

# OPTIMIZING A SUSTAINABLE AND INNOVATIVE WET-WHITE PROCESS WITH TARA TANNINS

by

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## ABSTRACT

This study considers the fruit of the tara tree (*Caesalpinia spinosa*) as a sustainable source for tanning agents and proposes alternatives to the commercial mineral salts and vegetable extracts to comply with an increasing demand that concerns low carbon footprint raw materials and health safety. Although tara tannins have been used in the leather industry and its properties being well known, the experimental part of the work aims to optimize innovative formulations using tara as wet-white pre-tanning agent. Combinations with naphthalene sulphonate and phenol condensation syntans will be used for wet white. Experiments have been designed by Simplex with centroid statistical calculations to obtain an optimized formulation. Tests are evaluated determining shrinkage temperature, tensile strength, elongation, tear resistance and light fastness.

## RESUMEN

Este trabajo considera el fruto del árbol de tara (*Caesalpinia spinosa*) como fuente sostenible de taninos para la curtición del cuero y propone alternativas para las sales minerales comerciales y los extractos vegetales como respuesta a la creciente demanda preocupada por reducir el impacto medioambiental y la seguridad de los materiales de consumo. Aunque los taninos de la tara ya se usan para la fabricación de cueros desde épocas remotas y sus propiedades están reconocidas, la sección experimental de este trabajo se orienta a optimizar fórmulas innovadoras utilizando la tara como agente de curtido wet-white. Combinaciones con naftaleno sulfónico y sintanes de condensación fenólica se emplean para wet white. Los experimentos se han diseñado por cálculos estadísticos utilizando el método Simplex con centroides para obtener una formulación optimizada. Los ensayos se evalúan determinando la temperatura de contracción, la resistencia y la elongación a la tracción, la resistencia al desgarro y la solidez a la luz.

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## INTRODUCTION

Since pre-Hispanic eras, plants were used for tanning and dyeing the hides and skins from the animals hunted for food. With the development of the knowledge and the technologies, humans have researched substances with specific properties to replace those from nature. Consumers concern today on the impact that the industry is causing to the environment and the health of the users, as well on social aspects, and claims for a just commerce and tackling poverty.

The tannins from tara are well known in the leather industry and it is appreciate because its light color and lightfastness. For this reason, demand of tara tannins increased during the last decades at the time leather production for automobile upholstery has experienced a highest demand. However, there are no specific promotions for the use of tara tannins. Its application as tanning agent remains in the technical departments of the chemical suppliers. Tannery technicians obtain very little information from technical sheets that only specifies few recommendations and provides minimum quality values such as concentration of tannins, solids and humidity. Therefore, the technical and scientific scope of this work is to fulfill the lack of specific literature and research focus on tara tannins. Also, it aims to provide technical information for its promotion to leather technicians.

*Cæsalpinia spinosa* (Molina) Kuntze, commonly known as tara<sup>1</sup>, is a small leguminous tree or thorny shrub. Tara is cultivated as a source of high value products from its pods as tannins based on a gallotannic structure used in the leather industry and seeds as gum for food industry. Having its origin in the Andean Region, pre-Incas civilizations used the fruits of the tree to produce dyes for textiles and ceramics, tannins for leather and medicines. Known, therefore, as “Incas green gold”, there is a strategic interest in Peru, Bolivia and Ecuador, supported by international organizations for cooperation, to promote productive processes under environmental sustainability criteria and social benefit.

Therefore, beyond the technical and scientific objectives of this research work, the two implicit pillars in the scope are:

- **Environment:** The study focus on the tannins obtained from the pods of the tara fruits. Tara is a tree, thus contributes to fix carbon and nitrogen, and, contrary to other vegetable tannins, production does not depend from other industries or requires deforestation. Regulations of chemicals, mainly in Europe, recognize the use of non-hazard substances from natural origin not chemically treated.

- **Social:** Tara tree is suitable for agro forestry and represents a source of economical activities for Andean Regions by exporting products to the leather markets. Also, other products from the fruit of tara are very valuable in other industries as gum for food and industrial applications and polyphenols with properties in medicine. The research has started as a cooperation work to engage in poverty in rural areas in Bolivia.

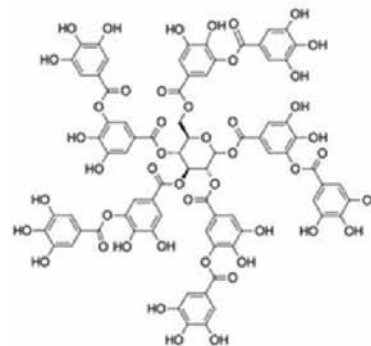


Figure 1: Tannic or Gallotannic acid

## EXPERIMENTAL

### Characterization of commercial tara tanning powder

Samples of tara tannin powder from different leather chemical suppliers were characterized. Table 1 indicates reference values for the tests carried out in this experimental work. The higher value corresponds to the mean value plus standard deviation and the lower the mean value minus the standard deviation:

**TABLE 1**  
**Reference values of tara characterization**

Determination	Values	Higher	Lower
pH analytical solution	3,42	3,57	3,27
Soluble solids (%)	65,53		
Total solids (%)	91,95		
Non tannins (%)	14,63	18,67	10,58
Tannins (%)	50,90	55,18	46,62
Insoluble (%)	26,43	32,31	20,54
Water (%)	8,05		

<sup>1</sup> Known names (Jones, 1987 and De la Cruz (2004): “Tara”, “Taya” (Peru), “Guarango” (Ecuador), “Cuica”, “Serrano”, “Vinillo”, “Acacia Amarilla” (Yellow acacia), “Andean Dividivi”

### Design of a pretanning process with tara

The experimental design focuses on finding the best combination of tara with syntans, by means, blending the tara powder with a condensation phenol syntan or a naphthalene sulphonic syntan, or the three of them. 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. Tara is well appreciated in the leather industry as vegetable tanning agent because its light fastness compared with other vegetable tannins. Therefore, influences of the components of the different mixtures on this property will be considered.

### Products, materials and equipment

To carry out the experimental tests, the following commercial products have been selected:

*Tara Powder:* Origen: Peru

Quality Control	pH	3,5
	Tannin content	45%
	Non tannin content	4,7%
	Water	7,1%
	Insolubles	33,2%

Soluble solids	59,7%
Total solids	92,9%
Iron	388,9mg/Kg (ppm) by atomic absorbance

#### *Synthetic tanning of phenol condensation:*

Fine powder, white, soluble in water. 90% of tanning content, pH 4 (+/-0,2) solution 1:10

#### *Synthetic tanning of naphthalene sulphonic:*

Yellowish liquid. Miscible in water. 35 % of tannin content. pH 3.3 – 3.7 (solution 1:10)

To obtain comparative tests, it was used hides of bovine, split in green. The were divided in 8 pieces and marked. The eight pieces were weight and their thicknesses were calibrated. The recipe used for the delimiting, bating and pickling processes is in Table 2.

The experimental design to evaluate ingredient blends is the Simplex method. It is applied when the sum of the percentages of the two or more factors or ingredients of a blend must be 100%. Therefore, the levels of the factors are not independent and the variation of them can determine the properties of the final product.

**TABLE 2**

Operation	°C	%	Product	Time	Comments
Washing	30	150	Water		
		0.2	Lactic acid	20 min.	Drain
Delimiting	35	100	Water		6 rpm
		2.5	Ammonium sulfate		
		0.3	Sodium bisulfite		
Bating		0.8	Lactic acid	90 min	pH = 8,1 Cut through
		1	Enzyme	60 min	Check bating pH 7.9 Temperature: 33°C Drain
Washing I	20	200	Water	15 min	Drain
Washing II	20	200	Water	15 min	Drain
Pickling	20	50	Water		8 rpm
		10	Sodium chloride	15 min	
		0.5	Formic acid (1:10)	20 min	
		1.0	Sulfuric acid (1:10)	120 min	
				Run overnight 15 min	pH 3.5
				Cut through	
		0.1	Preservative		Drain
					Horse up

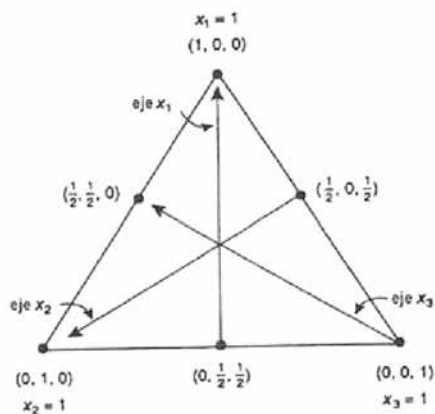


Figure 2: Coordinate axis for a mixture of three ingredients

If  $x_1, x_2, \dots, x_n$  are the variables representing the percentages of  $k$  ingredients or components of a blend, the values of  $x_i$  are restricted as follows:

$$0 \leq x_i \leq 1 \quad I = 1, 2, \dots, k$$

and the sum of the percentages of the  $k$  ingredients is 1:

$$\sum_{(i=1 \dots k)} x_i = x_1 + x_2 + \dots + x_k = 1$$

If the percentage of a component is  $x_i = 1$ , then there are no other components in the mixture. To design a blend with three components, the coordinated values are defined as:

$$x_1 + x_2 + x_3 = 1$$

The geometric description of the space of the factors for  $k$  components is a Simplex of  $(k-1)$  dimensions. Therefore, for three component blend, it will be a triangle which vertex represents one single component and the sides are the designed coordinates for mixtures of two components and a  $x_i=0$ . The coordinates inside the triangle represent the mixtures of two components where  $x_1 > 0, x_2 < 0$  and  $x_3 < 0$ . Any proportional combination of components for the mixture experiment must be placed either in the frontier or inside the triangle of coordinates. The axes of the variables  $x_i$  in the Simplex system of three variables are drawn in the figure 2. The axis of the ingredient  $i$  is the straight line that goes from the point base  $x_i=0$  and  $x_j=1/(k-1)$  for the ingredients,  $j \neq i$  in the vertex, where  $x_i=1$  and  $x_j=0$  for  $j \neq i$ .

As an example, for the mixture of three ingredients, the axis  $x_1$  goes from the base of coordinates  $(0, 1/2, 1/2)$  to the vertex  $(1, 0, 0)$ :

The Simplex design with centroids is based in the Simplex system coordinates when mixtures containing 1, 2, 3... or  $k$  ingredients with identical proportions. This means that there are  $k$  mixtures for each ingredient: all possible mixtures for

two components is  $1/2$ , for three  $1/3$  for  $k$ ,  $1/k$ . The trials are designed according to Simplex with centroids coordinates, and the percentages are adjusted to the tannin content of each ingredient according Table 3:

**TABLE 3:**  
**Simplex with centroids design**

Test	$X_1$	$X_2$	$X_3$	Tara	Phenol syntan	Naphtalen sulphonic syntan
1	1	0	0	12	0	0
2	0	1	0	0	6	0
3	0	0	1	0	0	14
4	1/2	1/2	0	6	3	0
5	1/2	0	1/2	6	0	7
6	0	1/2	1/2	0	3	7
7	1/3	1/3	1/3	4	2	4.7

The pretanning trials were carried out according to the following general process:

Operation	°C	%	Product	Time	Comments	
Pre-tanning pH 3.5	20	50	Water	15 min	°Bè: 7	
		4	Sodium chloride			
		1/2	Tanning agent			
		2	Sulphitated fatliquor			120 min
		1/2	Tanning agent			Overnight
		0,5	Formic acid	90 min	pH 3,2 Drain	

Horse up. Samming and stretching. Place and extend on a plate during 12 hours. Hanging for drying at 30°C. Conditioning and stake.

**TABLE 4**  
**Table of test results. Simplex design with centroids.**

#	Description	$S_T^\circ$	Tensile Strength (N) EN ISO 3376 – IUP6	% Elongation EN ISO 3376 – IUP6	Tear load (N/mm) EN ISO 3377-2, IUP8	Light fastness <sup>2</sup>
1	Tara powder	61.5	551.8	51.6	61.4	4
2	Phenol syntan	68.5	360.0	53.8	57.2	1
3	Naphthalene sulphonic	60.5	461.7	47.7	68.6	2
4	Tara + phenol	63.5	427.3	46.7	58.5	2
5	Tara + naphthalene	68.0	463.7	54.0	53.2	3
6	Phenol + naphthalene	65.5	495.2	48.7	89.0	2
7	Tara+phenol+naphthalene	67.5	477.7	51.8	56.3	2

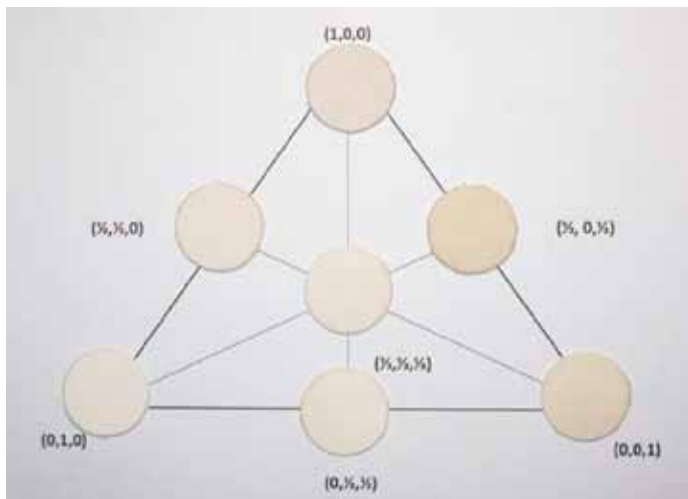


Photo 1: Design of a pretanning process with tara



Photo 2: Light fastness tests

## TEST RESULTS AND DISCUSSION

With the created experimental design, we have defined 5 statistics variables ( $S_T^\circ$ , Tensile, Elongation, Tear and Light) for three factors or components (tara, phenol syntan and naphthalene sulphonic), in a simplex-centroid model.

Results are analyzed for each variable in order to obtain the optimal response and the equation of the fitted model.

Shrinking temperature ( $S_T^\circ$ ):

Special Cubic Model Fitting Results for  $S_T^\circ$ :

Parameter	Estimate
A:Tara	61,5
B:Phenol syntan	68,5
C:Naphth sulfonic	60,5
AB	-6,0
AC	28,0
BC	4,0
ABC	30,0

The equation of the fitted model is:

$$TC = 61,5 * Tara + 68,5 * Phenol\ syntan + 60,5 * Naphth\ sulfonic - 6,0 * Tara * Phenol\ syntan + 28,0 * Tara * Naphth\ sulfonic + 4,0 * Phenol\ syntan * Naphth\ sulfonic + 30,002 * Tara * Phenol\ syntan * Naphth\ sulfonic$$

Optimize Response

Goal: maximize  $S_T^\circ$   
 Optimum value = 68,5

Factor	Low	High	Optimum
Tara	0,0	1,0	0,0
<b>Phenol syntan</b>	<b>0,0</b>	<b>1,0</b>	<b>1,0</b>
Naphth sulfonic	0,0	1,0	0,0

It is confirmed that phenol condensation tannins increase the shrinking temperatures more than plant polyphenol gallotannins. However, observing the estimated response surface, similar range of shrinking temperature is obtained with the combination of tara-naphthalene sulphonic syntan.

<sup>2</sup> For the mathematic model, the values of light fastness have been adjusted and the standard criteria have not been considered. The aim is to have a comparison between the trials carried out and not the value of light fastness.

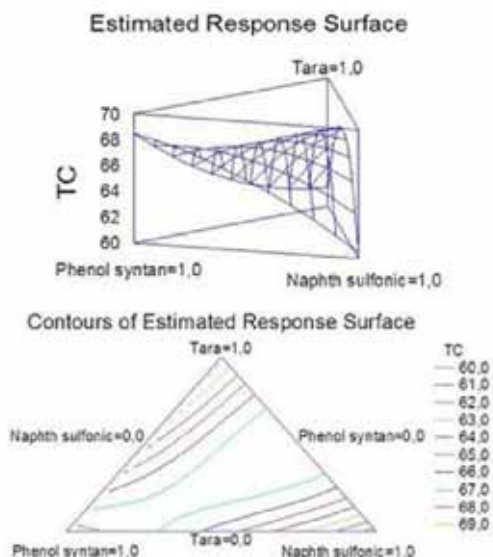


Figure 3: Estimated response surface for shrinking temperature

The synergy can be explained because, despite the low influence on shrinking temperature of the naphthalene sulphonic syntan, allows to penetrate tara in the inner layer of the leather, as is appreciate in the SEM photos 1 and 2.

Tensile strength

Special Cubic Model Fitting Results for Tensile

Parameter	Estimate
A:Tara	551,8
B:Phenol syntan	360,0
C:Naphth sulfonic	461,7
AB	-114,4
AC	-172,2
BC	337,4
ABC	384,0

The equation of the fitted model is

$$\text{Tensile} = 551,8 \cdot \text{Tara} + 360,0 \cdot \text{Phenol syntan} + 461,7 \cdot \text{Naphth sulfonic} - 114,4 \cdot \text{Tara} \cdot \text{Phenol syntan} - 172,2 \cdot \text{Tara} \cdot \text{Naphth sulfonic} + 337,4 \cdot \text{Phenol syntan} \cdot \text{Naphth sulfonic} + 384,014 \cdot \text{Tara} \cdot \text{Phenol syntan} \cdot \text{Naphth sulfonic}$$

Optimize Response

Goal: maximize Tensile  
Optimum value = 551,8

Factor	Low	High	Optimum
<b>Tara</b>	<b>0,0</b>	<b>1,0</b>	<b>1,0</b>
Phenol syntan	0,0	1,0	0,0
Naphth sulfonic	0,0	1,0	0,0

Pretanning with tara optimizes the values of tensile strength at the higher level, while the phenolic syntan do not help to

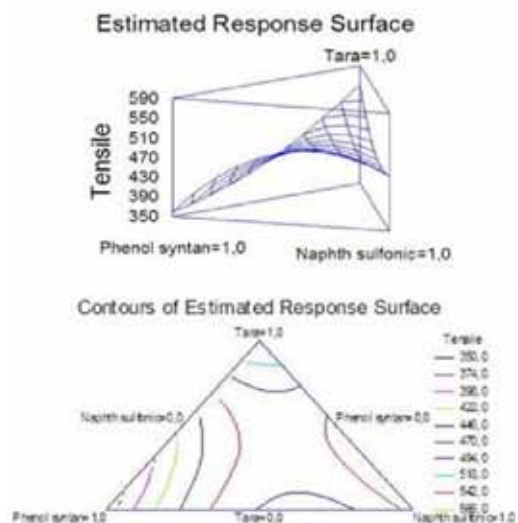


Figure 4: Estimated response surface for tensile strength

increase this resistance. Combinations of tara and naphthalene sulphonic syntans, as observed in the estimated response surface, have a range of the highest values. This is confirmed observing photos 1 to 4 as fibers keep compacted all through the leather than the other combinations.

Tensile strength elongation:

Special Cubic Model Fitting Results for Elongation

Parameter	Estimate
A:Tara	51,6
B:Phenol syntan	53,8
C:Naphth sulfonic	47,5
AB	-24,0
AC	17,8
BC	-7,8
ABC	64,5

The equation of the fitted model is

$$\text{Elongation} = 51,6 \cdot \text{Tara} + 53,8 \cdot \text{Phenol syntan} + 47,5 \cdot \text{Naphth sulfonic} - 24,0 \cdot \text{Tara} \cdot \text{Phenol syntan} + 17,8 \cdot \text{Tara} \cdot \text{Naphth sulfonic} - 7,8 \cdot \text{Phenol syntan} \cdot \text{Naphth sulfonic} + 64,5015 \cdot \text{Tara} \cdot \text{Phenol syntan} \cdot \text{Naphth sulfonic}$$

Optimize Response

Goal: maximize Elongation  
Optimum value = 54,2361

Factor	Low	High	Optimum
Tara	0,0	1,0	0,61
Phenol syntan	0,0	1,0	2,85E-8
Naphth sulfonic	0,0	1,0	0,38

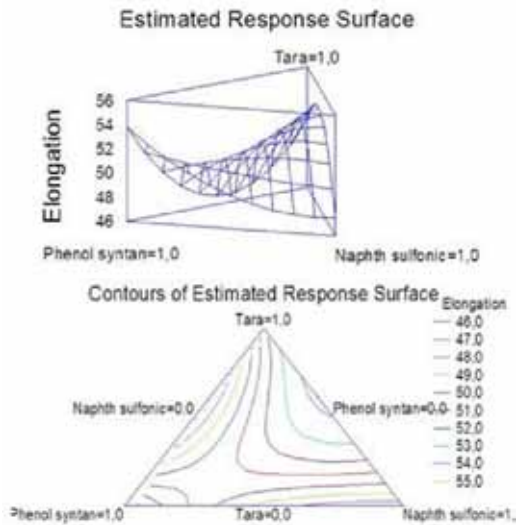


Figure 5: Estimated response surface for tensile elongation

Optimal is the combination of tara and naphthalene sulphonic tannin and similar elongation is obtained with phenol tannin. In any case, there are not significant different among the tests.

Light fastness

Special Cubic Model Fitting Results for Light fastness

Parameter	Estimate
A:Tara	4,0
B:Phenol syntan	1,0
C:Naphth sulfonic	2,0
AB	-2,0
AC	0,0
BC	2,0
ABC	-9,00

The equation of the fitted model is

$$\text{Light fastness} = 4,0 * \text{Tara} + 1,0 * \text{Phenol syntan} + 2,0 * \text{Naphth sulfonic} - 2,0 * \text{Tara} * \text{Phenol syntan} + 0,0 * \text{Tara} * \text{Naphth sulfonic} + 2,0 * \text{Phenol syntan} * \text{Naphth sulfonic} - 8,99996 * \text{Tara} * \text{Phenol syntan} * \text{Naphth sulfonic}$$

Optimize Response

Goal: maximize Light fastness  
Optimum value = 4,0

Factor	Low	High	Optimum
<b>Tara</b>	<b>0,0</b>	<b>1,0</b>	<b>1,0</b>
Phenol syntan	0,0	1,0	0,0
Naphth sulfonic	0,0	1,0	0,0

Tara itself has gives good light fastness to the leather. It is well know the use of tara in the automobile industry. It requires interior materials able to maintain its properties under extreme

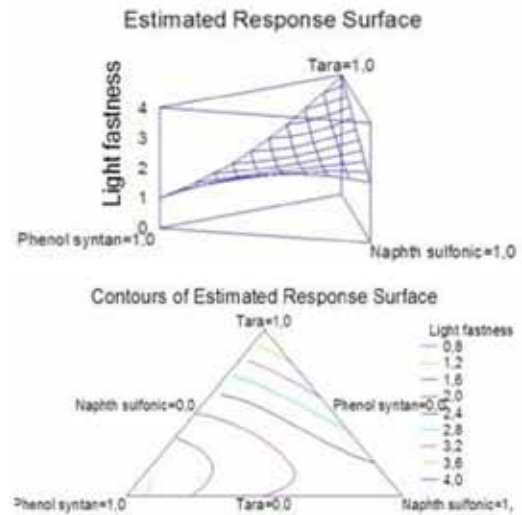


Figure 6: Estimated response surface for light fastness

expositions. Combinations with naphthalene sulphonic syntan have less negative influence in the light fastness values than the phenol condensation syntan.

There is a variety of results and the optimization of the mixtures will depend of the variables we analyze.

However we can observe that tara have, in general, good properties because its tanning effect, but in most of the cases, is not optimal due to certain limits to go through the leather.

With the help of an auxiliary syntan, naphthalene sulphonic type, penetration is improved considerably and the behavior of their combinations are able to obtain similar or even better values than a replacement syntan, phenol condensation type. This thesis is supported also, with the following SEM photographs:



Photo 1: SEM photo. Tara. 24x & 202x

The leather is well tanned on surface, while the inner layer fibers are open and well differentiated. The rapid superficial tanning effect of tara, due to its astringency, does not allows the unreacted tannins to penetrate inside the leather.

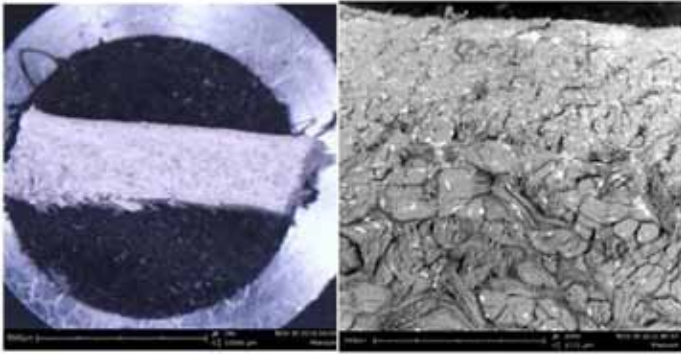


Photo 2: SEM photo. Tara + Naphthalene sulphonic syntan. 24x & 202x

The fibers are very compacted and they are not differentiated due to the crosslinking effect of the tannins.

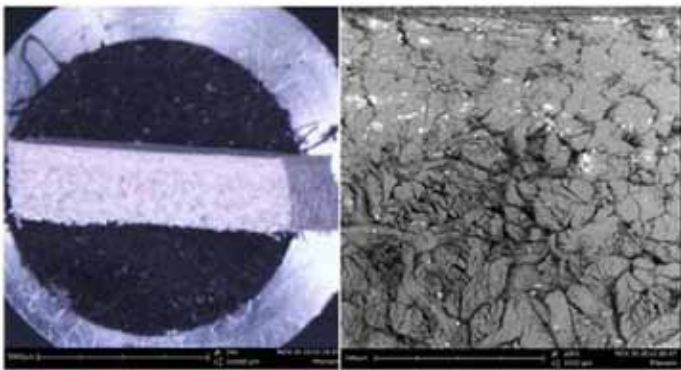


Photo 3: SEM photo. Tara + phenol condensation syntan. 24x & 202x

Fibers are very compacted and tanning is obtained all through the leather. Especially in the grain layer, fibbers have disappeared and material is tight and homogeneous.

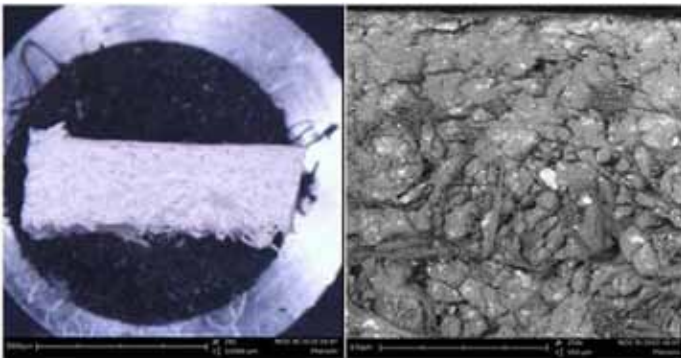


Photo 4: SEM photo. Tara + Naphthalene sulphonic syntan + phenol condensation syntan. 24x & 202x

Fibers are visible and there is certain uniformity among the grain and the inner layers.

## CONCLUSIONS

Differences between the tests are remarkable and the behavior of the leather depends much more of the variables than the combination of products. Considering the goals of the work, using tara as sustainable tanning agent, we observe that, further the test where tara alone has the best results (light fastness and tensile strength), good results and comparable to the ones achieved with the phenol condensation syntan, are the combinations of tara tannin and the naphthalene sulphonic syntan acting as tanning auxiliary. In these cases, a certain synergy is observed (Tensile elongation).

We assume that this combination (tara + naphthalene sulphonic syntan) will enhance the performance of the tara tannins what is the aim of this work. The chosen experimental design has only determined a mixture of equal proportions of the ingredients, calculated on the tanning content. The second experimental design will analyzed different percentages of the two products to define the most appropriate recipe for a sustainable wet white formulation.

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