Paper B7

Tara *(Caesalpinia spinosa)*:
The sustainable source of tannins for innovative tanning processes

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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. Although tara tannins have been used in the leather industry and its properties are well known, the 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 considering shrinking temperature, tensile strength, tensile elongation, tear load and lightfastness properties 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. Aunque los taninos de la tara ya se utilizan en la industria del cuero y sus propiedades son conocidas, el 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.

1. 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 claim 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.

Cæsalpinia spinosa (Molina) Kuntze, commonly known as tara[1], 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.

2. Materials and method

A preliminary work has been carried out to demonstrate the blend of tara powder and a naphthalene sulphonic syntan as the most appropriate compared with the mixture of tara powder and phenol condensation syntan. Photos 1 (tara), 2 (tara + naphthalene sulphonic syntan), 3 (tara + phenol condensation syntan) and 4 (tara + naphthalene sulphonic syntan and phenol condensation syntan).

Photo 1

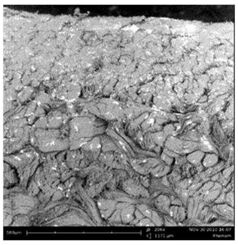


Photo 2

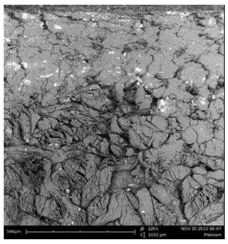
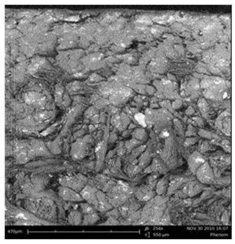


Photo 3



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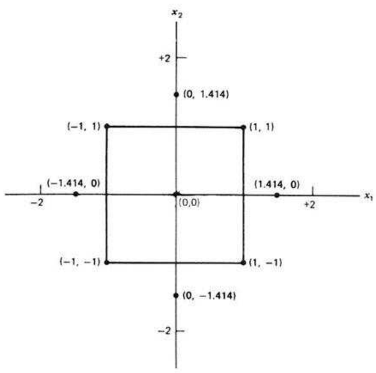

Figure 1: Quadratic, centralized, orthogonal and rotatable design

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… Tara is, up to now, used for retanning mainly wet-white using glutaraldehyde as a major tanning agent.

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. (Figure 1)

[1] Known names (Jones, 1987 and De la Cruz (2004): "Tara", "Taya" (Peru), "Guarango" (Ecuador), "Cuica", "Serrano", "Vinillo", "Acacia Amarilla" (Yellow acacia), "Andean Dividivi"

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

Tara Powder	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
Synthetic tanning of naphthalene sulphonic	Yellowish liquid. Miscible in water. 35 % of tannin content. pH 3.3 – 3.7 (solution 1:10)			

Table 1

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

Operation	ºC	%	Product	Time	Comments
Pre-tanning	20	50	Water		
		4	Sodium chloride	15 min	ºBè: 7
					pH 3.5
		1/2	Tanning blend		
		2	Sulphitated fatliquor	120 min	*Note 1*
		1/2	Tanning blend	Overnight	*Note 2*
		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 30ºC. Conditioning and stake.

Experimental factors: Tanning blend: % of tara powder and % Naphthalene sulphonic syntan

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
10	0	0	6	7
11	0	0	6	7
12	0	0	6	7
13	0	0	6	7

Table 2: Quadratic, centralized, rotatable and orthogonal design for tara and naphthalene sulphonic syntan. Codification table

3. Results and discussion:

Photo 5 shows the leather pieces test results in the coordinates according the described experimental design:

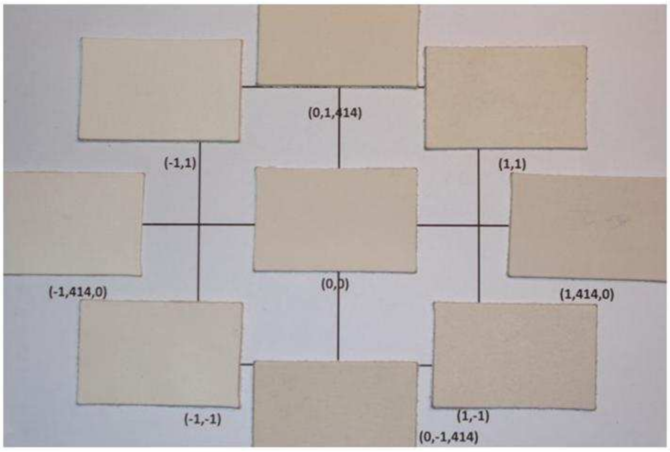

Photo 1: Optimization for a pretanning process with tara

Table 3: includes the physical test results to be statistically analyzed:

Test	**Coordinates**	**TCºC**	**Tensile Strength (N)** *EN ISO 3376-IUP6*	**% Elongation** *EN ISO 3376-IUP6*	**Tear load (N/mm)** *EN ISO 3377-2 IUP8*	**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
10	(0, 0)	65	903,0	44,7	82,3	2
11	(0, 0)	65	903,0	44,7	82,3	2
12	(0, 0)	65	903,0	44,7	82,3	2
13	(0, 0)	65	903,0	44,7	82,3	2

Table 3: Test results from experimental design

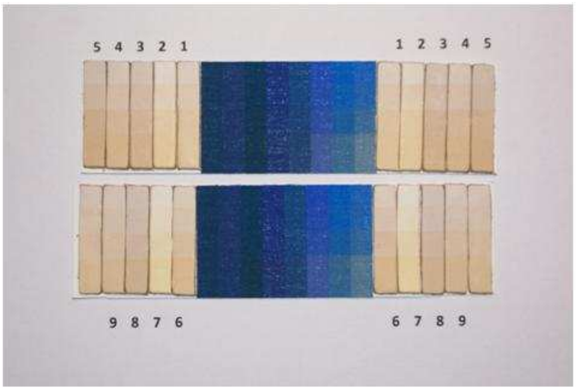

Photo 2: Light fastness test. Part 4

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

Shrinking temperature (ST°C):

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.

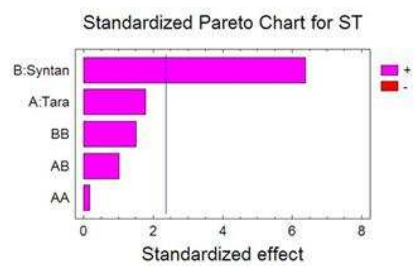

Figure 2: Pareto chart for shrinking temperature

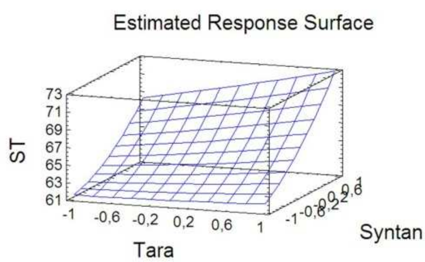

Figure 3: Estimated Response Surface for shrinking temperature

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

$$ST = 65,77 + 4,44*Syntan$$

Optimum value for syntan in shrinking temperature = 1,414 (14% Naphthalene sulphonic syntan).

Tensile strength (N)

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.

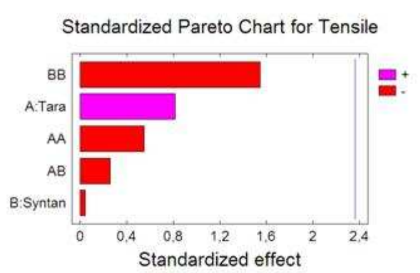

Figure 4: Pareto chart for tensile strength

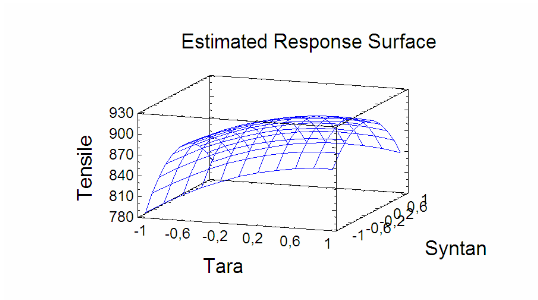

Figure 5: Estimated Response surface for tensile strength

Optimize Response			
Goal	maximize tensile strength (N)		
Optimum value	913,272		
Factor	Low	High	Optimum
Tara	-1,414	1,414	0,722
Syntan	-1,414	1,414	-0,091

Tensile elongation (%)

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

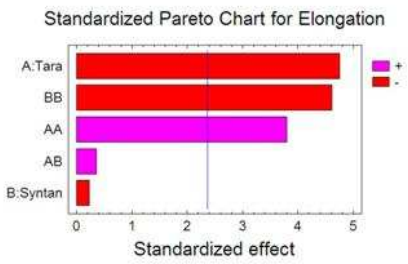

Figure 6: Pareto chart for tensile elongation

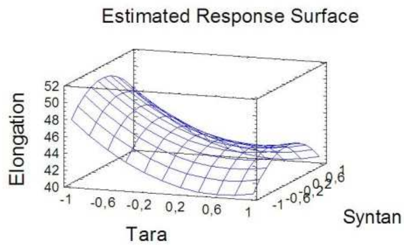

Figure 7: Estimated Response Surface for tensile elongation

Optimize Response			
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

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:

$$Elongation = 44,32 - 3,33*Tara$$

Tear load (N/mm)

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.

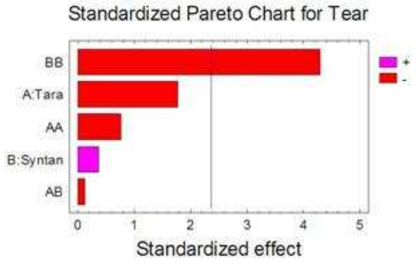

Figure 8: Pareto Chart for tear load Figure

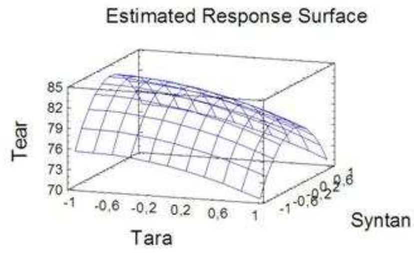

Figure 9: Estimated Response Surface for tear load

Optimize Response			
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

Lightfastness

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

For lightfastness, % Tara have P-values less than 0,05, indicating that they are significantly different from zero at the 95,0% confidence level.

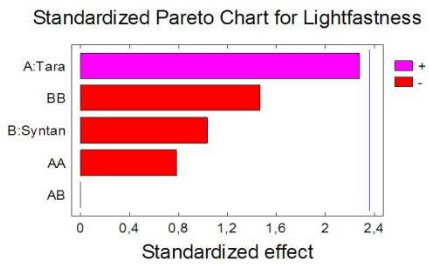

Figure 10: Pareto chart for lightfastness

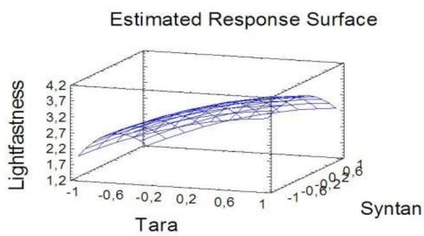

Figure 11: Estimated Response Surface for lightfastness

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

$$Lightfastness = 2{,}69 + 0{,}78*Tara$$

4. Conclusions

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

Optimize Response			
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

- The amount of tara in the recipe has very little influence on the shrinking 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 what is a general characteristic of vegetable tannins when compare with chrome tanning. Improvement with naphthalene sulphonic syntan has not been significantly proved. % of tara and % of syntan is optimized when concentrations are similar.

- Similar results are obtained for variable response tear load. % 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 appreciated because this property. Naphthalene sulphonic syntan may have a negative effect but results do not demonstrate a statistical significance effect.

- Synergy is obtained by increasing the values of naphthalene sulphonic when tara has limits: shrinking temperature due the improvement of the tara tannin penetration, tensile elongation an tear load. Again, syntan has a negative influence on light fastness.

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

Table 4: Conclusions effects of tara and syntan on wet-white properties

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

Optimal values for	Syntan	Tara
Shrinking 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

Table 5: Optimal values syntan and tara

Considering the means of the optimize response of table 7, the summary in table 6 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 32, 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 follow:

Operation	ºC	%	Product	Time	Comments
Pre-tanning	20	50 4	Water Sodium chloride	15 min	ºBè: 7 pH 3.5
		4,5 **3,5** 2	**Tara powder** **Naphthalene sulphonic** Sulphitated fatliquor	120 min	
		4,5 **3,5** 0,5	**Tara powder** **Naphthalene sulphonic** Formic acid	Overnight 90 min	pH 3,2
					Drain

Converting the % values in the recipe into proportional components and considering 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

The European Regulation REACH is a great argument to promote tara tannins in the European tanneries as they comply the definition of "substances which occur in nature" if they are not chemically processed. Therefore, they are exempt of such Regulation.

Tara is able to offer genuine leather being ecological and safe for the consumers at the time that social benefits by bringing to rural populations in remote Andean Regions an opportunity to deal with tara as a sustainable source of tannins for the leather industry.

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