

TARA (*CAESALPINIA SPINOSA*): THE SUSTAINABLE SOURCE OF TANNINS FOR INNOVATIVE TANNING PROCESSES*

by

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ABSTRACT

This study considers the fruit of the tara tree as a sustainable source for tanning agents and proposes alternatives to the commercial mineral salts and vegetable extracts to comply with environment and social concerns. Tara tannins have been used in retanning formulas in leather processing and its properties are well known. This work aims to optimize formulations using tara as a pre-tanning agent. Combinations with a naphthalene sulphonic syntan are used to obtain an innovative wet-white recipe in which shrinkage temperature, tensile strength, tensile elongation, tear load and lightfastness properties are considered as statistical variables.

RESUMEN

Este estudio considera el fruto del árbol de tara como fuente sostenible de taninos y propone alternativas a las sales minerales comerciales y los extractos vegetales para cumplir con demandas sociales y medioambientales. Los taninos de la tara ya se utilizan en los procesos de recurtición en la industria del cuero y sus propiedades son conocidas. Este trabajo propone la optimización de formulaciones utilizando la tara como agente de pre-curtición. Se utilizan combinaciones con un agente de curtición naftalén sulfónico para una formulación innovadora de wet-white considerando la temperatura de contracción, la resistencia y elongación a la tracción, la resistencia al desgarro y la solidez a la luz como variables estadísticas.

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INTRODUCTION

Since pre-Hispanic eras, plants were used for tanning and dyeing the hides and skins from the animals that were hunted for food. With onset of technology, humans have researched materials with specific properties to replace those from nature. Consumers are concern today on the impact that the industry is having on the environment and the health of the users, as well on social aspects, for a fair trade and addressing poverty.

The tannins from tara are well known in the leather industry and are valued for their ability to impart light color and lightfastness. For this reason, demand for tara tannins has increased at the time that leather production for automobile upholstery has experienced its highest demand.¹⁻¹⁰ *Cæsalpinia spinosa* (Molina) Kuntze, commonly known as tara,¹¹ (known names (Jones, 1987 and De la Cruz (2004): “Tara”, “Taya (Peru), “Guarango” (Ecuador), “Cuica”, “Serrano”, “Vinillo”, “Acacia Amarilla” (Yellow acacia), “Andean Dividivi”) 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.

In previous work,¹² combinations with naphthalene sulphonic and phenol condensation syntans have been carried out. This previous work was focused on finding the best combination of tara with the mentioned syntans. The best statistical design to evaluate ingredient blends is the Symplex method. In this preliminary work we demonstrated that the blend of tara powder and a naphthalene sulphonic syntan is the most

appropriate compared with the mixture of tara powder and phenol condensation syntan. The present study aims to optimize the formulation of tara with naphthalene sulphonic syntan to obtain an innovative wet-white recipe. To perform this study, we carry out a second experimental design to analyze different percentages of the two products and to define the most appropriate recipe for a sustainable wet-white formulation.

MATERIALS AND METHODS

The technical and scientific scope of this work is to propose innovative formulation based on tara powder for wet-white or metal-free article able to produce any kind of final leather good: shoe, apparel, upholstery, etc. Tara is, up to now, used for retanning mainly wet-white using glutaraldehyde as a major tanning agent. To carry out the experimental tests, the following commercial products have been selected:

The pretanning trials were carried out according to the general process seen in Table II.

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, according to a quadratic, centralized, rotatable and orthogonal model (See Figure 1).

In order to study the effect that each of the products used has on the final properties of the pretanned leather, as well as their interrelations, both a multilevel centralized factorial experimental design and an analysis of variance (ANOVA) have been employed as statistical tools. An experimental design with 2 variables and 2 levels⁽²²⁾ was chosen in order to carry out the experimentation. The variables to study were: amount of tara (%) and amount of naphthalene sulphonic syntan (%). Table 3 shows the nine experiments required to carry out this experimental design.

TABLE I
Characteristics of the commercial products.

<i>Tara Powder</i>	Origen	Peru		
	pH	3.5	Insolubles	33.2%
	Tannin content	45%	Soluble solids	59.7%
	Non tannin content	4.7%	Total solids	92.9%
	Water	7.1%	Iron by atomic absorbance	388.9 mg/Kg
<i>Synthetic tanning of naphthalene sulphonic</i>	Yellowish liquid. Miscible in water. 35% of tannin content. pH 3.3 – 3.7 (solution 1:10)			

RESULTS AND DISCUSSION

In the previous study,¹² we concluded that penetration of tara is improved considerably with the help of an auxiliary syntan. Specifically, using naphthalene sulphonic syntan. This thesis is supported with the SEM photographs shown in Figure 2.

In image a) 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 allow the unreacted tannins to penetrate inside the leather.

In image b) the fibers are very compacted and they are not differentiated due to the crosslinking effect of the tannins.

In image c) the fibers are very compacted and tanning is obtained all through the leather. Especially in the grain layer, fibers have disappeared and material is tight and homogeneous.

In image d) fibers are visible and there is certain uniformity among the grain and the inner layer.

Therefore, we assume that the combination of tara and naphthalene sulphonic syntan will enhance the performance of the tara tannins.

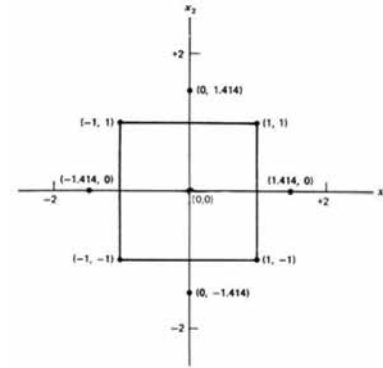
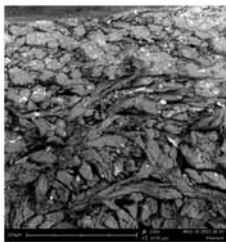


Figure 1. Quadratic, centralized, orthogonal and rotatable design.

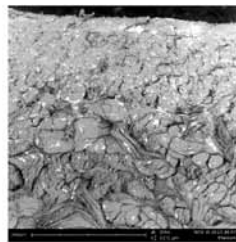
TABLE II
Recipe for the pretanning trials.

Operation	°C	%	Product	Time	Comments
Pre-tanning	20	50	Water		
		4	Sodium chloride	15 min	°Bè: 7 pH 3.5
		1/2	Tanning blend		
		2	Sulphitated fatliquor	120 min	<i>Note 1</i>
		1/2	Tanning blend	Overnight	<i>Note 2</i>
		0.5	Formic acid	90 min	pH 3.2
					Drain

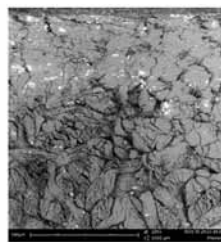
Horse up. Samming and stretching. Place and extend on a plate to be dried during 12 hours. Air drying at 30°C. Conditioning and stake.



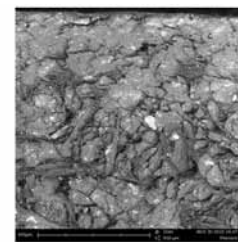
a) Tara



b) Tara + naphthalene sulphonic syntan



c) Tara + phenol condensation syntan



d) Tara + naphthalene sulphonic syntan + phenol condensation syntan

Figure 2. SEM images of the pretanned leathers.

TABLE III
Experimental design.

Test	x_1	x_2	% Tara powder	% Naphthalene sulphonic syntan
1	-1	-1	1,8	2
2	-1	1	1,8	12
3	1	-1	10.2	2
4	1	1	10.2	12
5	0	-1.414	6	0
6	0	1.414	6	14
7	-1.414	0	0	7
8	1.414	0	12	7
9	0	0	6	7

As mentioned in the materials and methods section, to define the most appropriate recipe for a sustainable wet-white formulation, a multilevel centralized factorial experimental design was carried

out. Figure 3 shows the leather pieces test results in the coordinates according the described experimental design.

Table 4 shows the physical test results to be statistically analyzed.

TABLE IV
Results of the physical tests.

Test	Coordinates	ST (°C)	Tensile Strength (N) <i>EN ISO 3376-IUP6</i>	% Elongation <i>EN ISO 3376-IUP6</i>	Tear load (N/mm) <i>EN ISO 3377-2 IUP8</i>	Lightfastness
1	(-1, -1)	61	743.0	49.0	76.9	2
2	(-1, 1)	69	725.3	44.1	79.5	2
3	(1, -1)	59	777.3	38.1	65.5	3
4	(1, 1)	71	709.5	39.5	64.3	3
5	(0, -1.414)	63	848.0	38.9	68.1	3
6	(0, 1.414)	74	900.5	37.0	72.3	1
7	(-1.414, 0)	63	875.0	52.8	81.9	1
8	(1.414, 0)	70	1022.0	48.4	82.8	4
9	(0, 0)	65	903.0	44.7	82.3	2

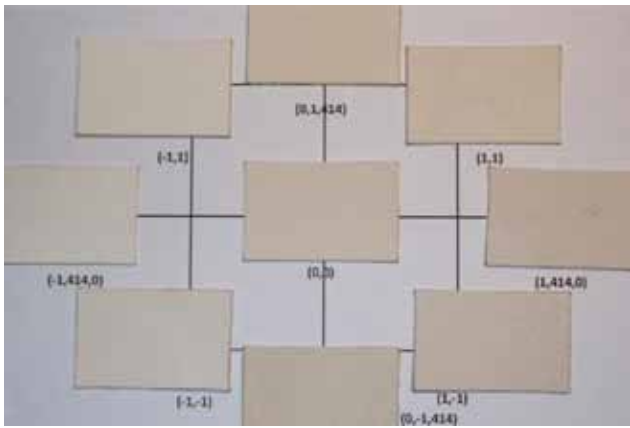


Figure 3. Optimization for a pretanning process with tara.

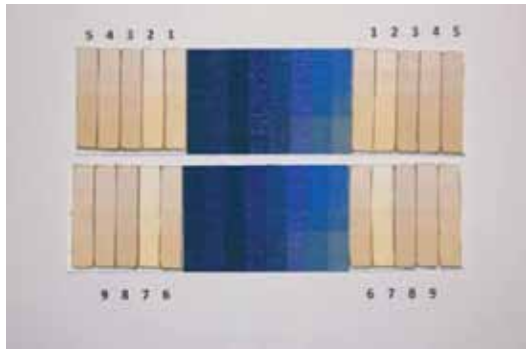


Figure 4. Lightfastness test.

Results are analyzed for each variable in order to obtain the optimal response:

Shrinkage Temperature (SToC):

TABLE V
Estimated effects for ST.

Average	65.00	+/- 0.88
A:Tara	2.47	+/- 1.39
B:Syntan	8.89	+/- 1.39

Analysis for Variance for ST

Source	Sum of Squares	Mean Square	F-Ratio	P-Value
A:Tara	12.25	12.25	3.15	0.1192
B:Syntan	158.03	158.03	40.64	0.0004

The ANOVA table partitions the variability in ST 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, % syntan has P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

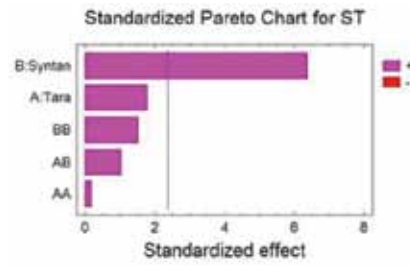


Figure 5. Pareto chart for shrinkage temperature.

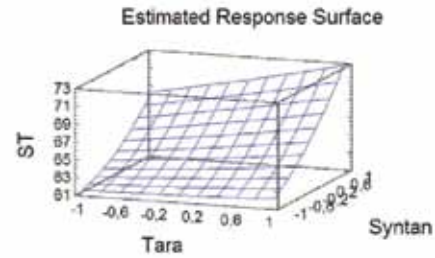


Figure 6. Estimated Response Surface for shrinkage temperature.

Since the effect of the % of syntan has statistical significance to the variable shrinkage temperature at 95% confidence, we can conclude that there is a correlation between the shrinkage temperature and the % of syntan according the following lineal equation:

$$ST = 65.77 + 4.44 * Syntan$$

Optimum value for syntan in shrinkage temperature = 1.414 (14% Naphthalene sulphonic syntan).

Tensile Strength (N)

TABLE VI
Estimated effects for tensile strength (N).

Average	903.00	+/- 43.84
A:Tara	56.60	+/- 69.31
B:Syntan	-2.81	+/- 69.31

Analysis for Variance for tensile strength (N)

Source	Sum of Squares	Mean Square	F-Ratio	P-Value
A:Tara	6406.51	6406.51	0.67	0.4411
B:Syntan	15.83	15.83	0.00	0.9688

None of the effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

TABLE VII
Optimize Response for tensile strength.

Goal	maximize tensile strength (N)		
Optimum value	913.272		
Factor	Low	High	Optimum
Tara	-1.414	1.414	0.722
Syantn	-1.414	1.414	-0.091

Tensile Elongation (%)

TABLE VIII
Estimated effects for tensile elongation (%)

Average	44.70	+/- 0.89
A:Tara	-6.66	+/- 1.40
B:Syntan	-0.32	+/- 1.40

Analysis for Variance for tensile elongation (%)

Source	Sum of Squares	Mean Square	F-Ratio	P-Value
A:Tara	88.60	88.60	22.56	0.0021
B:Syntan	0.21	0.21	0.05	0.8250

For % elongation % of tara have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

% Tara influences negatively to the tensile elongation and therefore the optimal value for tara is -1.414 = 0

By eliminating the interaction effects, and considering that the syntan has no significance influence in the tensile elongation, we can obtain a lineal equation where the variable is correlated to the % of tara:

$$\text{Elongation} = 44.32 - 3.33 * \text{Tara}$$

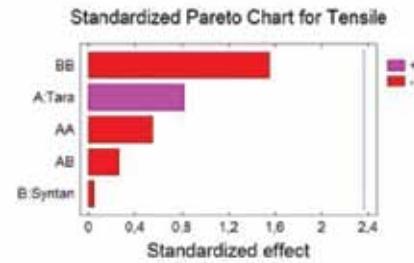


Figure 7. Pareto chart for tensile strength.

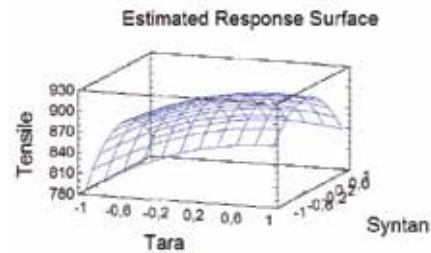


Figure 8. Estimated Response surface for tensile strength.

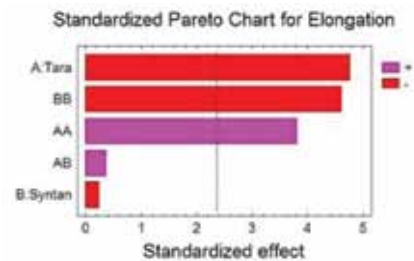


Figure 9. Pareto chart for tensile elongation.

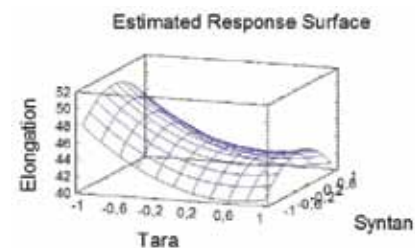


Figure 10. Estimated Response Surface for tensile elongation.

TABLE IX
Optimize Response for tensile elongation.

Goal	maximize tensile elongation (%)		
Optimum value	55.1497		
Factor	Low	High	Optimum
Tara	-1.414	1.414	-1.414
Syntan	-1.414	1.414	-0.095

Tear Load (N/mm)

TABLE X
Estimated effects for tear load (N/mm).

Average	82.30	+/- 2.03
A:Tara	-5.68	+/- 3.21
B:Syntan	1.18	+/- 3.21

Analysis for Variance for tear load (N/mm)

Source	Sum of Squares	Mean Square	F-Ratio	P-Value
A:Tara	64.57	64.57	3.14	0.1197
B:Syntan	2.81	2.81	0.14	0.7227

For tear load, the interaction of syntan has P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

To optimize variable response, no significant effects have been removed.

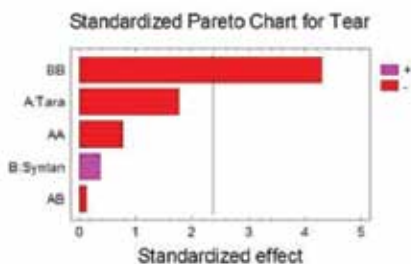


Figure 11. Pareto Chart for tear load.

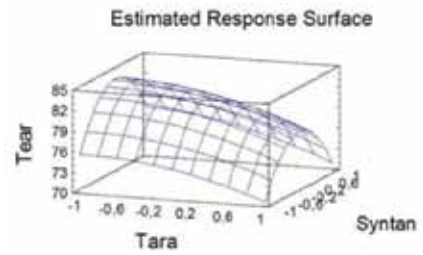


Figure 12. Estimated Response Surface for tear load.

Lightfastness

TABLE XI
Optimize Response for tear load.

Goal	maximize tear load (N/mm)		
Optimum value	85.40		
Factor	Low	High	Optimum
Tara	-1.414	1.414	-1.414
Syntan	-1.414	1.414	0.0

For lightfastness, % Tara have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

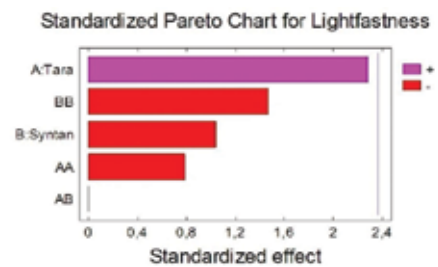


Figure 13. Pareto chart for lightfastness.

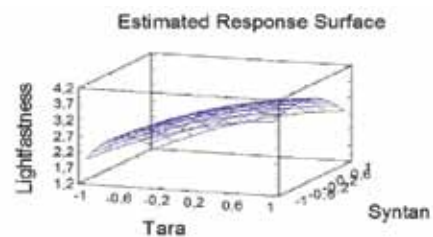


Figure 14. Estimated Response Surface for lightfastness.

TABLE XII
Estimated effects for lightfastness.

Average	3.00	+/- 0.32
A:Tara	1.56	+/- 0.63
B:Syntan	-0.71	+/- 0.63

Analysis for Variance for lightfastness

Source	Sum of Squares	Mean Square	F-Ratio	P-Value
A:Tara	4.87	4.87	6.15	0.0350
B:Syntan	1.00	1.00	1.26	0.2903

TABLE XIII
Optimize Response for lightfastness.

Goal	maximize lightfastness		
Optimum value	4.2		
Factor	Low	High	Optimum
Tara	-1.414	1.414	-1.41
Syntan	-1.414	1.414	-0.35

Excluding the % syntan and the interactions as they do not have statistical significant differ, we can calculate a lineal equation for tara:

$$\text{Lightfastness} = 2.69 + 0.78 * \text{Tara}$$

CONCLUSIONS

The values of the statistical results indicate the influence of the naphthalene sulphonic syntan with tara powder in the response variables of shrinkage temperature, tensile strength, tensile elongation, tear load and lightfastness;

- The amount of tara in the recipe has very little influence on the shrinkage temperature.
- Optimization for tensile strength cannot be proposed as the tests do not prove a significance correlation between this response variable and the effects of the factors % of tara and % of syntan. By observing the estimated response

surface the naphthalene sulphonic has an insignificant negative effect on this variable.

- With regard to the tensile elongation, the % of tara has a negative effect which is a general characteristic of vegetable tannins when compare with chrome tanning. Improvement with naphthalene sulphonic syntan has not been significantly proven. Percent of tara and % of syntan is optimized when concentrations are similar.
- Similar results are obtained for variable response tear load. Percent of tara has a negative effect and the naphthalene sulphonic syntan optimal responses are observed along the coordinate axis.
- Tests on lightfastness also confirm that tara tannins are valued because this property. Naphthalene sulphonic syntan may have a negative effect but results do not demonstrate a statistical significant effect.
- Synergy is obtained by increasing the values of naphthalene sulphonic when tara has limits: shrinkage temperature due to the improvement of the tara tannin penetration, tensile elongation an tear load. Again, syntan has a negative influence on light fastness.

TABLE XIV
Conclusions effects of tara and syntan on wet-white properties.

Variable responses	Effect of the factor		Influence of the syntan to the effect of the tara powder
	% Tara powder	% Naphthalene sulphonic syntan	
Shrinkage temperature	+	++	++
Tensile strength	+	()	()
Tensile elongation	--	()	+
Tear load	-	+	+
Lightfastness	++	-	-

Legend: ++ Very positive
+ Positive
() No influence
-- Very negative
- Negative

TABLE XV
Optimal values syntan and tara.

Optimal values for	Syntan	Tara
Shrinkage temperature	1.41	1.41
Tensile strength	-0.09	0.72
Tensile elongation	-0.09	-1.41
Tear loan	0.06	- 1.08
Light fastness	-0.32	1.36
Mean	-0.09	0.72
Average	0.19	0.20

Considering the means of the optimize response of table 15, the summary in table 14 and proposing to maximize the use of tara tannins as a main component in sustainable pre-tanning agent, we obtain the optimal value for the ingredients of a mixture of tara powder and a naphthalene sulphonic syntan as:

-0.09 Naphthalene sulphonic syntan + 0.72 tara powder

That, according to the codified table 3, corresponds to the following combination:

9% Tara powder

7% Naphthalene sulphonic syntan

Considering the optimal combinations for each variable, it is proposed a formulation of wet white as seen in the table below.

Converting the % values in the recipe into proportional components and taking into consideration the concentration of the tannin contained in the products used for the research, the relation between the tara tannin and the tannin of naphthalene sulphonic is:

62 parts tara tannin

38 parts Naphthalene sulphonic syntan

Tara tannins comply with the European Regulation REACH's definition of "substances which occur in nature" if they are not chemically processed and is a great argument to promote tara tannins in the European tanneries because they therefore, are exempt of such regulation.

The use of t produces leather that is ecological and safe for the consumers and, at the time, provides social benefits by bringing to rural populations in remote Andean Regions a source of employment in which they can supply a sustainable source of tannins for the leather industry.

ACKNOWLEDGEMENTS

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Operation	°C	%	Product	Time	Comments
Pre-tanning	20	50	Water	15 min	°Bè: 7 pH 3.5
		4	Sodium chloride		
		4,5 3,5 2	Tara powder Naphthalene sulphonic Sulphitated fatliquor	120 min	pH 3.2
		4.5 3.5 0.5	Tara powder Naphthalene sulphonic Formic acid	Overnight 90 min	
					Drain

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