APPLICATION OF SUSTAINABLE TANNINS WITH LOW CARBON FOOT PRINT

Jorge Díaz1, Concepciò Casas 1, Silvia Sorolla 1, Teresa Mir1 , Lluís Ollé1, Anna Bacardit1

1 Escuela de Ingeniería de Igualada (EEI), Universitat Politècnica de Catalunya (UPC), A3 Chair in Leather Innovation. Plaça del Rei, 15. 08700 – Igualada (Spain), e-mail: joger_diaz@hotmail.com

Abstract

Today we are living an “eco friendly boom”; this involves developing processes with less environmental impact and trying to make them as ecological as possible. That is the reason for carrying out this work; our aim is to use a vegetable extract as a sustainable source for the tanning process. This work considers the fruit of the Tara tree as a low carbon footprint raw material source for tanning agents and proposes alternatives to avoid the use of commercial vegetable extracts and mineral salts. Various designs have been developed for new tailored Tara tannins by chemical and physical modification, in order to obtain a higher percentage of tannins and therefore improve their tanning capability. In chemical modifications, several aqueous extractions at different temperatures have been developed and optimized in order to reduce the astringency and improve the penetration of the tannin molecules through the leather structure. The degree of hydrolysis has been controlled by means of the Gallic acid content by HPLC (High performance liquid Chromatography). In the physical modification part, the Tara has been milled and sieved, at several particle sizes, with the purpose of obtaining a smaller molecular size. Both chemical and physical modifications were tested in skin, in a wet-white pretanning process, combining them with the fewest possible commercial vegetable extracts and syntans. The formulations have been optimized by experimental design.

Keywords: Caesalpinia Spinosa, ecological, vegetable.

1. Introduction

Caesalpinia Spinosa (Molina) Kuntze; commonly knows as tara, , is a small leguminous tree or thorny shrub that grows spontaneously in South America, specially in Peru, and North Africa. From the precious fruits, and the pods the tara tannins are obtained, rich in piro-gallic substances and in a small quantity catequinic derivate.

The difference between Tara and other vegetable extracts is that the tara gives light color leathers and light fastness. For tanners, tara tannins are very important if they want to dye in light colors with a vegetable appearance. Tara has a very good light fastness; these tannins are very hard to oxidize because tara has a low quantity of free gallic acid.

Tara is also an extract with the highest ratio tannin/no-tannin with strong natural acidity. That’s why tara is the most astringent tannin in the market. This property is very interesting to produce levanted leather.

Today, chrome tanning is the most used world wide in about 85% of world leather production. However, the chromic wastewater disposal and the depuration mods, also the generation of skins wastes with chrome, represent several environmental impacts. These restrictions leads to the tanners to contemplate the implementation of new products based on wet-white production and following a vegetable tanning, with the aim of get chrome-free tanned leathers.

There are bibliography that shows some studies with use of Tara combined with other inorganic salts (aluminum, chromium) or with organic products (glutaraldehyde, syntans, quaternary phosphonium salts) to improve its tanning powder by means of penetration and blocking the reactive groups of collagen to facilitate the penetration and avoid an excess of tanning on the leather surface.

Ultrasound application in vegetable tanning process could improve the diffusion rate and an appreciable reduction in the particle size . The application of bacterial enzymes is also studied. The use of bacterial collagenase as an auxiliary agent in tanning bath has increased tanning absorption and better diffusion into leather .

Tara tannins are an alternative to commercial tanning and pre-tanning products obtained with chemical processes, like mineral salts, vegetable extracts, syntans or others. This tannin can supply the growing demand in materials with low carbon footprint and no human risks in their manipulation.

To stabilize the skin with the new products is important to enhance the penetration of the tara tannins. That's why some chemical and physical modifications are necessary to improve the entrance through the collagen structure. In this article just the physical modifications are shown.

The tara tannins are highly rated for the good light fastness, and the use has been increased lately in automotive industry world wide, for the promotion of the use of chrome-free leathers. Others applications are promoted in wet-white formulations to obtain upholstery for furniture, upper shoe leather and leather goods.

2.Objectives

The main objective of the project is to design new pre-tanning recipes using the tannins from tara fruit (Caesalpinia Spinosa) as vegetable tannin source, physically modified to promote the sustainability on the manufacture of high quality leather articles.

Investigation activities have been carried out to modify physically the commercial tara, where is pretended that the new fractions obtained present easiness to penetrate into the skin.

This objective will be carried out from the investigation activities based in structural modifications of the tannins. Those modifications include: improvements on the tannins concentrate homogenization and size particle size diminution.

Reduce or substitute the use of pre-tanning agents aldehyde type and syntans used in the wet-white leather production, using sustainable tannins. Also, the new modified tannins could substitute some current commercial vegetable extract, linked to deforestation.

The new designed products assessment will be done by the application on hides, where physical-chemical parameters has been done to determine the final quality of the leathers, also the pollutant loads of final wastewater has been assessed.

The specific objectives are as follows:

- Reduction of tara tannin astringency and avoid as much as possible formation of big molecular complex to improve the penetration of the tannins molecules through the skin.
- Increase the exhaustion of the baths in vegetable tanning, reducing insoluble matters and COD, which will help to reduce the environmental impact of the final floats from vegetable tannings and the exploitation of the tannin applied on the process.
- Avoid as much as possible the formation of iron complexes, present in the tara or in the mechanical processes on pre-tanned leathers with tara, with some sequestering agents. The presence of iron on this process forms black stains.
- Control the enzymatic activity of collagenase as precursor of improving the penetration of tannins, avoiding as much as possible the leather degradation.

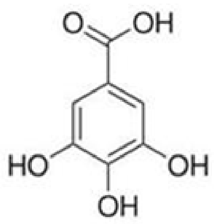
3.Backgrounds

Tara powder is hydrolysable tannin 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.

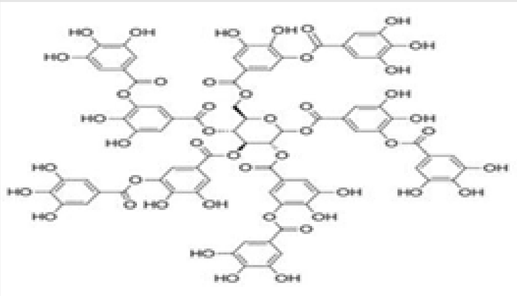
Turn, within the tara tannin structure, coexists with the quinic acid which also links to the gallic acid molecules with ester links substituting the –OH of the structure, as shows figure 1.

Depending on the Phenolic carboxylic acid nature, the hydrolysable tannins can sub-divide gallotannins and ellagitannins. The gallotannins hydrolysis produces gallic acid, mean while the ellagitannins produces hexahidroxidiphenilic acid.

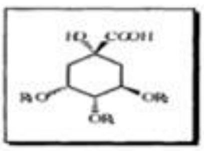
Tara extract is used to obtain tannic acid, and then used in very important applications, beside tanning industry they are used in the food industry to give some astringency to wine, teas, coffee and beer. Tara tannins are characterized for the high astringency and the soft acidic hydrolysis, the tannin gives gallic acid and alicyclic quinic acid instead of carbon hydrates as usually. The acidity of tannins is directly related to the presence of free carboxylic group in the structure.



Gallic acid



Tannic or Gallotannic acid



Quinic acid
($R_1 = R_2 = H$)

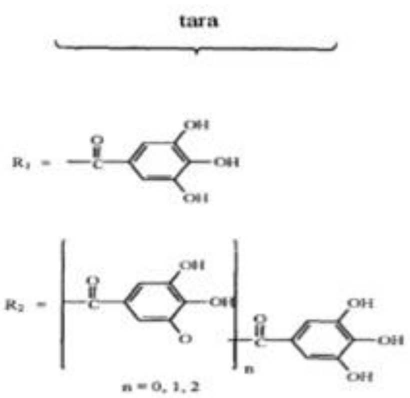


Figure 1: Molecular structure of tannic acid, gallic acid and quinic acid within the tara tannin molecule.

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.
-Penetration slows in the skin structure.
-Light fastness.
-High salt concentration buffers: are salts of weak organic acids, which provide good protection to the leather before ageing and acid hydrolysis.

4. Experimental development

4.1 Tara determinations

Determination of tannin content of several samples of tara powder has done, by the filter method, which consists in the tannin determination using filtration of a tannic solution through a hood containing leather powder slightly chromed; the tannic part remains linked inside of the hood, while the no tannin part can be evaluated from the liquid extracted by the filtration process.

The following table shows the results of the analysis of the different tara samples.

Parameter	S 1	S 2	S 3	S 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

Table1:Characterization of commercially available samples of Tara powder.

As can be observed, there is variability between different samples. The tannin content ranges between 45% and 50%. The concentration of insoluble matter, which is a negative factor for tanning process 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.

4.2 Physical modifications

A milled process in commercial tara has been made, with a methodology presented bellow, and the particle size has been determined on modified tara and original tara by sieved. Next tannin determination is carried out on different particle size.

4.2.1 Milling process

A powder sample of commercial Tara is applied a milling process. The methodology is as follows:
•The powder sample is placed in canisters 1L capacity to 1/3 of its capacity. (Photo 9, Annex 7)
•The introduction of bearing steel balls of various sizes.
•Let it roll for 50 h in laboratory rotary shaker (speed 15 rev / min.).
Powder samples of Tara (commercial and milled) was applied 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 um, 125µm, 100µm, 80 microns, 63 microns, 50 microns, 45 microns and 40 microns), mounted on a column of greater too low, as the following pictures.

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

The following charts show the granulometric of the samples studied.

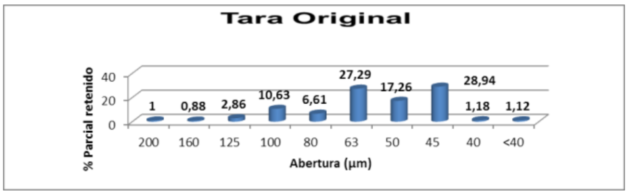


Figure 1: Graph Original Tara weight percent as it passes through various sieves

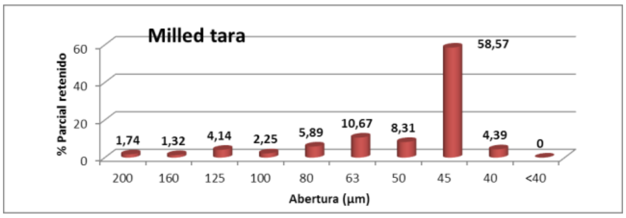


Figure 2: Distribution in weight percent after grinding Tara retained on each sieve

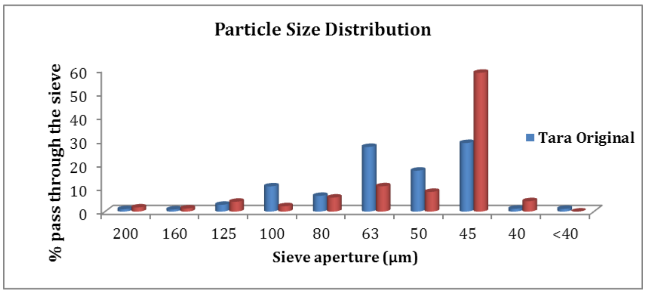


Figure 2: Comparison of particle size between original and milled Tara

It can be seen that grinding the original Tara has increased particle fraction smaller than 63 microns, homogenizing the particles to a size of 45 microns. You 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.

4.2.2 Tanins Determination

Samples are analyzed according to the milled Tara at different particle size fractions.
•Tara milled (total sample)
• Milled Fraction Tara 200-80 microns
• Milled fraction Tara <80-50 microns
• Milled fraction Tara <50-40 microns
•Original Tara

This separation is performed by size fractions due to the results obtained and the homogenization of Tara, ground in a particle size less than 50 microns, and it is with these fractions with which later was applied to the skin at laboratory scale.

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 1: Fraction and percentage obtained after milling and sieving process

The determination of tannins content of the samples is as follows in Table 22.

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 3: Determination of tannins (Part 2)

As can be observed in the table, there is variability across the different samples once again. The tara powder with a particle size 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 of smaller particle size has a higher percentage of tannins and presents a low content of insoluble matter. Therefore, we will follow the work with the application of three samples of tara to the leather: i) original tara, ii) milled tara, and iii) milled tara, particle size fraction of 50-40 microns.

4.2.3 Application of the physical modified Tara to the leather

For a second application of the tara at different particle sizes and because of the results obtained, tests on hides has been done at laboratory scale, using milled tara, sieved tara at particle size of 50 µm and original tara.

The base formulation used is described as follows:

STAGE	ºC	%	PRODUCT	Time	
Pre-tanning	20	50	Water with salt	15'	10 ºBé
		11	**Modified tara**		
		7	Synthetic X		
		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 4: Pre-tanning formulation

We started with pickled hides and a then neutralization process was done to increase the pH and starts the pre-tanning process. Then each piece was pre-tanned in different drums.

Three trials has been done:
1. Original Tara
2. Milled tara
3. Sieved tara

Results

Shrinkage temperature was determined to evaluate the thermal stability of leathers obtained. Better the hides are tanned better the shrinkage temperature.

Leathers were evaluated regarding colour and organoleptic parameters of hardness by applying the "Softness Test". The results obtained are shown in following table.

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 5: Shrinkage temperature, leather cross-section and softness

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

Table 6: Analysis of residual floats

The decrease of suspended matter and chemical oxygen demand is especially noticeable. Both the suspended matter and chemical oxygen demand decrease with the particle size, which is something to be taken into account. However, the softness obtained is not desirable; all the test leather samples were significantly hard.

Conclusions of physical modifications of tara

In general, all tests gave very rigid; this could be for drying excess before the staking. The softness tests prove it with their low values.

The colors of the trials are very similar with a yellowish appearance.

Something very important to notice on these trials is the improvement of the products penetration, which is one of the aims of this project.

The shrinkage temperatures are very similar, but in the case of final baths assessment, there is a big decrease of COD with the milled tara and even more for sieved tara, where shows a decrement in about 36% against the original tara.

Even more noticeable is the decreasing on suspended matter and the table shows how the value decreases as the particle size does it.

4.3 Application of modified tara on hides

4.3.1 Mixtures of Tara and other products

Different combinations of Milled and sieved Tara, at particle size around 40-50 microns, with other products have been studied: vegetable tannins (quebracho, mimosa), dispersants and synthetic tannins.

An experiment has been developed for the application of the Milled and sieved Tara products on skin at laboratory scale to determine their tanning power, analyzing the degree of penetration and stabilization on the skin structure and the physical and organoleptic properties acquired.

The obtained hides were characterized and the result obtained allows raising the optimization process of the methodology developed and designing formulations of pre-tanning.

Mixes of modified tara with different products

The products to be analyzed correspond to different mixtures of milled and sieved Tara (2:1) with vegetable extracts, synthetic tanning agents and auxiliaries.

The following table describes their composition:

Samples	Composition	% Theoretical tannins, mixture	% Real tannins, mixture
1	S. Tara/Mimosa	52.8	50.1
2	S. Tara/Quebracho	52.8	53.0
3	S. Tara/Naftalensulphonic	47.6	40.4
4	S. Tara/phenolic	48.0	45.7
5	S. Tara/Dihidroxidiphenilsulfone	44.8	44.3
6	S. Tara/Sodium [illegible]	36.1	36.1
0	Original Tara	47.0	43.9

Table 7: Description of the different mixtures of Milled Tara

It starts from pickling cowhide at pH 3.5, weighed and measured the thickness (2.2 / 2.5 mm). Is performed the process of neutralized to pH 5.0, in DD Simplex Drum (10 rpm). Once neutralized, the skin is divided into several samples of 250 g. about to go to pre-tannage test.

It is performed to determine the shrinkage temperature of the hides to evaluate their stability at the temperature. The better the skin is tanned, the higher the shrinkage temperature.

The skins are assessed to determine the organoleptic parameters such as color and toughness, determination by the equipment Data Color and Method "Softness test". Also the penetration values of the pre-tanning agents are valued by observing the cut skin.

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

Test	Composition	Ts (°C)	Soft ness (mm)	Cuts photos
1	S. Tara/Mimosa	60	1.1	
2	S. Tara/Quebracho	59	1.0	
3	S.Tara/ Naftalensulphonic	64	0.7	
4	S. Tara/ phenolic	64	0.6	
5	S.Tara/ Dihidroxidiphenilsulfone	62	1.1	
6	S. Tara/ sodium Pyrophosphate acid	62	0.9	
0	Original Tara	61	0.6	

Table 8: Results of skin tests Ts, softness and cut-penetration

Conclusions

The best shrinkage temperature observed in mixtures is with synthetics. An increase in the tanning properties is not observed in mixtures with Sieved Tara and other vegetable extract.

The best results, regarding the shrinkage temperature corresponding to the naphthalene mixture and with phenolic mixture followed by pyrophosphate, Dihidroxidiphenilsulfone.

Because of the results in the pre-tannage of product X are not as expected, will consider replacing it with a product naftalen sulphonic of Leather Química for improving the penetration of Tara. It will assess the possibility of using different lubricants agents that promote the spread of Tara.

4.3.2 Optimization of a mixture of modified Tara, naphthalene sulfonic and pyrophosphate

Tacking into account that the goal is to improve the penetration of the products, with the help of syntan naphthalene sulphonic, penetration is improved considerably and the behaviour of their combinations are able to obtain similar or even better values than a replacement syntan, phenol condensation type.

An experimental design is performed where it is used the Milled and sieved Tara (50 – 40 µm), with the aim to improve the formulation and minimize the use of synthetic tanning auxiliaries.

Products:
•Milled and sieved Tara (50 – 40 µm)
•Naphthalene Sulphonic syntan: Leathersyn NO
•Sodium acid Pyrophosphate
•Oil: Leatheroil EFA.

Factors to consider:

•Improved mechanical effect to enhance penetration (in pilot scale the mechanical effect is reduced by the characteristics of the drums). Use "plastic pieces".
•Using sodium pyrophosphate (4%) and decrease the amount of sodium chloride to achieve 10 °Be in the pretanning process.
•Experimental design will be further described below
•This products will be applied together as a mix (M) as follows:

-X1% Milled and sieved Tara (50 – 40 µm)
-X2% Leathersyn NO
-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 .

It is started with skin pieces neutralized following the base formulation as follows:

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

Table 9: Base formulation for experimental part III.5

Experimental Design

The study of wet white formulations is centralized factorial experimental design where two levels are defined for each factor. They studied two variables and two levels each (22) adding four central points. The variables to consider are the concentration of Tara and synthetic dispersant. This design has 12 different trials.

The experimental design ratios are described in this table:

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

Table 10: Variables, levels for experimental design

Experimental factors: % of tara powder and % Naphthalene sulphonic syntan added to the pre-tanning process according application recipe of table 4:

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 11: % of Tara and syntans for each trial

Process is performed on skin samples of 2370 g pickled (3550 gr pelt weight) in Simplex-4 Drum. First neutralized to pH = 5 and Cut through. Then washed and pretanning assays are performed.

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

Pre-tannins penetration is controlled into the skin, determining the shrinkage temperature and measured their organoleptic characteristics after drying operations and softened skin samples.

Results

Results from this experimental part are summarized in table 36, as follows:

Test	x_1	x_2	% Tara	% Syntan	Ts (ºC)	DSC (ºC)	Thickness (mm)	Tear Load (Strenght, N/mm)	Tensile Strenght (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

All results were introduced in the Statgraphics Plus version 5.1.To analyze the results of design, first look at the ANOVA table, tells us what factors (in this case, %Tara and % synthetic) that influence the Shrinkage Temperature (Ts) , Tear Resistance, Tensile Strength and Softness test (which are the observed variables).

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

There is another analysis done, which is the Light fastness for this experimental design.

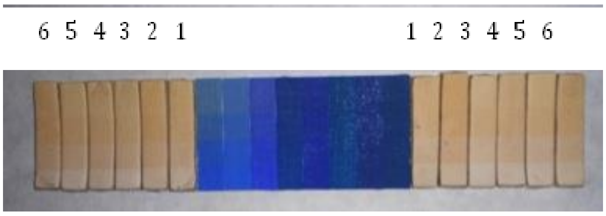


Photo 2: Light Fastness for experimental part III.5, (samples 1-6)

Photo 3: Light Fastness for experimental part III.2, (samples 7-12)

As can be seen, there is a change of color in all processes, nevertheless they are too similar with each other, this is too difficult to asses and make a conclusion in lightfastness basis. However, even when changes can be observed, there are not very dark final colours.

All leather were assessed by three different technicians, members of the European project party, their impressions about organoleptic Fool feel, smooth feel and tightness are described in Table 37. Taking into account that the symbols '+' means that the leather has a better behaviour against each analysis.

Test	**x_1**	**x_2**	**% Tara**	**% Syntan**	**Fool feel**	**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 13: Assessment of three different technicians, in order to obtain organoleptic

Conclusions

After seeing the statistical results from Statgraphics and 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 sulfonic synthetic, is as follows:

9% Modified Tara
2% Naphthalene sulphonic Syntan

That percentages means in terms of all Mix:

81.81% Milled Tara
18.18% of Naphthalene sulphonic Syntan

Based on the objectives of the work, to use sustainable products and reduce the use of synthetic auxiliary products, we can say that the goal has been met and that the use of syntans has been decreased by about 20%, and therefore increased the use of natural products, in this case the Tara. It is noteworthy that the changes made in the tare are physical processes that do not need extra chemicals to manufacture, such as synthetic products so they will not be subject to revision defined in Reach.

It is important to mention that the tara modifications are just physical, and it does not need any chemical product to obtain it, which allows not been under the REACH regulation.

The use of sodium Pyrophosphate acid, improves the penetration of the tara and also acts as an iron sequestering. This could be prove after the mechanical process of shaving, because it does not show any black stain on the leather.

4.3.3 Manufacture of three leather articles with modified tara: Automotive upholstery, leather goods and shoe upper leather.

Objective:

Use of milled Tara, from physical modifications of the project for the development of three leather articles:

•Automotive upholstery
•Footwear
•Leather goods.

Taking the results of the experimental design of section 4, which were made with mixtures of Tara milled, Synthetic naphthalene sulfonic and sodium acid pyrophosphate, which concluded that would be used the following percentages:

9% Milled Tara
2% Synthetic naphthalene sulfonic
4% Sodium acid pyrophosphate

Procedure:

The hides were collected in pelt and deliming, bating and pickle process were performed in laboratory, following a standard formulation, with the exception of automotive upholstery since the side leather was divided into two parts, one of which was subjected to acid enzymatic treatment in separately pickle.

Pickle formulation with enzymatic treatment for upholstery was conducted as follows:

		WET PHASE				
		Nº:		Date:		13/12/12
		Enterprise:	I+D Lowest	Skin:		½ side Bovine
		Article:	**Enzymatic Pickle**	Status:		batting
		Technician:	JDM	% (weight):		hide
		Drum	Simplex - 4	Weight (gr):		4.71
OPERATION	**ºC**	**%**	**PRODUCT**	**Gr.**	**TIME**	**OBSERVATIONS**
Pickle	20	50	Water	4.71kg		
		10	salt	471 g	10’	ºBé= 6
		1.0	Formic Acid		30’	
		0.5	Sulphuric Acid		60’	
		1.0	DEFAT 80 PA		180’	
					night	pH=3.0

Table 14: Pickle formulation with enzymatic treatment

Standard neutralization was performed with all skins in the same drum to homogenize and to obtain a pH value of around 5.0, which is the optimum value, founded to work with the Tara.

Pretanning was performed with all the skins together in the same drum, and then they were sent to Combalia to Sammy and shaved. A final tanning bath was taken and a chemical analysis was performed. Pretanning formulation was followed according to the latest experimental design.

At the end of pretanning a check was done and the penetration of the product was very good and showed a color characteristic of Tara, but insoluble matter appeared over the leather.

After shaving process the flesh-side was monitored to see iron stains, a couple of spots were seen, however after a couple of days when they went to retanning had disappeared.
The shaved skins returned to the laboratory for Retanning, dyeing and greasing process following formulations delivered by Leather Chemistry, described in the annexes.

Results

Once re-tanned and greased the automotive upholstery leathers were machined in Combalia, where they made the Sammy process and toggling for drying. Later they were staked in Machine.

The sides for Leather Goods and Footwear were drained and were reviewed in Combalia and passed through the vacuum machine at 45 ° C for 2 minutes. Then they were staked in machine. When they were collected seemed rigid and there was some sort of curtain effect on grain so they were sent to Curtits Aqualata for conditioning and later stake, which was a big improvement.

The results of chemical and physical analysis are presented below.

Results of chemical analysis for a final bath taken from pre-tanning process.

DETERMINATION	SIEVED TARA	MILLED Tara	UNITS	INTERN METHOD
pH	**3.8**	**3,7**		
SUSPENDED MATTER (M.E.S.)	**7976**	**10117**	mg/L	UNE-EN 872:2006
Chemical Oxygen Demands Kit. Decanted	**25560**	**40800**	mgO2/L	Kit Merck
Chemical Oxygen Demands Kit. No Decanted	**31000**	**67200**	mgO2/L	Kit Merck
Organic Nitrogen Ammonia Kit	**390**	**1903**	mgN/L	Kit Merck
Conductivity	**69855**	**69729**	µS/cm	UNE-EN 27888:1994
Solids	**16.6**	**14,3**	%	
Ashes a 500º	**7.5**	**8,1**		
pH Analytic Solution	**4.0**	**3,9**	%	Método de la Campana
Soluble solids	**9.1**	**11,1**	%	
Total solids	**9.3**	**12**	%	
No tannins	**8.3**	**8,8**	%	
Tannins	**0.8**	**2,3**	%	
Insolubles	**0.7**	**0,9**	%	
Agua	**90.2**	**88**	%	
pH Solución al 100%	**3.8**	**3,7**		
Densidad	**9.7**	**12**	ºBe	

Table 15: Results of chemical analysis of pre-tanning residual bath

Results Automotive Upholstery physical tests: comparative between the process with enzymatic pre-treatment and without enzymatic treatment.

DETERMINATION	without enzima	with enzima	Minimum	Units
THIKNESS	1,46	1,39		mm
Tensile Strength				
Strength	259,9	180,9	100	N
Elongation at break	46,7	43,6	<50	%
Tear Resistance	107,1	94,1	40	N/mm
Softness test	3	2,7		mm
Shrinkage Temperature (Ts)	74	74		ºC
DSC (dry leather)	118	119		ºC

Table 17: Leather goods physical tests

Results Footwear physical tests:

DETERMINATION	RESULTS	MINIMUM	UNIT	INTERN METHOD
THIKNESS	1,82		mm	IUP4 / EN ISO 2589
Tensile Strength				IUP6 / ISO 3376
Strength	389	150	N	
Elongation at break	44,5	40	%	
Tear Resistance	70,6	50	N/mm	IUP 8/ ISO3377
Softness test	2,3		mm	IUP 36/ EN ISO 17235
Shrinkage Temperature (Ts)	75		ºC	IUP 16 / ISO 3380
DSC (dry leather)			ºC	

Table 2: Footwear physical tests

Conclusions part 4.3.3

The skins have a very good appearance with a uniform dyeing and acceptable smoothness, the results are within the parameters established for each item.

In the case of the two automotive upholstery leathers, were expected to have a better smoothness, but had a bit of stiffness, so it was decided to strake in drum on dry skin, where achieving a better look.

In all tests have been completed some optimal percentages found, these percentages are based on pelt weight, reaching values of up to 18% of product mix for pre-tanning. For a next perform a test seek pretanning using the same ratio to the sample percentage is used, but only 10% on pelt weight mixture. After these trials chemical and physical analysis will be carried out.

5. General Conclusions

In physical modifications, a process of milled and sieved was performed to determine the tara tannins particle size. The tannins determination showed that at low particle size (40-50µm) the tannin content increases against original tara. Also on hides application showed a better penetration at lower particle size. That is why we decided to use that modified tara.

Applications of modified tara with different products has been done y we decided that the best auxiliary to improve the penetration is the naphthalene sulphonic syntan. This syntan was used in the experimental design to obtain the optimal combination with modified tara.

The optimal value gave by the statistical program (Statgraphics), taking into account the physical assays like shrinkage temperature, DSC, Tensile strength and tear load, is as follows:

9% Modified Tara
2% Naphthalene sulphonic Syntan

Based on the objectives of the project, of increase the use of sustainable products and decrease the use of auxiliary products, it can be said that the goal has been reach because the use of synthetics has been decrease in about 25%, comparing it with other studies carried out previously, and therefore the use of natural products has been increase considerably.

The final leather manufactures, are within the parameters established for each article.

Other objectives has been achieved, like the decrement of pollutant loads on final wastewater. This is because there is a decreasing on CDO and suspended matter using the modified tara. Also the exhaustion of tannins on final wastewater has been decreased, which means that almost every tannin fraction are linked to the leather processed.

6. **REFERENCES**

A. Brack Egg. Diccionario Enciclopédico de Plantas Útiles del Perú Cusco, Perú: CBC. 1999.
http://es.silvateam.com/Productos-y-Servicios/Leather/Extractos-vegetales/Taninos-de-tara.

http://www.scrd.net/scrd_new/espagnol/c_nat/extraits_veg/tara.htm

Madhan B. et al. “Combination tanning based on Tara: an attempt to make chrome-free garment leathers”, Journal of the American leather Chemists Association, vol. 102, No. 6, 182, 2007

Vitolo S. et al. “Tara Aluminium as an alternative to traditional chrome tanning: Development of a pilot-scale process for high-quality bovine upper leather”, Journal of the American leather Chemists Association, vol. 98, 123. 2003

Covington A.D., “New tannages for the new millennium”, Journal of the American leather Chemists Association, 1993, 168, 1998

Sivakumar V., “Ultrasound assisted diffusion in vegetable tanning for leather processing”. Journal of the American leather Chemists Association, vol. 103 (10), p. 330. 2008.

S. Kanth, et al., “Studies on the Use of Enzymes in Tanning Process: Part II. Kinetics of Vegetable Tanning Process”, Vol.: 105, N.: 1, 16-24, 2010

ICT, Leather Trade House, , Kings Park Road, Moulton Park, Northampton, NN3 6JD, UK, (Date of consultancy May, 15, 2010) www.tannerscouncilict.org

The physical tests on leather determine the capacity of finished leather to resist loads and actions that will be submitted by consumers according the manufactured leather goods. Such tests measure the properties that depend on the whole leather structure, considering all its thickness. The results will depend on factors like the parts of the hides or skins where samples are taken and its dimensions, the technical characteristics of the apparatus, the atmospheric conditions and the procedures. Therefore, the standard ISO methods have to be strictly followed to assure the maximum repetitiveness and reproducibility