where the natural fat content is about 10-20% on dry weight. The nature of this fat makes it difficult to remove because of the presence of cerides and a high melting temperature. The three methods commonly used for degreasing are: with organic solvent and non-ionic surfactant, in aqueous medium with non-ionic surfactant and in solvent medium.

- *Pickling:* Is carried out to reduce pH of the pelt prior to mineral tanning and some organic tannages. The choice of the exact pickling parameters depends on the subsequent tanning step. Very often is carried out in the tanning liquor; however, pickled pelts can be traded, especially sheepskins, using fungicides to protect them from mould growth during storage.

- *Tanning:* In the tanning process the collagen fiber is stabilized by the tanning agents such that the hide is no longer susceptible to putrefaction or rotting. In this process the collagen fibers are stabilized by the cross-linking action of the tanning agents. Furthermore their dimension stability, resistance to mechanical action and heat increase. Various agents can be categorized in three main groups: mineral tannins, vegetable tannins, alternative such as syntans, aldehydes, oil… Chromium and vegetable tanning agents are the most commonly used tanning agents.

- *Draining, samming and setting:* After tanning, the leathers are drained, rinsed and either horsed up to age, or unloaded in boxes and subsequently sammed to reduce the moisture content prior to further mechanical action, such as splitting and shaving. The setting our operation can be carried out to stretch out the leather. There exist machines, which combine the samming and setting action. After samming and setting, hides and skins can be sorted into different grades after which they are processed further or sold on the market.

- *Shaving:* The shaving process is carried out to achieve an even thickness throughout the skin/hide, and it can be carried out on tanned or crusted leather. Shaving is carried

out where splitting is not possible or where minor adjustments to the thickness are required.

Post-tanning operations:

- Post-tanning involves neutralization and washing, followed by retanning, dyeing and Fatliquoring, mostly done in a single processing vessel. At this stage of the process, specialist operations may also be carried out to add certain properties to the leather such as water repellence or resistance, oleo-phobic, gas permeability, flame retarding, abrasion, anti-electrostatics, etc.

- *Neutralization:* Is the process by which the tanned hides are brought to a pH suitable for the process of retanning, dyeing and Fatliquoring.

- *Bleaching:* Vegetable tanned skins and leathers with wool or hair may need to be bleached in order to remove stains, or to reduce the coloring in the hair, wool or leather prior to retanning and dyeing.

- *Retanning:* The retanning process can be carried out with the following objectives:
  - To improve the feel and handle of the leathers
  - To fill the looser and softer parts of the leather in order to produce leathers or more uniform physical properties and with more economical cutting value to the customer
  - To assist in the production of corrected grain leathers
  - To improve the resistance to alkali and perspiration
  - To improve wetting back property of the hides which will help the dyeing process.
  - A wide variety of chemicals can be used for the re-tannage of leather. They can generally be divided into the following categories: vegetable extracts, syntans, aldehydes, mineral tanning agents and resins.

- *Dyeing*: The dyeing process is carried out to produce level colors over the whole surface of each hide and skin and exact matching between hides in a commercial pack. Typical dyestuffs are water-based acid dyes.

- *Fatliquoring:* Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or might be synthetics based on mineral oils.
  The re-tanning, dyed and fatliquored leather is usually washed before being horsed up (piled on “horses”) to rest.

- *Drying*: The objective is to dry the leather whilst optimizing the quality and area yield. There is a wide range of drying techniques and some may be used in combination. Each technique has a specific influence on the characteristics of the leather. The most used drying techniques include samming, setting out, hang drying, vacuum drying, and toggle drying. Generally samming and setting out are used to reduce the moisture content mechanically before another drying technique is used dry the leather further. After drying, the leather may be referred as curst. Crust is a tradable intermediate product.

Finishing:

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished with respect to: color, gloss, handle, flex, adhesion, rub fastness, as well as other properties including extensibility, break, light and perspiration fastness, water vapor permeability and water resistance as required for the end use. Generally, finishing operations can be divided into mechanical finishing processes and applying a surface coat.

- *Mechanical finished processes:* a wide range of mechanical finishing operations may be carried out to improve the appearance and the feel of the leather. The following list includes, among others, commonly used mechanical finishing operations:

- *Conditioning*: optimizing the moisture content in leather for subsequent operations
- *Staking:* softening and stretching of leather
- *Buffing/de-dusting:* abrading of the leather surface and removing the resulting dust from the leather surface.
- *Dry milling:* mechanical softening
- *Polishing*
- *Plating / embossing:* flattering or printing a pattern into the leather.
- These operations may be carried out before or after applying a coat, or between the applications of coatings.

- *Applying a surface coat:* The purpose of applying a surface coat is:
- To provide protection from contaminants (water, oils, soil…)
- To provide color either to modify dyed color or reinforce that provided by the dyes, to even the color or to disguise defects.
- To provide modifications to handle and gloss performance
- To provide attractive fashion or fancy effects
- To meet other customer requirements
- There is a wide range of application methods each of which has its advantages and disadvantages. A combination of methods can be used to achieve the desired effect on the finished product. In principle, the following types of application methods can be distinguished:

- Padding or brushing the finishing mix onto the leather surface
- Spray coating, which involves spraying the finishing material with, pressurized air in spry cabinets.
- Curtain coating, which is passing the leather through a curtain of finishing material
- Roller coating, which is an application of finishing mix through a roller
- Transfer coating, which is the transfer of a film/foil onto leather previously treated with an adhesive.

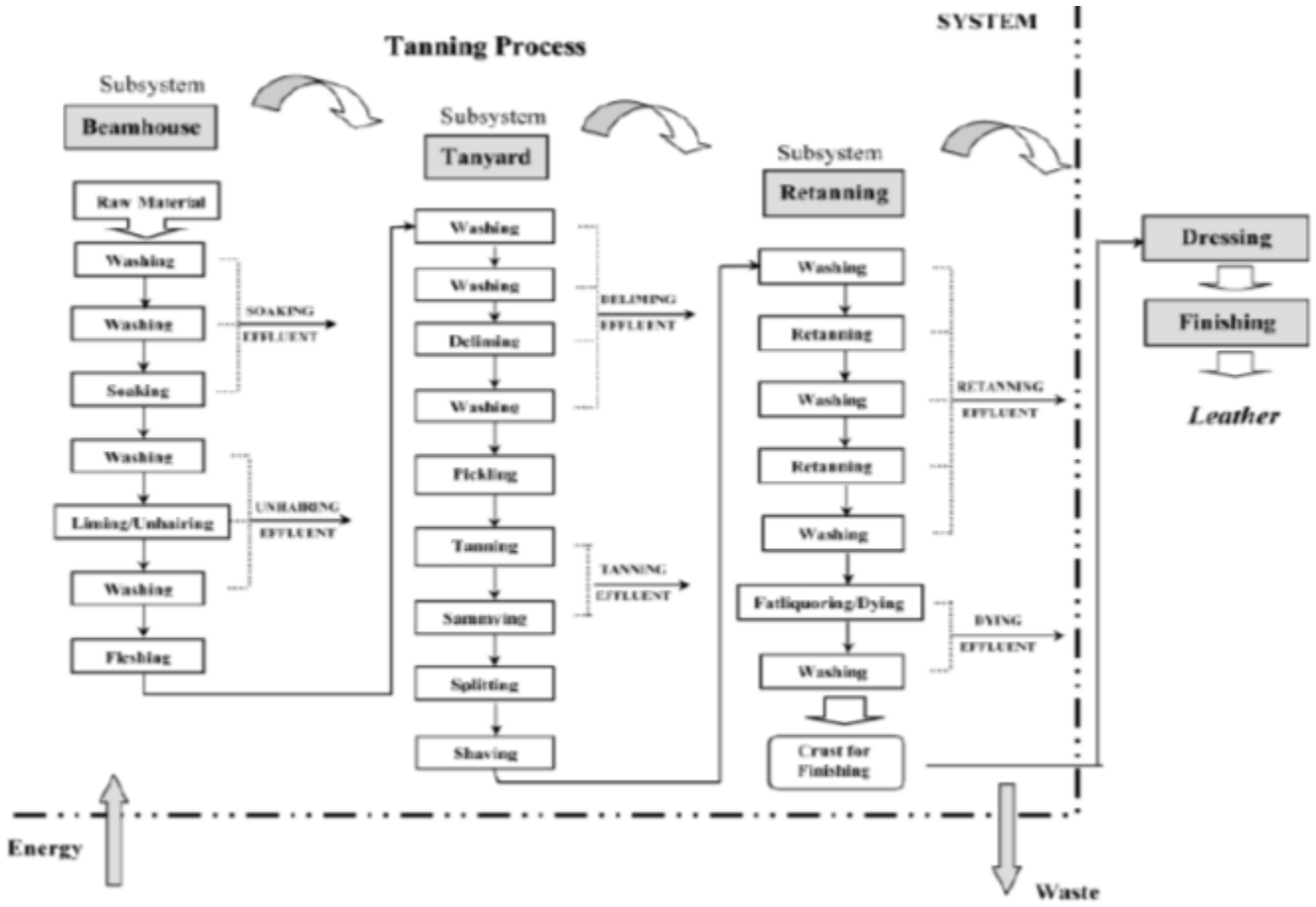

Figure 1: Flow chart of Tanning process system

Annex 2: Inputs and outputs in tannin process.

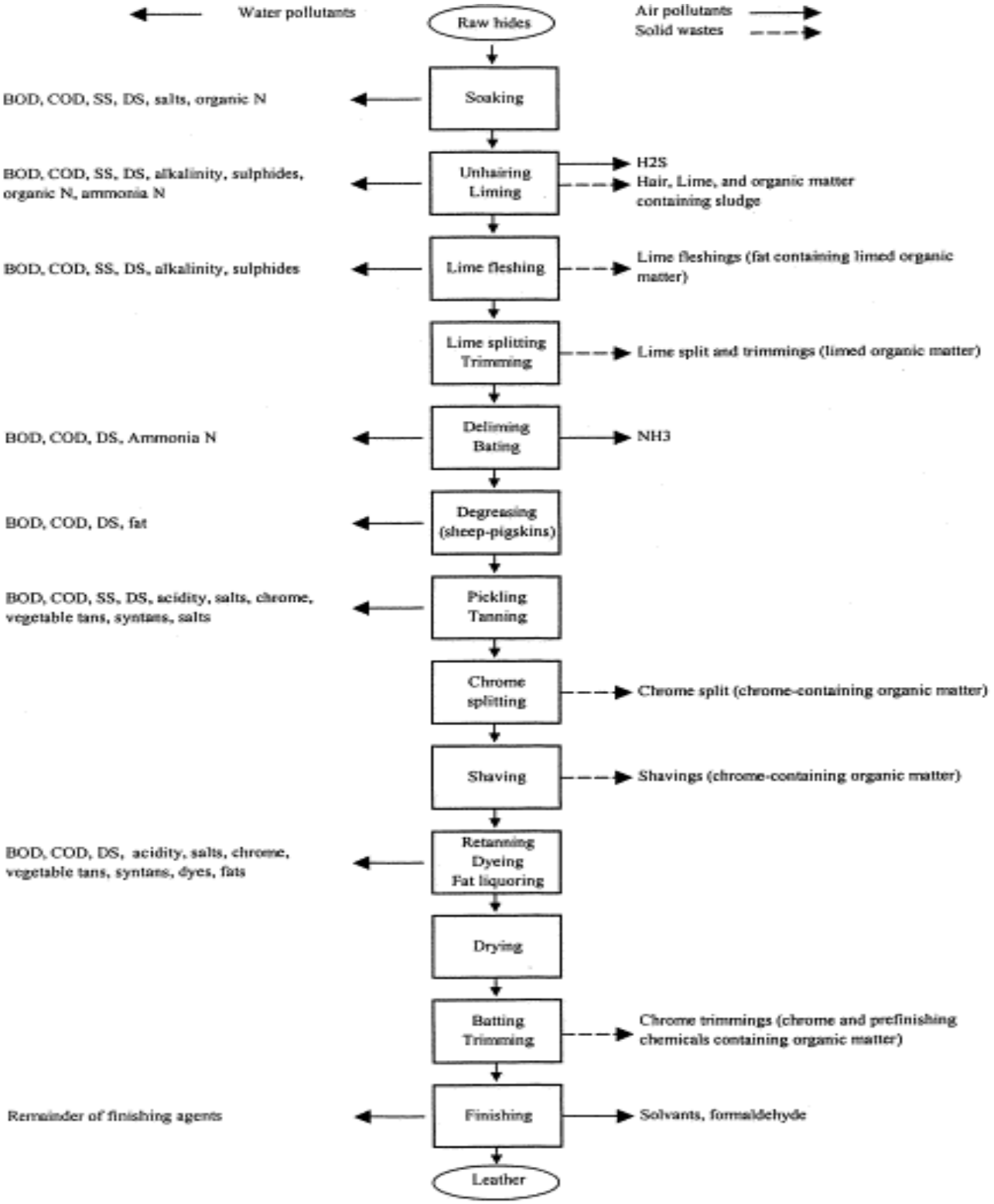

Figure 2: Inputs and outputs in tannin process.

This figure expresses the input and output overview for a conventional (chrome tanning) process for bovine salted hides per ton of raw hide treated. The quantities and qualities of emissions and waste produced by tanneries strongly depend on the type of leather processed, the source of hides and skins and the techniques applied.
Environmental concerns in a tannery include waste water, solid waste, air pollution, soil protection and safety aspects. The releases potentially contain toxic, persistent or otherwise harmful substances.

Most of the steps of the tannery's operation are performed in water. Consequently waste water effluent is one of the major concerns in tanneries. The characteristics of waste water are a high chemical and biological oxygen demand, high salt content and toxic releases. The table bellow shows the consumption level of the main process chemicals, tanning agents and auxiliary chemicals for a conventional tanning process for salted bovine hides.

A further aspect to be aware of in the tanneries is the potential hazard to human health and the environment for handling, storing, transporting and packaging of chemicals.

When effluents discharge to water treatment plants, either municipal or plants operated for large tanning complexes, it is produced a high amount of sludge, about 5 to 10% of the total volume of effluent being discharged. The settle sludge resulting is normally in the form of a liquid with a solids content of 3-5% dry solids. Typically, sludge are dewater to have a dry matter content if 25-40%.

For sludge and other residues further re-use and recycling options exists. The viability of these options is strongly dependent on the composition of the residues. Landfilling of wastes with high organic content and toxic substances is increasingly coming under pressure in many countries. Other strategies include reduction measures by means of recycling, composting, biogas production or materials/energy recovery. However, an average of more than 80% of these solid residues and sludge contain chromium.

Probably, the most debated issue with regards to the leather industry impact in the environment is the chrome tanning, thus the utilization of chromium (III) salts. They are used in the tanning industry and its toxicity shall not be confused with chromium (VI). Hexavalent chromium is known to be a skin irritant and thought to be carcinogen.

Despite toxicity of chromium (III) salts is similar to the table salt, there are concerns because potential oxidation, either in leather articles, effluents after chrome tanning or solid wastes. It is know the effect of certain fatliquors and other chemicals to oxidize tanned leather, but also, some other that prevent such formation. Polyphenols, contained in vegetable tannins have shown anti-oxidation properties.

Due to the fact that chromium has been under pressure from regulatory authorities, and other collectives, some leather users are beginning to demand the use of alternative tanning agents, such as glutaraldehyde, aluminum and vegetable tannins. In any case, nowadays, chrome tanning is the most efficient and versatile tanning agent available and it is relatively cheap.

The amount of chemicals used varies significantly with the specification of the final product, the pelts treated and the process chosen. Figures for consumption of chemicals can therefore only be given within a broad range. Besides the main process chemicals, a great variety of substances is used for auxiliary process purposes. For reasons of workplace health and safety,

some barely soluble agents are applied as aqueous suspensions or dispersion, which may have to be stabilized with auxiliaries, thus adding even further to the number of chemicals used.

It is common for tanneries to use more than 300 different chemicals in the lather making process. The potential impact of chemicals will depend of many factors:

- The selected chemicals
- The medium in which it is released (solid waste, atmosphere, effluent, soil…)
- The actual concentration received by the environment. It should be noted that the quantities in the wastewater are not strictly a function on the input quantities. Some agents are almost totally absorbed, react in the process or are precipitated in the wastewater treatment.
- Transformation of the chemicals due to chemical and biological processes before and after discharge o the environment. The substances might react during the process or with other constituents; or they are degraded in the wastewater treatment plant; they can also be distributed to different outlets of a factory.
- Continuous or batch discharge.
- Characteristics of the receiving environment. For example in a water course, essential factors are: the stress of organisms due to other constituents; inhibitory or synergetic effects due to other chemicals; flow characteristics; light and temperature.

Chemical consumption	**%**
Standard inorganic (without salt from curing, acids, bases, sulphides, ammonium-containing chemicals)	40
Standard organic, not mentioned bellow (acids, bases, salts)	7
Tanning chemicals (chrome, vegetable and alternative tanning agents)	23
Dyeing agents and auxiliaries	4
Fatliquoring agents	8
Finish chemicals (pigments, special effect chemicals, binders and crosslinking agent)	10
Organic solvents	5
Surfactants	1
Biocides	0,2
Enzymes	1
Others (sequestering agents, wetting agents, complexing agents…)	
Total	100

Table 1: Consumption of chemicals in leather processes (Source IPPC)[1]

[1] European Commission. Integrated Pollution Prevention and Control (IPPC). Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), p. 42. 2013.

Annex 3: Tara (Photos and description)

The tree:

Photo 1: Tara tree

The tara tree is small, only 2 – 3 meters high, but oldest species can achieved up to 12 meters; short, cylindrical and sometimes twisted trunk with a dark grey bark with scattered prickles, with dense and rising branches and twigs, sometimes from the lowest part, and leafy and umbrella-shaped top. Pivot roots and abundant secondary roots. It is a leguminous plant and fixes the nitrogen. BASFOR[2] reports selected trees to supply germoplasma of 3 – 11 m. high, trunk diameter average 22 cm, and top diameter of average 5 m.

Alternate composed, like feathers, slightly prickly, ovoid and brilliant leaflets of dark green color measuring 15 cm of length.

[2] BASFOR: Semillas Forestales – Plantas y Asesoramiento técnico. Centro de Semillas Forestales. ESFOR (School of forest science. Universidad San Simón. IC) http://www.umss.edu.bo/Academia/Centros/Basfor/

Photo 2*: Tara flower*

Hermaphrodites, yellow to red color, grouped in grapes at the extreme of the terminal branches. Flowers are 15 to 20 cm long, irregular and tubular calyx, short twice bigger than stamens, long sepals, corolla with free petals, grapes 8 – 15 cm. long.
Fruits and pods:

Photo 3: Tara pods

The fruit of Caesalpinia spinosa is a flat yellow to orange pod up to 10 cm long and 2 cm wide. They are fragile when are dry. Every pod contains up to 7 round seeds with a diameter of 5 to 7 mm. The color of the seeds is dark red when mature.

They weight 3,3 g average, what means one kg of seed needs 305 fruits.

Annex 4: Determination of tannin content by filter method

Preparation of the analytical solution:

The appropriate quantity of vegetable tanning agents were weighted on a analytical balance to obtain an analytical solution containing between 3,75 and 4,25 grams of substances absorbed by the hide powder and 800 ml of hot distilled water 60 °C to 80 °C was added in a calibrated 1000 ml flask. It was shacked to fully dissolve the tanning agents, leave to cool down in water bath at (20 ± 2)°C and distilled water up to the mark was added.

Preparation of the bell:

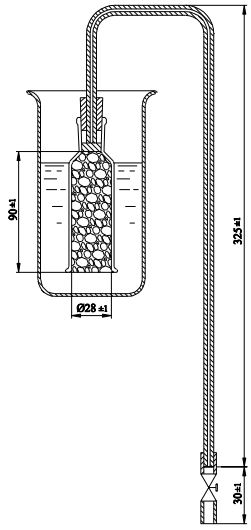

Photo 4: Bell, from the extraction method

A layer of cotton wool was placed at the top of the bell to prevent the hide powder from entering the capillary tube.

A rubber cork containing the glass capillary tube was put in the bell.

7 g of hide powder was weighted on a technical balance and introduced uniformly in the bell pressing it down, up to the top of the rim.

The polyethylene tube was put in the glass capillary tube and a Hoffman clamp was used.

The non-tanning agents were determined as follows:

The bell containing hide powder was placed in a beaker of suitable capacity. The beaker was filled with the unfiltered analytical solution up to the neck of the bell. When the hide powder was completely soaked, it was sucked on the longer end of the capillary tube to create a slight depression and the solution started siphoning.

The Hoffman clamp was used to adjust the flow of the solution so that about 8-10 drops of the de-tanned solution drip through per minute.

A total of 90 ml in (120 ± 10) min was collected.

The first 30 ml of the filtrate were collected in a 50 ml glass measuring cylinder (5.16) and disposed of.

The resulting solution was clear.

Photo 5: Photographs of the tannin determination method assembly.

To control the breakthrough of tanning agents, 5 ml of the collected solution were used and added 0,5 ml gelatine solution.
The next 60 ml were collected in a perfectly dry 100 ml glass-measuring cylinder to determine the non-tanning agents. To avoid side reactions, temperature was kept between 18ºC to 20ºC
With a pipette 50 ml, the filtered solution was transferred into a previously dried and weighted silver dish.
The dish was placed on the water bath for complete evaporation.
The dish was put in a drying oven at (102 ± 2) °C to attain constant weight (about 18 h ± 2 h).
The dish was put in the silica gel 173xcel173ators (5.2) and weighs it after 15 min on analytical balance.

Determination of soluble substances

To filter the analytical solutions, a filter system was used according to this draft:
Cellulose acetate membranes with 0,45 µm pores were used.
About 100 ml of filtrate were collected.
The filtered solution was transfer with a pipette into a previously dried and weighed silver dish.
The dish was placed on the water bath until complete evaporation Then in an oven at (102 ± 2) °C to attain constant weight (about 18h ± 2h).
The dish (5.3) was put in a silica gel dryer and weight if after 15 min on analytical balance.

Determination of total solids

A silver dish was calibrated in an oven at (102 ± 2) °C and then cool it off in a dryer, for about 15 min, down to ambient temperature. The dish was weighted with the analytical balance.
About 3 g – 5 g of the sample were added to the dish.
The dish was put in the oven without air circulation at (102 ± 2) °C to attain constant weight (about 18h ± 2h). Then was put in a silica gel dryer and weighted after 15 min on analytical balance.

Calculation of results:

The percentage content of dry substances (S_{to}) (% total solid) was calculated using the equation (1).

$$S_{to}=\frac{m_1 \times 100}{m_{P0}} \quad (1)$$

where:

S_{to} percentage content of dry substances (% total solid) in %;

m_1 is the dry residue as determined (determination of total solids) in g;

m_{P0} is the product's weight (determination of total solids) in g.

The percentage of soluble solids (S_{so}) was calculated using the equation (2).

$$S_{so}=\frac{m_2 \times 20 \times 100}{m_{P1}} \quad (2)$$

where:

S_{so} percentage content of soluble solids in %;

m_2 is the dry residue of 50 ml of the filtered analytical solution in g;

m_{P1} is the initial weighing of the product (analytical solution) in g.

The percentage of non-tanning solid (S_{nt}) was calculated using the equation (3).

$$S_{nt}=\frac{m_3 \times 20 \times 100}{m_{P1}} \quad (3)$$

where:

S_{nt} percentage of non-tanning solid in %;

m_3 is the dry residue of the non-tanning agent solution, deducted from the blank value in g;

m_{P1} is the initial weighing of the product (analytical solution) in g.

The percentage of tanning agents (T) shall be calculated using the equation (4).

$$T=S_{so}-S_{nt} \quad (4)$$

The percentage of insoluble matter (I_M) shall be calculated using the equation (5).

$$I_M = S_{to} - S_{so} \quad (5)$$

The percentage of water (W) shall be calculated using the equation (6).

$$W = 100 - S_{to} \quad (6)$$

The ratio of tanning agent to non-tanning agent (R) shall be calculated using the equation (7).

$$R = = \frac{T}{S_{nt}} \quad (7)$$

Annex 5: Characteristics and classification of Syntans

Syntans Characteristics.

The synthetic tanning is obtained treating aromatic substances type phenol, naphthol, resorcinol, pyrocatechol, piragalol, lignosulfonic acids, etc. with formaldehyde to condense them and subsequently make them water-soluble with sulfuric acid introducing them sulphonic groups.

Among the characteristics in synthetic tanning that influence tanning ability is the size of molecules, being important their average molecular weight. When the phenol is condensed with formaldehyde thermosetting resin is formed, the hardness and molecular weight depends on the relationship with the condensing agent (formaldehyde) a greater amount of formaldehyde, the higher the molecular weight. If the molecule is too small gives a poor tanning action and, on the contrary, it is too large there is a poor penetration into the leather.

The commercial synthetic phenolic base have a molecular weight of 400-800, the higher molecular weight is not good fixing on the reactive groups of collagen, but may have a filling effect when applied on skin.

The synthetic tanning can be:

1. Synthetic tanning with own tanning power, called substitution. Are synthetic tannins whose chemical structure is similar to that of natural tannins because they contain phenolic hydroxyl groups and thus are able to react with protein producing tanned leather, namely that can be used as sole tanning. Have the following characteristics:

- High light fastness and oxidation also, while vegetable tanning tend to darken light and oxidized with air oxygen.
- Clarify leather color.
- Further clarify the post-dyeing because being highly anionic they would occupy the dye anilines position.
- Their aggregates of molecules and particles are smaller, with a minor colloid that natural vegetable tannins that give less filling leather. For example an acacia or quebracho tend to fill leather much more than synthetic substitute tannins, but in return also achieved much softer leathers.
- They are less sensitive to iron and electrolytes.

2. Tanning with nothing or little synthetic tanning power, called auxiliary.
   They are used to facilitate the process of tanning to other tanning substances, modify the behavior of vegetable extracts or the synthetic replacements.

Classification and properties of syntans according to their behavior:

1. Main Tannings or complete tannings. For its quality of tanning alone, can completely replace or in part vegetable tanning and tanned leathers give the desired properties.

2. Tanning whites. They can also be counted, in most cases, as main tanning agents. They possess most of the time, a lesser effect of fullness, while a high white effect and high light fastness. The white-tanning agents can be used for white retanning chrome leather tanning and as unique in some cases, depending on their manufacture. They tan giving white-pigmented fine, giving soft feeling, are particularly light fastness and fillers.

3. Tanning to levant (Crispado). They are highly acidic and astringent, for a combined effect of the flower and thereby achieve a high tense granular. Along with phenolic tanning is also used for years, glutaraldehyde for tense line effects.

4. Pre-Tannings. They were developed for improving the diffusion of large parts tanning and highly concentrated, to accelerate or reduce the tanning time. They give tanning colors clearer, smoother and tightness.

5. Re-tannings. They are lot of products. Mainly used for further processing of chrome leather, to achieve special effects and properties, tightness, grain resistant and texture, softness or full strength, light colored or dyed equalization, fitness for grinding, light fastness or aging stability and improved physical properties.

6. Tanning auxiliaries. They serve to support special tannages as dissolution of sludge in vegetable tanning floats, tanning or distribution or pH regulation.

7. Tanning bleaching. They are used for bleaching or correct the color of leather, vegetable tanned or to clean the surface of the grain.

8. Tanning dispersant. They are used with untreated Vegetable extracts, tanned slow and difficult, for example quebracho. This avoids adding large amounts of sulfite.

9. Tanning of fullness. They serve as filler of heavy leather, for plane leather padding on the re-tannage. Along with syntans and some polymeric tanning agents, may be mentioned resins tanning with a filling effect selective for the parts of the skin of loose structure.
10. Tanning neutralization. These products, which by the strong buffering masked cause decreased sensitivity to acids and good light fastness, in neutralization, along a retanning effect a neutralization is done. There is no danger of excessive neutralization.

The synthetic Tannings are used bit as unique tanner, only when it wants to get a white leather or leather with unique characteristics. The synthetic tanning have less filling power than the

vegetable extracts, and tanning leather gives a stiff appearance. They usually exhibit poor light fastness.

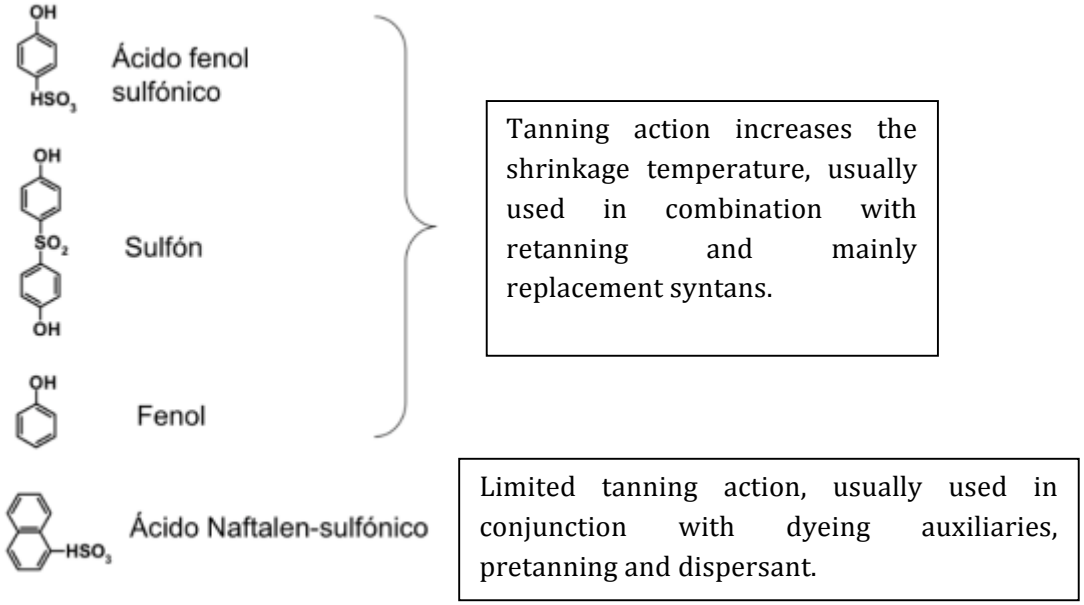

Figure 3: Main components of syntans.

Annex 6: Some Photos of the project

- **Chemical modifications**

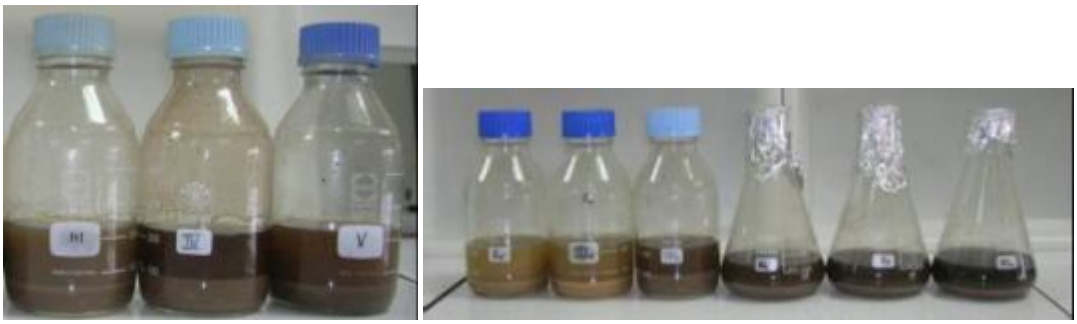

Photo 6: Chemical and aqueous extraction processes at 70ºC and Solutions obtained after sulphitation process at 70ºC.

- **Physical modifications**

Photo 7: Laboratory Rotary shaker for milling process

Photo 8: Sieves used for experimental part II.

- **Leather production**

Photo 9: Products used in Experimental part III.5

Photo 10: Drums laboratory scale and pilot scale used in this project

Photo 11: Original Tara and Milled Tara

Photo 12: DSC, Differential Scanning Calorimeter

Annex 7: The surface graphic for a quadratic, centralized, orthogonal and rotatable design.

Design of a pretanning process with tara aims to obtain the components of a mixture that better fits tara by improving its performance for a sustainable wet white pretanning process. This part 4 optimizes the best working conditions of the selected blend components to maximize the values of shrinking temperature, tensile strength, tensile elongation and tear resistance.

To optimize a magnitude that depends from one o more variables X = (x, y, …z), it is necessary to determine the values of the parameters which the function obtains the absolute optimal, maximal or minimal values.

There exists several techniques to optimize a function, but to simplify and better understand the behavior of the blend, the experiments will be based on a design with a response surface. Visually, best fitted response can be analyzed in a certain area of interest factor levels and the sensibility to the factors can be evaluated.

The response surface and the analysis strategy will assume that the average of the response variable μ_y is a function of the quantitative factor levels represented by the variables x_1, x_2, …, x_k. The polynomials models are used in the practice to estimate the real function. Normally, the real function is unknown and polynomial function often gives a good loom in areas relatively small of the quantitative factor levels.

The polynomial models used to analyze variable response surfaces are normally lineal:

$$\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2$$

or quadratic:

$$\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2$$

When the optimal surface region is identified, a new design is necessary to characterize the variable response surface. 2^k factorial models are useful designs to identify significant factors and optimal response regions but require a big number of tests.

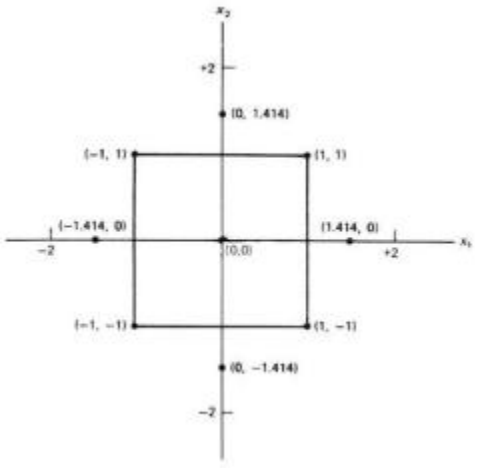

Figure 4: Surface graph of a quadratic equation, centralized design, orthogonal and rotatable

Box and Wilson (1951) proposed decentralized designs reducing the number of combinations, based on 2^n factorials with 2n additional combinations, or axial points, through the coordinated axis of codified factor levels: (±α,0,0,…,0),(0,±α,0,…0),…(0,0,0…±α) and m replications in the designed center of the coordinates.

In order to obtain the same accuracy for all the mean estimations, it is necessary a rotatable design. In this case, the accuracy of the estimated surface is independent of the design orientation with regard to the real response.

Figure 5: The surface graphic for a quadratic, centralized, orthogonal and rotatable design

Centralized design becomes rotatable establishing axial points values a $\alpha = (2^n)^{1/4}$.

The α value for a 2 factor design is:

$$\alpha = (4)^{1/4} = \sqrt{2} = 1{,}414$$

The surface graphic for a quadratic, centralized, orthogonal and rotatable design is in Figure 30.

Trials are carried out in the same conditions as described in Section 4: Part 3: Design of a pretanning process with tara, and designed according to the following quadratic, centralized, rotatable and orthogonal design. The percentages are also adjusted to the tannin content of each ingredient.

Annex 8. Technical information for some products used in recipes.[3]

- **LeatherOil EFA**

Synthetic phosphoric ester
Phosphoric ester

LEATHEROIL EFA is a general use fatliquor for all skin types. It has good light fastness and given its synthetic nature eliminates the risk of fatty spew. No oxidizable. Because of its high stability allows use in tanning and retanning bath, helps in better distribution of chrome.
LEATHEROIL EFA has a great fixation capacity and dispersing power, helping to the penetration of the fatliquor mixture. It makes a silky dry touch leathers, soft and flexible.
It is completely anionic and has no problem to use with vegetable extracts.

Characteristics:

- Appearance: Clear yellowish liquid
- Active content: 55 % ± 2
- pH 10%: 6.5 ± 1
- Character: Anionic

- **LeatherOil SS**

Synthetic sulphited Fatliquor
Synthetic and natural sulphited Fatliquor

LEATHEROIL SS has low oxidability and high penetration.
It uses in tanning floats as pre-fatliquoring because has good stability to electrolytes.
LEATHEROIL SS lends a natural bright to suede plush and have a good light fastness.

- **LeatherOil XL**

Lecithin oil
Lecithin and natural oils

LEATHEROIL XL is fatliquor for all types of articles especially for nappa touch. It's used as a complement of other oils. It's very suitable for nappa and upholstery articles, giving no heavy leather with light weight feeling, round and silky touch and good fullness.
It provides a good penetration alone or in combination with other fatliquors. It's stable to acids and electrolytes in normal retanning conditions.

[3] www.leatherquimica.com

- **LeatherOil P-4**

Sulphated fatliquor
Sulphated natural and synthetic oils.

LEATHEROIL P-4 performs in any kind of leathers and skins.
LEATHEROIL P-4 provides excellent fullness, softness and round feel. Light fastness recommended for white leather.
It can be used as the main fatliquor, or to improve the fatliquoring composition penetration.
LEATHEROIL P-4 is stable to anionic and to non-ionic auxiliaries.

- **LeatherOil PI-90**

Sulphited natural fatliquor
Sulphited fish oil.

LEATHEROIL PI-90 is a fatliquor developed for soft leather, it has a good penetration and it is distributed very well in the structure of skin giving stability to the oil emulsion.

LEATHEROIL PI-90 is stable to electrolytes concentrations, and to hard water. It use chrome floats, improving tanning evenness and tear strength values.

- **LeatherSyn WRP**

Synthetic tanning
Universal Synthetic tanning

LEATHERSYN WRP has a good stability in front of chrome salts and a good light fastness.
A reaction with chrome skins gives a complex that improves fullness and grain tightness.
LEATHERSYN WRP can be used in tanning.

- **LeatherSyn NO**

Neutralizing and dispersing agent
Neutral salts of aromatic sulphonic acids.

LEATHERSYN NO in vegetable tanning, or in chrome leather retanning with vegetable extracts, helps to the penetration and distribution of natural and synthetic tannins. The affinity for cationic dyes is increased.

LEATHERSYN NO is a chrome-masking agent. If used in chrome basification, softness, fullness, grain tightness and elasticity are enhanced. It reduces the affinity for anionic tannins, fatliquors and dyes, when used as a soft neutralizing agent in wet-blue. Uniformity of fatliquoring, softness, fullness, and evenness of dyeing are improved.

Characteristics:

Appearance: Light brown powder
Active content: > 95 %
pH 10%: 7.0 ± 1
Character: Anionic

- **LeatherTan MM**

Retanning resin
Melamine polymer.

LEATHERTAN MM performs in any kind of leathers and skins. It has a selective filling action in the emptiest parts.
LEATHERTAN MM provides excellent fullness, softness and round feel, with tight and fine grain. It can be used to obtain short and even nap, when buffing suede, nubuck or corrected grain.
LEATHERTAN MM is compatible with anionic and non ionic auxiliaries.

- **LeatherTan FP-30**

- Retanning Resin
- Polymeric aqueous solution.

LEATHERTAN FP-30 is a retanning resin that gives fullness and versatility to the leather.
LEATHERTAN FP-30 keeps the chrome character in leather, suitable for empty structure retanning, and it is possible to replace all vegetable tannins and some synthetic tannins.
LEATHERTAN FP-30 clear dye used before dyeing, but if used then its effect is reduced.

Annex 9: Experimental design 3.4

3.4.4.1 Statistical analysis of Experimental Design for Shrinkage Temperature (Ts)

Analysis Summary

Estimated effects for Ts		
Average	69,75	+/- 0,335528
A: Tara	1,03033	+/- 0,474509
B: Syntan	-1,48744	+/- 0,474509
AA	-2,25001	+/- 0,530518
AB	-0,5	+/- 0,671056
BB	-0,750002	+/- 0,530518

Table 2: Estimated effects for Ts

Standard errors are based on total error with 6 d.f.

The following table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error.

Analysis of Variance for Ts

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	2,12316	1	2,12316	4,71	0,0729
B: Syntan	4,42493	1	4,42493	9,83	0,0202
AA	8,10001	1	8,10001	17,99	0,0054
AB	0,25	1	0,25	0,56	0,4844
BB	0,899998	1	0,899998	2,00	0,2072
Total error	2,7019	6	0,450316		
Total (corr.)	17,75	11			

Table 3: Analysis of variance for Ts

R-squared = 84,7781 percent
R-squared (adjusted for d.f.) = 72,0931 percent
Standard Error of Est. = 0,671056
Mean absolute error = 0,405943
Durbin-Watson statistic = 2,37398 (P=0,2319)
Lag 1 residual autocorrelation = -0,296779
The ANOVA table partitions the variability in Ts into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 84,7781% of the variability in Ts. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 72,0931%. The standard error of the estimate shows the standard deviation of the residuals to be 0,671056. The mean absolute error (MAE) of 0,405943 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they

occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart, shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Ts.

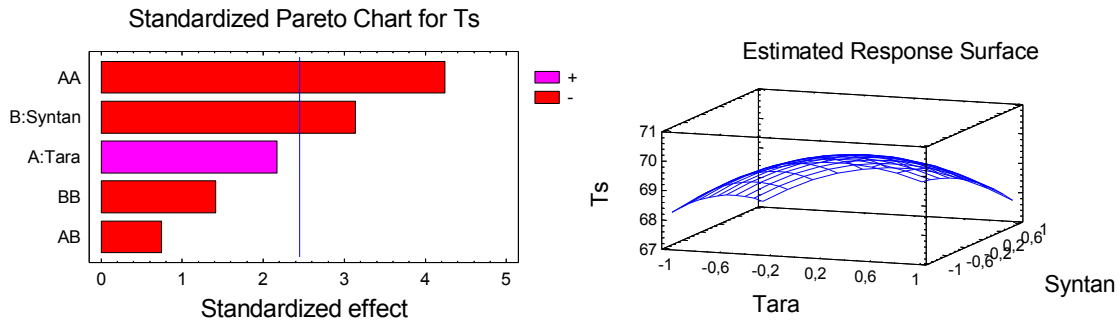

Figure 6: Standardized Pareto Chart and Response surface for Ts.

Excluding the values that are not statistically significant (P-value >0.05), the optimization tables and the Regression Coefficients comes like this:

Regression coefficients for Ts	
Constant	69,45
B: Syntan	-0,743719
AA	-1,05001

Table 4: Regression coefficients for Ts

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is

Ts = 69,45 - 0,743719*Syntan - 1,05001*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Ts

Goal: maximize Ts

Optimum value = 70,5018

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 5: Optimize response for Ts.

This table shows the combination of factor levels, which maximizes Ts over the indicated region.

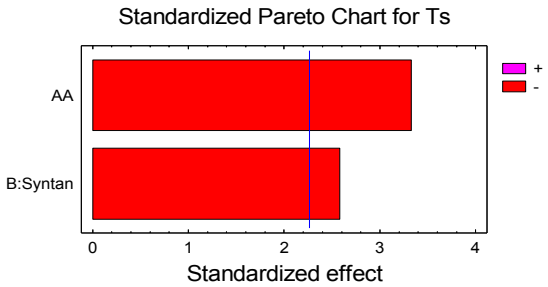

Figure 7: Pareto chart for Ts with the values not statistically significant excluded.

4.2.4.2 Statistical analysis of Experimental Design for DSC (Differential Scanning Calorimeter)

Analysis Summary

Estimated effects for DSC	
Average	99,925 +/- 0,235003
A: Tara	0,441422 +/- 0,332344
B: Syntan	-0,971752 +/- 0,332344
AA	-1,46251 +/- 0,371573
AB	-0,4 +/- 0,470005
BB	-0,512503 +/- 0,371573

Table 6: Estimated effects for DSC

Standard errors are based on total error with 6 d.f.

This table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error.

Analysis of Variance for DSC

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	0,389706	1	0,389706	1,76	0,2324
B: Syntan	1,8886	1	1,8886	8,55	0,0265
AA	3,42226	1	3,42226	15,49	0,0077
AB	0,16	1	0,16	0,72	0,4274
BB	0,420251	1	0,420251	1,90	0,2170
Total error	1,32543	6	0,220905		
Total (corr.)	7,26667	11			

Table 7: Analysis of variance for DSC

R-squared = 81,7601 percent

R-squared (adjusted for d.f.) = 66,5602 percent

Standard Error of Est. = 0,470005

Mean absolute error = 0,266665

Durbin-Watson statistic = 1,15775 (P=0,0541)

Lag 1 residual autocorrelation = 0,28199

The ANOVA table partitions the variability in DSC into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level. The

R-Squared statistic indicates that the model as fitted explains 81,7601% of the variability in DSC.

The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 66,5602%. The standard error of the estimate shows the standard deviation of the residuals to be 0,470005. The mean absolute error (MAE) of 0,266665 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the DSC.

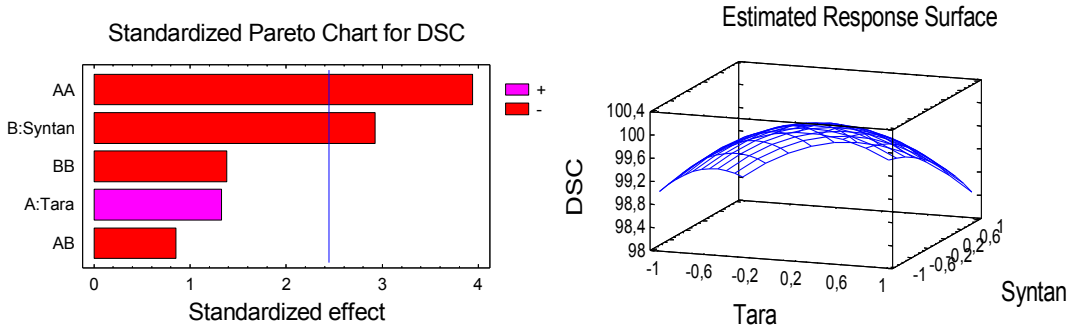

Figure 8: Standardized Pareto Chart and Response surface for DSC.

Excluding the values that are not statistically significant the optimization tables and the Regression Coefficients comes like this:

Regression coefficients for DSC	
Constant	99,72
B: Syntan	-0,485876
AA	-0,680004

Table 8: Regression coefficients for DSC.

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is

DSC = 99,72 - 0,485876*Syntan - 0,680004*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response

Goal: maximize DSC

Optimum value = 100,407

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 9: Optimize response for DSC.

This table shows the combination of factor levels, which maximizes DSC over the indicated region. .

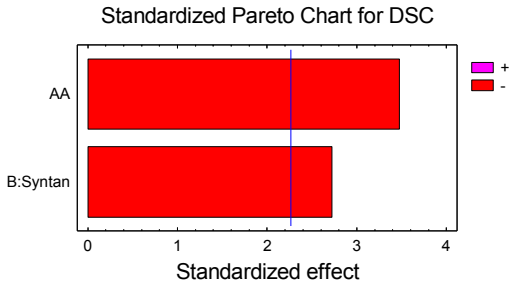

Figure 9: Pareto chart for DSC with the values not statistically significant excluded.

4.2.4.3 Statistical analysis of Experimental Design for Tensile Strength

Analysis Summary

Estimated effects for Tensile Strength	
Average	33,075 +/- 1,5017
A: Tara	3,03345 +/- 2,12372
B: Syntan	-5,06691 +/- 2,12372
AA	-9,65003 +/- 2,3744
AB	-0,5 +/- 3,00339
BB	-0,849982 +/- 2,3744

Table 10: Estimated effects for Tensile Strength

Standard errors are based on total error with 6 d.f.

This table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error.

Analysis of Variance for Tensile strength

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	18,4036	1	18,4036	2,04	0,2031
B: Syntan	51,3469	1	51,3469	5,69	0,0543
AA	148,996	1	148,996	16,52	0,0066
AB	0,25	1	0,25	0,03	0,8732
BB	1,15594	1	1,15594	0,13	0,7326
Total error	54,1222	6	9,02036		
Total (corr.)	275,063	11			

Table 11: Analysis of variance for Tensile Strength

R-squared = 80,3237 percent

R-squared (adjusted for d.f.) = 63,9267 percent

Standard Error of Est. = 3,00339
Mean absolute error = 1,50985
Durbin-Watson statistic = 2,17682 (P=0,3492)
Lag 1 residual autocorrelation = -0,0887702

The ANOVA table partitions the variability in Tensile strength into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 1 effect has P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 80,3237% of the variability in Tensile strength. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 63,9267%. The standard error of the estimate shows the standard deviation of the residuals to be 3,00339. The mean absolute error (MAE) of 1,50985 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Tensile Strength.

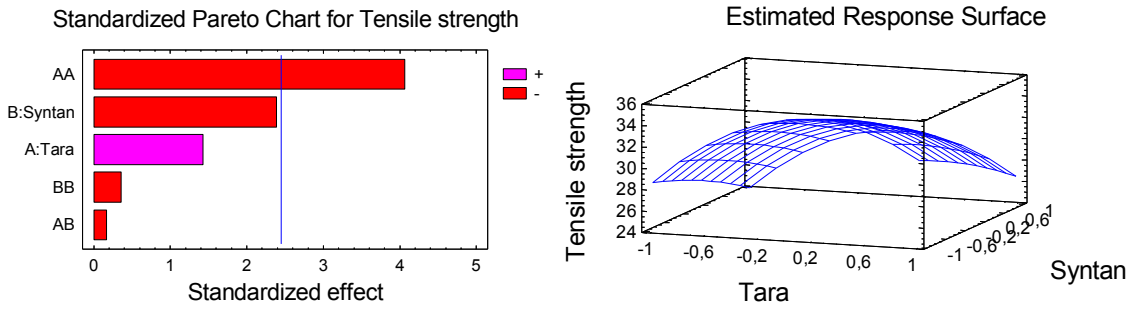

Figure 10: Standardized Pareto Chart and Response surface for Tensile Strength.

Excluding the values that are not statistically significant the optimization tables and the Regression Coefficients comes like this:

Regression coefficients for Tensile strength	
Constant	32,735
B: Syntan	-2,53345
AA	-4,74002

Table 12: Regression coefficients for Tensile Strength.

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is:

Tensile strength = 32,735 - 2,53345*Syntan - 4,74002*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Tensile Strength

Goal: maximize Tensile strength

Optimum value = 36,3178

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 13: Optimize response for Tensile Strength.

This table shows the combination of factor levels, which maximizes Tensile strength over the indicated region.

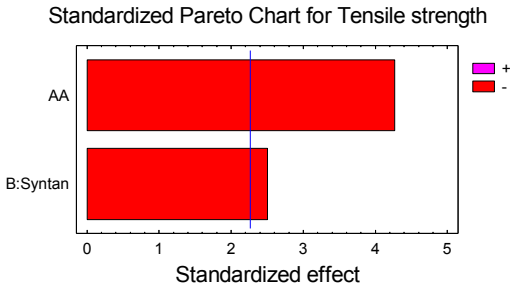

Figure 11: Pareto chart for Tensile Strength with the values not statistically significant excluded.

4.2.4.4 Statistical analysis of Experimental Design for Tear Load

Analysis Summary

Estimated effects for Tear load	
Average	108,375 +/- 2,91997
A: Tara	6,99068 +/- 4,12946
B: Syntan	-14,3378 +/- 4,12946
AA	-27,6938 +/- 4,61689
AB	-5,54 +/- 5,83994
BB	-10,7587 +/- 4,61689

Table 14: Estimated effects for Tear Load

Standard errors are based on total error with 6 d.f.

This table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error.

Analysis of Variance for Tear load

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	97,7388	1	97,7388	2,87	0,1414
B: Syntan	411,141	1	411,141	12,06	0,0133
AA	1227,11	1	1227,11	35,98	0,0010
AB	30,6916	1	30,6916	0,90	0,3794
BB	185,2	1	185,2	5,43	0,0586
Total error	204,629	6	34,1048		
Total (corr.)	2016,72	11			

Table 15: Analysis of variance for Tear Load.

R-squared = 89,8534 percent

R-squared (adjusted for d.f.) = 81,3979 percent

Standard Error of Est. = 5,83994

Mean absolute error = 2,96745

Durbin-Watson statistic = 2,21547 (P=0,3247)

Lag 1 residual autocorrelation = -0,165279

The ANOVA table partitions the variability in Tear load into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 89,8534% of the variability in Tear load. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 81,3979%. The standard error of the estimate shows the standard deviation of the residuals to be 5,83994. The mean absolute error (MAE) of 2,96745 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based in the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.

The Pareto Chart, shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Tear Load.

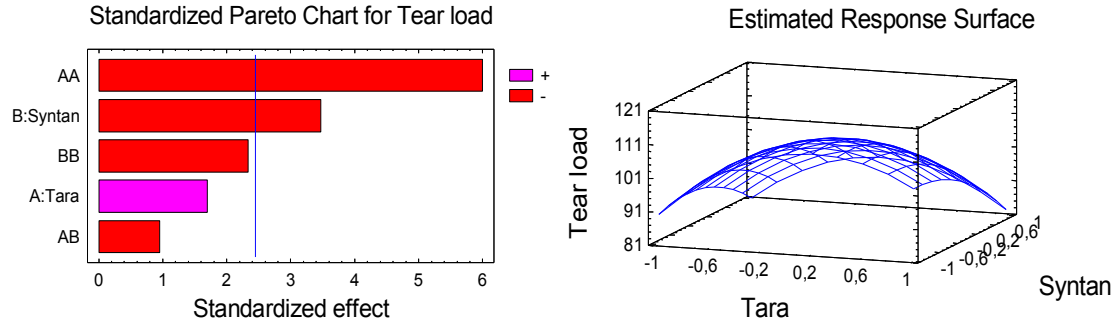

Figure 12: Standardized Pareto Chart and Response surface for Tear Load.

Excluding the values that are not statistically significant the optimization tables and the Regression Coefficients comes like this:

Regression coefficients for Tear load	
Constant	104,072
B: Syntan	-7,16888
AA	-12,7711

Table 16: Regression coefficients for Tear Load

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is

Tear load = 104,072 - 7,16888*Syntan - 12,7711*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Tear Load

Goal: maximize Tear load

Optimum value = 114.21

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 17: Optimize response for Tear Load.

This table shows the combination of factor levels, which maximizes Tear load over the indicated region.

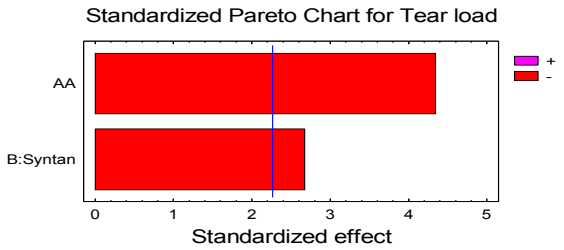

Figure 13: Pareto chart for Tear Load with the values not statistically significant excluded.

4.2.4.5 Statistical analysis of Experimental Design for Softness test

Analysis Summary

Estimated effects for Softness Test		
average	1,8	+/- 0,0524841
A:Tara	0,145711	+/- 0,0742238
B:Syntan	-0,201777	+/- 0,0742238
AA	-0,450001	+/- 0,0829849
AB	-0,05	+/- 0,104968
BB	-0,0999994	+/- 0,0829849

Table 18: Estimated effects for Softness Test

Standard errors are based on total error with 6 d.f.

This table shows each of the estimated effects and interactions. Also shown is the standard error of each of the effects, which measures their sampling error.

Analysis of Variance for Softness

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A: Tara	0,0424632	1	0,0424632	3,85	0,0973
B: Syntan	0,0814275	1	0,0814275	7,39	0,0347
AA	0,323999	1	0,323999	29,41	0,0016
AB	0,0025	1	0,0025	0,23	0,6507
BB	0,0159997	1	0,0159997	1,45	0,2736
Total error	0,0661098	6	0,0110183		

Table 19: Analysis of variance for Softness Test

R-squared = 87,2045 percent
R-squared (adjusted for d.f.) = 76,5417 percent
Standard Error of Est. = 0,104968
Mean absolute error = 0,0515168
Durbin-Watson statistic = 2,0258 (P=0,4496)
Lag 1 residual autocorrelation = -0,0188444

The ANOVA table partitions the variability in Softness into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 2 effects have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 7,2045% of the variability in Softness. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 76,5417%. The standard error of the estimate shows the standard deviation of the residuals to be 0,104968. The mean absolute error (MAE) of 0,0515168 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 0.05, there is no indication of serial autocorrelation in the residuals.
The Pareto Chart shows the standardized effect in decreasing order of importance. Also an estimated Response surface plot is shown next, to see the behavior of the variables against the Softness.

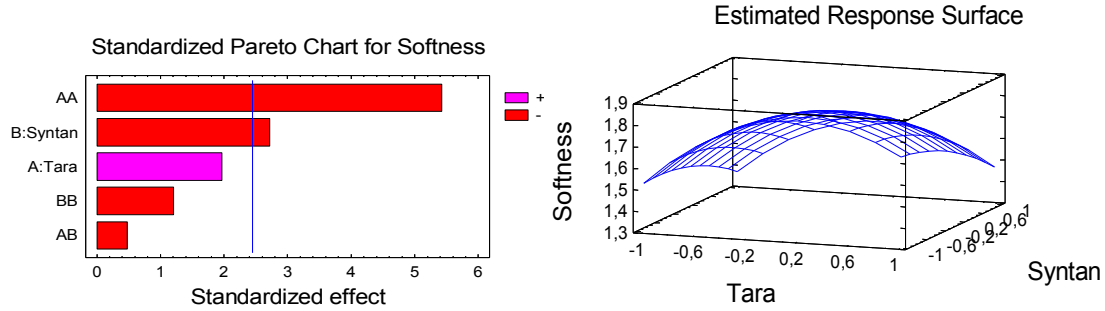

Figure 14: Standardized Pareto Chart and Response surface for Softness Test.

Excluding the values that are not statistically significant the optimization tables and the Regression Coefficients comes like this:

Regression coefficients for Softness Test	
Constant	1,76
B: Syntan	-0,100888
AA	-0,215001

Table 20: Regression coefficients for Softness Test.

This pane displays the regression equation, which has been fitted to the data. The equation of the fitted model is

Softness = 1,76 - 0,100888*Syntan - 0,215001*Tara^2

Where the values of the variables are specified in their original units.

Optimize Response for Softness Test

Goal: maximize Softness

Optimum value = 1,90268

Factor	Low	High	Optimum
Tara	-1,41421	1,41421	0,0
Syntan	-1,41421	1,41421	-1,41421

Table 21: Optimize response for Softness Test.

This table shows the combination of factor levels, which maximizes Softness over the indicated region.

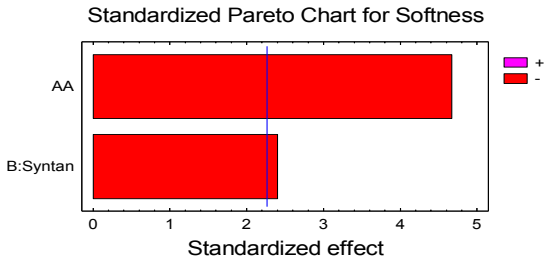

Figure 15: Pareto chart for Softness Test with the values not statistically significant excluded.

Annex 10. Life Cycle Assessment (LCA). Inputs and outputs of global tanning process

Process: **Conventional**
Operation: **Soaking**
Base Unit: Wet salted hides **1 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	H_2O (20ºC)	8000	*kg/tn*	8000	kg
C5	I	Ch: Surfactant	Anionic surfactant	0,5	%	5	kg
C6	I	Ch: Sodium Carbonate	Na_2CO_3	0,2	%	2	kg
D1	I	Drum 1 (beamhouse proc.)	Run	19,5	h	19,5	h
TE	I	Thermal energy	Drum 1 (beamhouse)		MJ/tn		MJ
EE	I	Electrical energy	Drum 1 (beamhouse)	1014	MJ/tn	1014	MJ

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from soaking	8	m3/tn	8	m3
LW_DQO	O	LiqWaste: DQO	DQO content	28	kg/tn	28	kg
LW_DBO5	O	LiqWaste: DBO5	DBO_5 content	12	kg/tn	12	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	13	kg/tn	13	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	1,5	kg/tn	1,5	kg
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	150	kg/tn	150	kg

Process: **New pre-tanning**
Operation: **Soaking**
Base Unit: Wet salted hides **1 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	H_2O (20ºC)	8000	*kg/tn*	8000	kg
C5	I	Ch: Surfactant	Anionic surfactant	0,5	%	5	kg
C6	I	Ch: Sodium Carbonate	Na_2CO_3	0,2	%	2	kg
D1	I	Drum 1 (beamhouse proc.)	Run	19,5	h	19,5	h
TE	I	Thermal energy	Drum 1 (beamhouse)		MJ/tn		MJ
EE	I	Electrical energy	Drum 1 (beamhouse)	1014	MJ/tn	1014	MJ

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from soaking	8	m3/tn	8	m3
LW_DQO	O	LiqWaste: DQO	DQO content	28[4]	kg/tn	28	kg
LW_DBO5	O	LiqWaste: DBO5	DBO_5 content	12[3]	kg/tn	12	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	13[3]	kg/tn	13	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	1,5[3]	kg/tn	1,5	kg
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	150[5]	kg/tn	150	kg

Table 22: Inputs and outputs of soaking process (New and conventional)

Process: **Conventional**
Operation: **Unhairing-Liming**
Base Unit: Wet salted hides **1 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	H_2O (20ºC)	2500	*kg/tn*	2500	kg
W	I	Water	H_2O (25ºC)	1500	*kg/tn*	1500	kg
C7	I	Ch: Calcium hydroxide	$Ca(OH)_2$	5	%	50	kg
C3	I	Ch: Sodium sulphide	Na_2S	2	%	20	kg
C9	I	Ch: Amino compound	Amine	0,5	%	5	kg
D1	I	Drum 1 (beamhouse proc.)	Run	28,5	h	28,5	h
TE	I	Thermal energy	Process water heating (25ºC)		MJ/tn		MJ
EE	I	Electrical energy	Drum 1 (Beamhouse)	1482	MJ/tn	1482	MJ

Process: **New pre-tanning**
Operation: **Unhairing-Liming**
Base Unit: Wet salted hides **1 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	H_2O (20ºC)	2500	*kg/tn*	2500	kg
W	I	Water	H_2O (25ºC)	1500	*kg/tn*	1500	kg
C7	I	Ch: Calcium hydroxide	$Ca(OH)_2$	5	%	50	kg
C3	I	Ch: Sodium sulphide	Na_2S	2	%	20	kg
C9	I	Ch: Amino compound	Amine	0,5	%	5	kg
D1	I	Drum 1 (beamhouse proc.)	Run	28,5	h	28,5	h
TE	I	Thermal energy	Process water heating (25ºC)		MJ/tn		MJ
EE	I	Electrical energy	Drum 1 (Beamhouse)	1482	MJ/tn	1482	MJ

OUTPUTS

Type	I/O	Type name	Description	Reference	Quantity
WW_H2O	O	LiqWaste: Water	Wastewater from unhairing-liming	2,5 m3/tn	2,5 m3
LW_DQO	O	LiqWaste: DQO	DQO content	50 kg/tn	50 kg
LW_DBO5	O	LiqWaste: DBO5	DBO5 content	20 kg/tn	20 kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	15 kg/tn	15 kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	3 kg/tn	3 kg
LW_Ntot	O	LiqWaste: Nitrogen	Ammonia nitrogen content	0,4 kg/tn	0,4 kg
LW_S2-	O	LiqWaste: Sulphides	Sulphides content	2,8 kg/tn	2,8 kg
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	15 kg/tn	15 kg
EW_Ch	O	Emissions to air: Chemicals (S)	Possible H_2S Emissions	kg/tn	kg
SW	O	SolidWaste	Hair recovery	40 kg/tn	40 kg

Type	I/O	Type name	Description	Reference	Quantity
WW_H2O	O	LiqWaste: Water	Wastewater from unhairing-liming	2,5 m3/tn	2,5 m3
LW_DQO	O	LiqWaste: DQO	DQO content	50[6] kg/tn	50 kg
LW_DBO5	O	LiqWaste: DBO5	DBO5 content	20[5] kg/tn	20 kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	15[5] kg/tn	15 kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	3[5] kg/tn	3 kg
LW_Ntot	O	LiqWaste: Nitrogen	Ammonia nitrogen content	0,4[5] kg/tn	0,4 kg
LW_S2-	O	LiqWaste: Sulphides	Sulphides content	2,8[7] kg/tn	2,8 kg
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	15[5] kg/tn	15 kg
EW_Ch	O	Emissions to air: Chemicals (S)	Possible H_2S Emissions	kg/tn	kg
SW	O	SolidWaste	Hair recovery	40[8] kg/tn	40 kg

Table 23: Inputs and outputs of unhairing and liming process (New and conventional)

[6] Frendrup (1999), wastewater loads per tone rawhide, salt free raw hides IPPC, Summary of pollution loads discharged in effluents, p. 115, 2009.
[7] Bath concentration of S_2. Extracted from the Project ACA (AIICA).
[8] Frendrup, Dry hair/tn raw bovine hide. UNIDO, p. 26, 2000.

Process:	Conventional		
Operation:	Fleshing-Splitting		
Base Unit:	Wet salted hides		1

INPUTS

Type	I/O	Type name	Description	Reference		
W	I	Water	Cleaning water	*300*	*kg/tn*	300
EE	I	Electrical energy	Energy supply for Fleshing	399,6[8]	*MJ/tn*	399,6
EE	I	Electrical energy	Splitting machine	466,2[8]	MJ/tn	466,2

OUTPUTS

Type	I/O	Type name	Description	Reference		
SW	O	SolidWaste	Fleshings	300	*kg/tn*	300
SW	O	SolidWaste	Lime trimmings	100	*kg/tn*	100
IN	O	Intermediates	Unusable lime splits	107	*kg/tn*	107
WW_H2O	O	LiqWaste: Water	Cleaning water	0,3	*m3/tn*	0,3

Process:	New pre-tanning		
Operation:	Fleshing-Splitting		
Base Unit:	Wet salted hides		1 tn

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Cleaning water	*300*	kg/tn	300	kg
EE	I	Electrical energy	Energy supply for Fleshing	399,6[9]	*MJ/tn*	399,6	MJ
EE	I	Electrical energy	Splitting machine	466,2[8]	MJ/tn	466,2	MJ

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity	
SW	O	SolidWaste	Fleshings	300	*kg/tn*	300	kg
SW	O	SolidWaste	Lime trimmings	100	*kg/tn*	100	kg
IN	O	Intermediates	Unusable lime splits	107	*kg/tn*	107	kg
WW_H2O	O	LiqWaste: Water	Cleaning water	0,3	*m3/tn*	0,3	m3

Table 24: Inputs and outputs of fleshing and splitting process (New and conventional)

[9] IPPC 2013, p. 83, 203

Process: **Conventional**
Operation: **Deliming-Bating**
Base Unit: Split hides **0,715 tn**

INPUTS

Type	I/O	Type name	Description	Reference	Quantity
W	I	Water	H_2O (30ºC)	2000 *kg/tn*	1430 kg
W	I	Water	H_2O (35ºC)	1500 *kg/tn*	1072,5 kg
W	I	Water	H_2O rinsing (25ºC)	1000 *kg/tn*	715 kg
C13	I	Ch: Dicarboxylic Acid	Dicarboxylic acids	1,5 *%*	10,725 kg
C10	I	Ch: Enzyme	Pancreatic enzyme	0,7 *%*	5,005 kg
D2	I	Drum 2 (tanning proc.)	Run	1,75 *h*	1,75 h
EE	I	Electrical energy	Drum 2 (Deliming-batting)	121,63 MJ/tn	86,962 MJ

Process: **New pre-tanning**
Operation: **Deliming-Bating**
Base Unit: Split hides **0,715 tn**

INPUTS

Type	I/O	Type name	Description	Reference	Quantity
W	I	Water	H_2O (30ºC)	2000 *kg/tn*	1430 kg
W	I	Water	H_2O (35ºC)	1500 *kg/tn*	1072,5 kg
W	I	Water	H_2O rinsing (25ºC)	1000 *kg/tn*	715 kg
C13	I	Ch: Dicarboxylic Acid	Dicarboxylic acids	1,5 *%*	10,725 kg
C10	I	Ch: Enzyme	Pancreatic enzyme	0,7 *%*	5,005 kg
D2	I	Drum 2 (tanning proc.)	Run	1,75 *h*	1,75 h
EE	I	Electrical energy	Drum 2 (Deliming-batting)	121,63 MJ/tn	86,962 MJ

OUTPUTS						
Type	I/O	Type name	Description	Reference	Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from deliming-bating	4,5 m3/tn	3,2175 m3	
LW_DQO	O	LiqWaste: DQO	DQO content	22,378 kg/tn	16 kg	
LW_DBO5	O	LiqWaste: DBO5	DBO5 content	9,7902 kg/tn	7 kg	
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	13,986 kg/tn	10 kg	
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	1,6783 kg/tn	1,2 kg	
LW_Ntot	O	LiqWaste: Nitrogen	Ammonia nitrogen content	0,4196 kg/tn	0,3 kg	
LW_S2-	O	LiqWaste: Sulphides	Sulphides content	0,028 kg/tn	0,02 kg	
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	1,3986 kg/tn	1 kg	
LW_SO42-	O	LiqWaste: Sulphates	Sulphates content	2,0979 kg/tn	1,5 kg	

OUTPUTS					
Type	I/O	Type name	Description	Reference	Quantity
WW_H2O	O	LiqWaste: Water	Wastewater from deliming-bating	4,5 m3/tn	3,2175 m3
LW_DQO	O	LiqWaste: DQO	DQO content	22,378[10] kg/tn	16 kg
LW_DBO5	O	LiqWaste: DBO5	DBO5 content	9,7902[9] kg/tn	7 kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	13,986[9] kg/tn	10 kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen content	1,6783[9] kg/tn	1,2 kg
LW_Ntot	O	LiqWaste: Nitrogen	Ammonia nitrogen content	0,4196[9] kg/tn	0,3 kg
LW_S2-	O	LiqWaste: Sulphides	Sulphides content	0,028[9] kg/tn	0,02 kg
LW_Cl-	O	LiqWaste: Chlorides	Chlorides content	1,3986[7] kg/tn	1 kg
LW_SO42-	O	LiqWaste: Sulphates	Sulphates content	2,0979[7] kg/tn	1,5 kg

Table 25: Inputs and outputs of de-liming and bating process (New and conventional)

[10] Frendrup (1999), Wastewater loads per tone raw hide, average unit (Table 3.13, 3.14, 3.12)

Process: **Conventional**
Operation: **Pickling**
Base Unit: Split hides **0,715 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	H_2O (20ºC)	1000	*kg/tn*	715	kg
C12	I	Ch: Formic Acid	HCOOH	0,5	%	3,575	kg
C15	I	Ch: Sulphuric Acid	H_2SO_4	0,7	%	5,005	kg
C1	I	Ch: Sodium chloride	NaCl	7	%	50,05	kg
D2	I	Drum 2 (tanning proc.)	Run	2	*h*	2	h
EE	I	Electrical energy	Drum 2 (Pickling-tanning)	139	MJ/tn	99,385	MJ

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity
-	O				-	-

There are not outputs; due the bath is the same for tanning

Process: **New pre-tanning**
Operation: **Pickling**
Base Unit: Split hides **0,715 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	H_2O (20ºC)	500	kg/tn	357,5	kg
C12	I	Ch: Formic Acid	HCOOH (1:10)	1	%	7,15	kg
C1	I	Ch: Sodium chloride	NaCl	4	%	28,6	kg
D2	I	Drum 2 (tanning proc.)	Run	2	h	2	h
EE	I	Electrical energy	Drum 2 (Pickling-tanning)	139	MJ/tn	99,385	MJ
-	I				-	-	

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity
-	O				-	-

Table 26: Inputs and outputs of pickling process (New and conventional)

Process: Conventional
Operation: **Pre-tanning**
Base Unit: Split hides **0,715tn**

INPUTS

Type	I/O	Type name	Description	Reference	Quantity
W	I	Water	Water (20ºC)	500*kg/tn*	357,5kg
C17	I	Glutaraldehyde	Glutaraldehyde 50%	2,5*%*	17,875kg
C18	I	Syntan sulphone type	Synthetic sulphone type	5*%*	35,75kg
W	I	Water	Rinsing Water (20ºC)	3000*kg/tn*	2145kg
D2	I	Drum 2 (tanning proc.)	Run	10*h*	10h
EE	I	Electrical energy	Drum 2 (pickling-tanning)	695*MJ/tn*	496,93MJ

OUTPUTS[11]

Type	I/O	Type name	Description	Reference	Quantity
WW_H2O	O	LiqWaste: Water	Wastewater from pickling-tanning	4,5m3/tn	3,2175m3
LW_DQO	O	LiqWaste: DQO	DQO content	146,5kg/tn	104,75kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	40,94kg/tn	29,272kg
LW_Ntot	O	LiqWaste: Nitrogen	Total Nitrogen Content	1,6kg/tn	1,144kg

Process: New pre-tanning
Operation: **Pre-tanning**
Base Unit: Split hides **0,715tn**

INPUTS

Type	I/O	Type name	Description	Reference	Quantity
W	I	Water	Water (20ºC)	500*kg/tn*	357,5kg
C14	I	Ch: Tara sieved (40-50 microns)	Tara pretanning	9*%*	64,35kg
C11	I	Ch: Naphtalenesulphonic synthan, pretanning	Pretanning Precursor	2*%*	14,3kg
C16	I	Sodium, Pyrophosphate acid	Pretanning Precursor	4*%*	28,6kg
C12	I	Ch: Formic Acid	Fixing agent	0,8*%*	5,72kg
W	I	Water	Rinsing Water (20ºC)	3000*kg/tn*	2145kg

OUTPUTS[10]

Type	I/O	Type name	Description	Reference	Quantity
WW_H2O	O	LiqWaste: Water	Wastewater from tanning	4m3/tn	2,86m3
LW_DQO	O	LiqWaste: DQO	DQO content	102,24kg/tn	73,1016kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	31,9kg/tn	22,8085kg
LW_Ntot	O	LiqWaste: Nitrogen	Total Nitrogen Content	1,5kg/tn	1,0725kg

Table 27: Inputs and outputs of pre-tanning process (New and conventional)

[11] Values extracted from this thesis. Manufacture of three leather articles with modified Tara (chapter 4, section 4.1).

Process: **Conventional**
Group: **Wet-end processes**
Operation: **Samming-Shaving**
Base Unit: Limed hides **1,1 tn**

INPUTS[12]

Type	I/O	Type name	Description	Reference		Quantity		
EE	I	Electrical energy	Shaving operation	266,4	MJ/tn	293,04	MJ	
EE	I	Electrical energy	Sammying operation	199,8	MJ/tn	219,78	MJ	

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity		
SW	O	SolidWaste	leather shavings	99	*kg/tn*	108,9	kg	
SW	O	SolidWaste	Leather cuts	20	*kg/tn*	22	kg	
LW_Cr	O	LiqWaste: Chromium (III)	Sammying liquor		*kg/tn*		kg	

Process: **New pre-tanning**
Group: **Wet-end processes**
Operation: **Samming-Shaving**
Base Unit: Limed hides **1,1 tn**

INPUTS[11]

Type	I/O	Type name	Description	Reference		Quantity	
EE	I	Electrical energy	Shaving operation	266,4	MJ/tn	293,04	MJ
EE	I	Electrical energy	Sammying operation	199,8	MJ/tn	219,78	MJ

OUTPUTS

Type	I/O	Type name	Description	Reference		Quantity	
SW	O	SolidWaste	Leather shavings	99	*kg/tn*	108,9	kg
SW	O	SolidWaste	Leather cuts	20	*kg/tn*	22	kg
LW_Cr	O	LiqWaste: Chromium (III)	Sammying liquor		*kg/tn*		kg

Table 28: Inputs and outputs of samming and shaving process (New and conventional)

[12] IPPC 2013, p. 83, 203

Process:	Conventional		
Group:	Wet-end processes		
Operation:	Washing + Neutralisation		
Base Unit:	WW Shaved hides	0,262	tn

INPUTS							
Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water 30ºC	2000	kg/tn	524,04	kg
C20	I	Sodium formate	Sodium formate	1	%	2,6202	kg
C21	I	Sodium bicarbonate	Sodium bicarbonate	0,8	%	2,0962	kg
W	I	Water	Washing Water	2000	kg/tn	524,04	kg
EE	I	Electrical energy	Drum 3	149,6	MJ/tn	39,198	MJ
D3	I	Drum 3 (wet-end proc.)	Run	2,2	h	2,2	h

*The outputs are summarized in the fatliquoring process.

Process:	New pre-tanning		
Group:	Wet-end processes		
Operation:	Washing + Neutralisation		
Base Unit:	WW Shaved hides	0,262	tn

INPUTS							
Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water	600	kg/tn	157,21	kg
C19	I	Oxalic Acid	Oxalic Acid	0,5	%	1,3101	kg
C20	I	Sodium formate	Sodium formate	1	%	2,6202	kg
C21	I	Sodium bicarbonate	Sodium bicarbonate	0,5	%	1,3101	kg
D3	I	Drum 3 (wet-end proc.)	Run	2,2	h	2,2	h
EE	I	Electrical energy	Drum 3	149,6	MJ/tn	39,198	MJ
W	I	Water	Washing Water	2000	kg/tn	524,04	kg

Table 29: Inputs of neutralizing process (New and conventional)

Process:	Conventional		
Operation:	Retanning		
Base Unit:	WW Shaved hides	0,262	tn

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
C23	I	Synthan (substitution)	Phenol condensation syntan	10	%	26,202	kg
C25	I	Original Tara	Original tara	5	%	13,101	kg
C23	I	Synthan (substitution)	Copolimer syntan	2	%	5,2404	kg
C23	I	Synthan (substitution)	Phenol condensation syntan	10	%	26,202	kg
C25	I	Original Tara	Original tara	5	%	13,101	kg
C26	I	Dye	Dye	1	%	2,6202	kg
C12	I	Ch: Formic Acid	Formic acid (1:10) to fix	1	%	2,6202	kg
W	I	Water	Washing water (50ºC)	2000	kg/tn	524,04	kg
D3	I	Drum 3 (wet-end proc.)	Run	8	h	8	h
EE	I	Electrical energy	Drum 3	544	MJ/tn	142,54	MJ

Process:	New pre-tanning		
Operation:	Retanning		
Base Unit:	WW Shaved hides	0,262	tn

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
C22	I	Compact product	Pre-tanning mixed product	5	%	13,101	kg
C23	I	Synthan (substitution)	Substitution syntan	2	%	5,2404	kg
C24	I	Oil	Sulphited synthetic oil	3	%	7,8606	kg
C24	I	Oil	Lecithin	3	%	7,8606	kg
W	I	Water	Water 30º	500	kg/tn	131,01	kg
C23	I	Synthan (substitution)	Substitution syntan	3	%	7,8606	kg
C25	I	Original Tara	Tara	5	%	13,101	kg
C23	I	Synthan (substitution)	Substitution syntan	4	%	10,481	kg
C25	I	Original Tara	Tara	6	%	15,721	kg
W	I	Water	Water 50 ºC	500	kg/tn	131,01	kg
D3	I	Drum 3 (wet-end proc.)	Run	4,2	h	4,2	h
EE	I	Electrical energy	Drum 3	285,6	MJ/tn	74,833	MJ

Table 30: Inputs of re-tanning process (New and conventional)

Process: **Conventional**
Operation: **Fatliquoring**
Base Unit: WW Shaved hides **0,262 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water 50ºC	2000	kg/tn	524,04	kg
C24	I	Oil	Comb. synthetic and natural oil	4	%	10,481	kg
C24	I	Oil	Sulphited fish oil	8	%	20,962	kg
C12	I	Ch: Formic Acid	Formic acid. Fixing	1,5	%	3,9303	kg
W	I	Water	Rinsing water 40ºC	2000	kg/tn	524,04	kg
D3	I	Drum 3 (wet-end proc.)	Run	2	h	2	h
EE	I	Electrical energy	Drum 3	136	MJ/tn	35,635	MJ
TE	I	Thermal energy	Water heating (45-50ºC)	3840	MJ/tn	1006,2	MJ
TE	I	Thermal energy	Drying	3840	MJ/tn	1006,2	MJ
	I						
	I						
	I						
-	I				-	-	

Process: **New pre-tanning**
Operation: **Fatliquoring**
Base Unit: WW Shaved hides **0,262 tn**

INPUTS

Type	I/O	Type name	Description	Reference		Quantity	
W	I	Water	Water 45 ºC	1500	kg/tn	393,03	kg
C24	I	Oil	Sulphited synthetic oil	2	%	5,2404	kg
C24	I	Oil	Lecithin	2	%	5,2404	kg
C24	I	Oil	Sulphated (semi-synthetic) oil	2	%	5,2404	kg
C12	I	Ch: Formic Acid	Formic acid. Fixing	1	%	2,6202	kg
C24	I	Oil	Sulphited synthetic oil	2	%	5,2404	kg
C24	I	Oil	Lecithin	2	%	5,2404	kg
C24	I	Oil	Sulphated (semi-synthetic) oil	4	%	10,481	kg
C12	I	Ch: Formic Acid	Formic acid. Fixing	1	%	2,6202	kg
W	I	Water	Water to wash (30ºC)	2000	kg/tn	524,04	kg
D3	I	Drum 3 (wet-end proc.)	Run	4,5	h	4,5	h
EE	I	Electrical energy	Drum 3	306	MJ/tn	80,178	MJ
TE	I	Thermal energy	Water heating (45-50ºC)	3840	MJ/tn	1006,2	MJ

OUTPUTS[13]							
Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from post-tanning operations	8,001	*m3/tn*	2,0964	m3
LW_Cr	O	LiqWaste: Chromium (III)	Chromium (III) content	0,001	*kg/tn*	0,0003	kg
LW_DQO	O	LiqWaste: DQO	DQO content	351,2	kg/tn	92,021	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	26,41	kg/tn	6,9199	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen Content	3,7	kg/tn	0,9695	kg

OUTPUTS[12]							
Type	I/O	Type name	Description	Reference		Quantity	
WW_H2O	O	LiqWaste: Water	Wastewater from post-tanning operations	5,101	*m3/tn*	1,3366	m3
LW_Cr	O	LiqWaste: Chromium (III)	Chromium (III) content	0,0006	*kg/tn*	0,0002	kg
LW_DQO	O	LiqWaste: DQO	DQO content	211	kg/tn	55,286	kg
LW_MES	O	LiqWaste: Susp. Matter	Suspended matter content	16	kg/tn	4,1923	kg
LW_Ntot	O	LiqWaste: Nitrogen	Total nitrogen Content	2,2	kg/tn	0,5764	kg

Table 31: Inputs and outputs of fatliquoring process (New and conventional)

The wastewater value is the total amount of wastewater of Washing + Neutralizing, Re-tanning and Fatliquoring.

[13] Bath concentration of final post-tanning operations. Extracted from the Project ACA (AIICA).

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Dissemination of the research work

Publications:

- ***Low carbon products for the design of innovative leather processes. Part I: determination of the optimal chemical modification of tara. . (JALCA, Vol. 108, p. 386-391, 2013)***

- ***Low carbon products for the design of innovative leather processes. Part II: determination of the optimal physical modification of tara. (JALCA, Vol. 109, p. 25-31, 2014)***

Congress:

62nd Congress of AQEIC (Spanish Leather Chemists Association), Lorca (Murcia), May 10th and 11th, 2013

Presentation: 'Aplicación de taninos sostenibles con baja huella de carbono'

Author: Jorge Gerardo Díaz Muñoz

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Les pàgines 210 a 227 de la tesi contenen els treballs citats, que es poden consultar a la web de l'editor.

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Las páginas 210 a 227 de la tesis contienen los trabajos que pueden consultarse en la web del editor.

ATTENTION ¡

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PROGRAMA

62 CONGRESO DE LA ASOCIACIÓN QUÍMICA ESPAÑOLA DE LA INDUSTRIA DEL CUERO

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10 y 11 de mayo de 2013 Lorca

ASAMBLEA GENERAL EXTRAORDINARIA

Viernes, 10 de Mayo

Sesión de tarde

ASAMBLEA DE SOCIOS

17,30 - 18,00 Recepción y registro de asistentes

18,00 - 20,00 Junta General. Lectura del resultado de las votaciones y proclamación de los resultados.

Sábado, 11 de Mayo

JORNADA TÉCNICA

Sesión de mañana

Presidentes de la sesión: Sr. Luis Labastida Azemar y Sr. Juan Pérez Gil

9,00 - 9,45 Recepción, registro de asistentes y entrega de documentación.

9,45 - 10,15 Ceremonia de apertura del 62 Congreso.

10,15 -10,45 "Lorca: pasión, desgracia, esperanza. Bienvenidos"

Sr. Gerónimo Gil Arcas

10,45 – 11,05 "Influencia de la recurtición con sintanes en la tintura del cuero"

Autores: Olga Ballús y Ramón Palop

11,05 – 11,25 "Fungicidas alternativos para la industria de la piel: DIMPTS e IPBC"

Autores: Sara Cuadros, Joaquim Font, Mª A. Manresa, Agustí Marsal y Lluís Ollé

11,25 – 11,45 PAUSA – CAFÉ

Presidentes de la sesión:Sr. Gerónimo Gil Arcas y Dr.Agustín Marsal Monge

11,45 – 12,05 "Caracterización por microextracción en fase sólida de compuestos orgánicos volátiles en piel"

Autores: Rosa Cuadros, Joaquim Font, Lluís Ollé, Anna Bacaradit y Agustí Marsal

12,05 – 12,25 "Alternativas ambientales a los procesos de rendido y engrase."

Autores: M.Roig, V.Segarra, J.Ferrer y M.A. Martínez

12,25 – 12,45 "Aplicación de ultrasonidos en curtición vegetal"

Autores: Felip Combalia, Josep Morera y Esther Bartolí

12,45 – 15,15 ALMUERZO DE TRABAJO

Sesión de tarde

Presidentes de sesión: Dr. Lluis Ollé Otero y Sr. José Ramón Martínez Pardo

15,15 – 15,35 "Aplicación de taninos sostenibles con baja huella de carbono"

Autores: Jorge Gerardo Díaz, Concepció Casas, Teresa Mir, Lluís Ollé y Anna Bacardit

15,35 – 15,55 "Curtidos: residuos y legislación"

Sra. Luz Gil Jodar

15,55 – 17,00 COLOQUIO

PROGRAMA PARA ACOMPAÑANTES

Día 11 mayo de 2013

10 horas : Recogida en hoteles con microbus.

10,30 horas : Reunión en Plaza de España.

10,35 horas : Recorrido por el casco antiguo, Palacio de Guevara, museos de bordados del paso blanco y paso azul, subida al castillo, con visita a la sinagoga y demás instalaciones.

La subida al castillo se realizará en el tren turístico.

13,00 horas : Vuelta a la Plaza de España.

13,30 horas : Almuerzo en el restaurante "La Cofradía", junto a los congresistas.

Tarde libre.

A elección se puede visitar la llamada zona cero en donde los terremotos del 11 marzo de 2011 fueron más devastadores.

21,00 horas. Cena de Clausura en el Parador Castillo de Lorca .

Entrega Premio AQEIC 2013