

LOW CARBON PRODUCTS TO DESIGN INNOVATIVE LEATHER PROCESSES. PART III: OPTIMIZATION OF AN ECO-FRIENDLY FORMULATION USING TARA

by

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ABSTRACT

The aim of this work was to design a new pretanning formulation by using the fruit of the Tara tree (*Cæsalpinia Spinosa*) as the sole source of vegetable tannin. The innovative aspect of this work embodies a new-tailored tara product which gave its tannin the enhanced ability to readily penetrate the leather cross section, and thus made it unnecessary for the tanner to add aldehydes, syntans, other common vegetable tannins and mineral salts.

Specifically, physical modifications had been developed in part II of this broad study to obtain a modified tara with a higher percentage of tannins and with a better ability to penetrate/fix in leather by sieving and milling (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara¹ and Low carbon products to design innovative leather processes. Part II: determination of the optimal physical modification of tara).² We developed in this work an innovative, eco-friendly and optimal wet white formulation which has a maximum offer to leather of 9% modified tara and a maximum 2% naphthalene sulphonic syntan dispersing agent.

INTRODUCTION

The tara tannin powder comes from the fruit of the tara tree, which can be obtained without the need to deforest entire areas, unlike vegetable extracts that come from cutting down trees. *Cæsalpinia spinosa* (Molina) Kuntze, commonly known as tara, is a small leguminous tree or thorny shrub. Tara pods and seeds are a source of high value products that contain tannins of a galloylated quinic acid structure, used in the leather industry and gum for food industry.³

Tara powder is a hydrolysable tannin formed by a core of sugar molecules such as glucose, coupled with phenol carboxylic acids, like gallic acid and its derivatives. The ester linkages are formed between the alcohol groups (-OH) of the

sugar molecule and the carboxylic groups (-COOH) of the molecules of phenol-carboxylic acids. The number of ester linkages in a molecule of tannin depends on the sugar molecules present at the core of the tannin molecule.⁴

Tara tannins are very astringent and react strongly with the skin, leaving this material on the surface, and preventing its penetration through the entire skin. As a result of these undesirable properties, this work was focused on obtaining an eco-friendly formulation using physical-modified tara in order to increase its tanning power, decrease its astringency, and to reduce the offer to leather of syntans and other kinds of auxiliaries, meaning to increase the use of natural products.

Bibliography from studies examining the use of tara combined with other inorganic salts (aluminum, chromium) or with organic products (gluteraldehyde, syntans, quaternary phosphonium salts) show the improvement of its tanning power by means of penetration, and the blocking of collagen reactive groups so as to avoid an excess of tanning on the leather surface. However, an industrial application has not been generated.⁵⁻⁸

Ultrasound application in vegetable tanning processes could improve the diffusion rate and generate an appreciable reduction in the particle size,⁹ but the overall results were impractical. As to the application of bacterial enzymes, which was also studied, the use of bacterial collagenase as an auxiliary agent in tanning bath has increased tanning absorption and better diffusion into leather.¹⁰

The objective of this work is to obtain an optimized innovative formulation based on tara for wet-white or metal free leather article, and to produce all kinds of final leather goods like shoe, apparel, upholstery, etc.

There is an opportunity for the leather industry to replace synthetic chemicals and to obtain sustainable processes and articles. Tara tannins offer a wide range of advantages if quality and prices fulfill the expectations of the market. Due to this fact, we used a modified tara with a higher percentage

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of tannins and with a better level of penetration by sieving and milling.^{1,2} The use of tara, tannins avoids cutting down other trees; for example the quebracho tree which requires 100 years to grow to maturity; the chestnut tree which takes 40 years to mature, and the mimosa tree which takes approximately 10 years by comparison.

In addition, it is important to notice that the Tara products are not subject to review by REACH. REACH was created to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances. At the same time, REACH aims to enhance the innovation and competitiveness of the EU chemicals industry. The benefits of the REACH system will come gradually, as more and more substances are phased into REACH.¹¹

MATERIALS AND METHODOLOGY

An experimental design was developed in order to obtain an optimized innovative formulation based on tara for wet-white or metal free leather article, and to produce all kinds of final goods like shoe, apparel, upholstery, etc. By using this new modified product (milled and sieved tara) and a naphthalene sulphonic syntan dispersing agent we improved the penetration and distribution of the tara in the leather cross-section section. Another product we used in this innovative formulation is sodium acid pyrophosphate. It a sequestering agent of iron, and further helped distribute the products in the leather cross section.

The variables of the experimental design were the different percentage offer to leather of the two products (Modified Tara

TABLE I
Pre-tanning formulation.

%	PRODUCT	TIME	OBSERVATIONS
50	WATER + SALT 20°C	15'	6 °Bé
X	X ₁ % Milled and sieved Tara (50 – 40 µm) X ₂ % Naphthalene Sulphonic syntan 4% Pyrophosphate		
2	Sulphited oil	Over night	Cut
0.8	Formic acid	2h	pH=3.75
			Drain

TABLE II
Factors and levels studied.

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

TABLE III
Experimental design.

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 IV
Gluteraldehyde pre-tanning formulation.

%	PRODUCT	TIME	OBSERVATIONS
50	WATER + SALT 20°C	15'	6 °Bé
2.5	Gluteraldehyde 50%	3.5 h	pH = 4.2 – 4.4
5	Sulphonic synthetic	5 h	pH = 4.0 – 4.2
200	Water	20'	Drain. Horse up.
			Sammy

+ naphthalene sulphonic syntan), which are needed to define the most appropriate recipe for a sustainable wet white formulation. A 4% offer of Pyrophosphate was constant in all the tests. Table I shows the formulation.

The aim of the experimental design was to optimize the formulation of Table 1 by maximizing the offer of natural products (tara), and by simultaneously minimizing the use of synthetic tanning auxiliaries. The design consists of a centralized, rotatable and factorial design with two levels defined for each factor. Two factors were studied which are the concentration of Tara and the concentration of naphthalene sulphonic syntan. This design has 12 different wet end trials. Table II shows the levels or concentrations [offers to leather] of the products that were studied. Table III shows the twelve experiments, which enabled the execution of this experimental design.

A comparison trial of an established wet-white formulation using gluteraldehyde was done in order to study, and confirm the feasibility of the new formulation. This control or reference formulation is shown in Table IV.

RESULTS AND DISCUSSION

The results from this experimental design are summarized in Table V.

The results were analyzed for each variable in order to obtain the optimal response by means of the software named Statgraphics Plus version 5.1.

Figure 1. represents the Pareto chart that shows each of the estimated effects and interactions for the leather property of Shrinkage temperature [Ts].

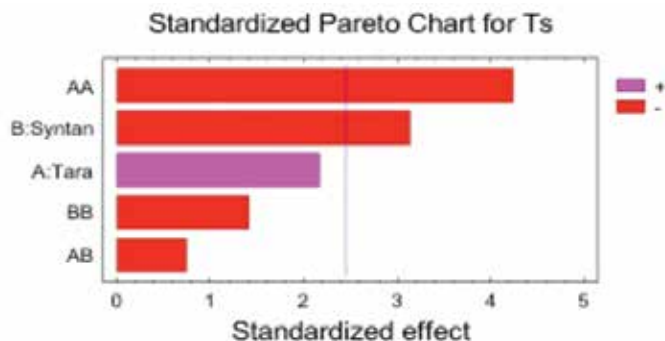


Figure 1. Pareto chart for Shrinkage temperature.

The amount of tara in the quadratic response (AA in the vertical axis of the Pareto chart) and the amount of syntan (B in the vertical axis of the Pareto chart) are statistically significant. As the tara presents a quadratic response, there is a maximum value of its concentration which increases

shrinkage temperature, but above this value, the shrinkage temperature decreases. In addition, the higher the amount of synthetic and tara lower Ts.

By excluding the values that are not statistically significant (P-value >0.05), the resultant regression equation, the optimization table, and the response surface plot are shown below, in Table VI and Figure 2.

The regression equation of the fitted model is:
 $T_s = 69.45 - 0.74 \cdot \text{Syntan} - 1.05 \cdot \text{Tara}^2$

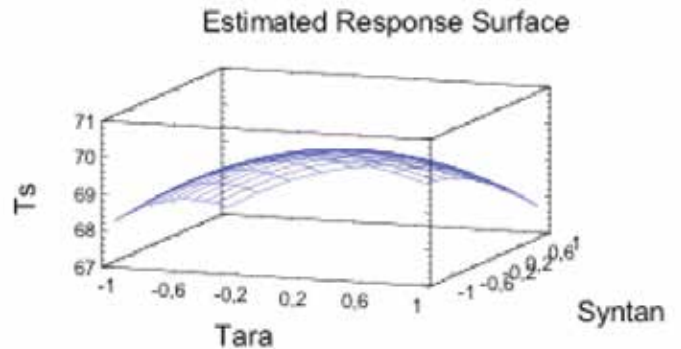


Figure 2. Response surface for Ts.

Table VI shows the combination of factor levels, which maximizes Ts over the indicated region. For a better understanding of the table, it is important to remember that the value 0.0 for Tara factor is the central point, representing 9%; and that the value -1.41421 represents the minor value for Syntan, which is 2%.

Figure 3. represents the Pareto chart, which shows each of the estimated effects and interactions for the Tensile strength of the resultant leather.

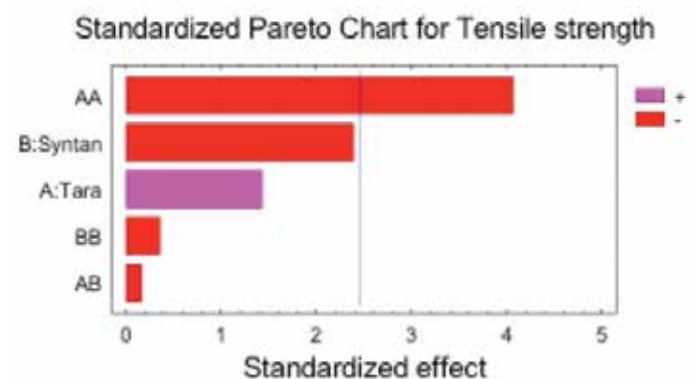


Figure 3. Pareto chart for Tensile strength.

As can be seen in the Pareto chart, the effect has P-value less than 0.05, indicating that it is significantly different from zero at the 95.0% confidence level. That effect is the amount of tara

TABLE V
Results of the experimental design.

Test	% Tara	% Syntan	Ts (°C)	Thickness (mm)	Tear Load (N/mm)	Tensile Strength (N/mm ²)	Softness Test (mm)
1	7.6	2.9	67.5	2.33	85.2	28.5	1.5
2	7.6	7.2	67.5	2.32	84.6	28.2	1.5
3	10.4	2.9	69.0	2.59	102.6	30.4	1.7
4	10.4	7.2	68.0	2.50	90.9	29.1	1.6
5	9	2	71.0	2.35	111.8	37.6	1.9
6	9	8	67.5	2.60	80.0	24.4	1.4
7	7	5	67.0	2.72	77.5	18.9	1.2
8	11	5	68.5	2.73	80.5	25.5	1.4
9	9	5	70.0	2.24	108.1	33.2	1.8
10	9	5	69.5	2.13	108.4	33.5	1.8
11	9	5	69.5	2.08	108.7	32.7	1.8
12	9	5	70.0	2.26	108.3	32.9	1.8

in its quadratic response (AA in the vertical axis of the Pareto chart) as shown below in its regression equation.

Excluding the values that are not statistically significant (P-value >0.05), the regression equation, the optimization table, and the response surface plot are obtained below, in Table VII and Figure 4.

The equation of the fitted model is:

$$\text{Tensile strength} = 32.73 - 2.53 * \text{Syntan} - 4.74 * \text{Tara}^2$$

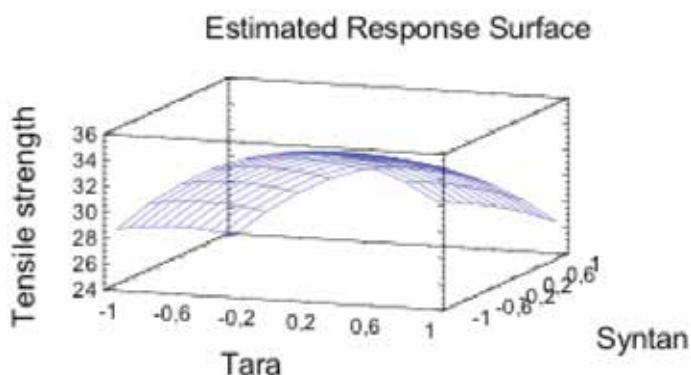


Figure 4. Response Surface for Tensile strength.

TABLE VI
Optimize response for Ts.

Factor	Low	High	Optimum
Tara	-1.41421	1.41421	0.0
Syntan	-1.41421	1.41421	-1.41421

TABLE VII
Optimize response for Tensile Strength.

Factor	Low	High	Optimum
Tara	-1.41421	1.41421	0.0
Syntan	-1.41421	1.41421	-1.41421

This table shows the combination of factor levels, which maximizes Tensile strength over the indicated region. **Again, the optimal formulation used 9% of tara and 2% of dispersing syntan.**

Figure 5. represents the Pareto chart, which shows each of the estimated effects and interactions for Tear Load

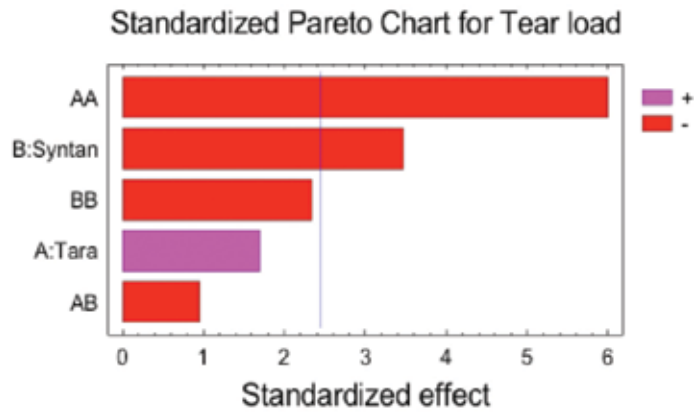


Figure 5. Pareto chart for Tear load.

As can be seen in the Pareto chart, the amount of tara has a quadratic response and the amount of syntan are statistically significant. The statistical analysis follows the same pattern of the previous properties studied.

Excluding the values that are not statistically significant (P-value >0.05), the regression equation, the optimization table, and the response surface plot are shown below, in Table VIII and Figure 6.

The equation of the fitted model is:
 Tear load = 104.07 – 7.16*Syntan – 12.77*Tara²

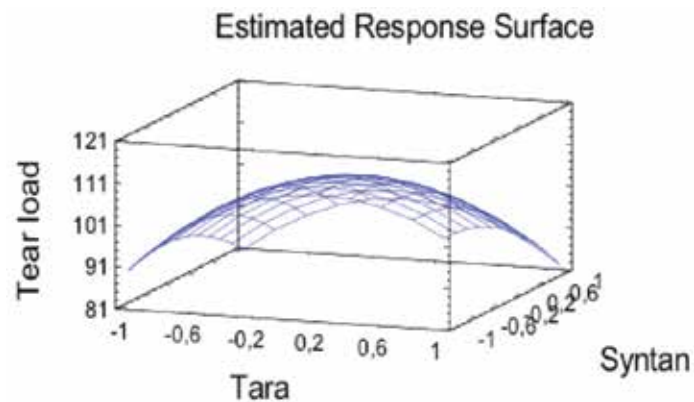


Figure 6. Response Surface for Tear load.

Table 8 shows the combination of factor levels, which maximizes Tear load over the indicated region. **Again, the maximum value for tear load was observed with offers to leather of 9% tara and 2% syntan.**

TABLE VIII
Optimize response for Tear load.

Factor	Low	High	Optimum
Tara	-1.41421	1.41421	0.0
Syntan	-1.41421	1.41421	-1.41421

Figure 7. represents the Pareto chart, which shows each of the estimated effects and interactions for Softness.

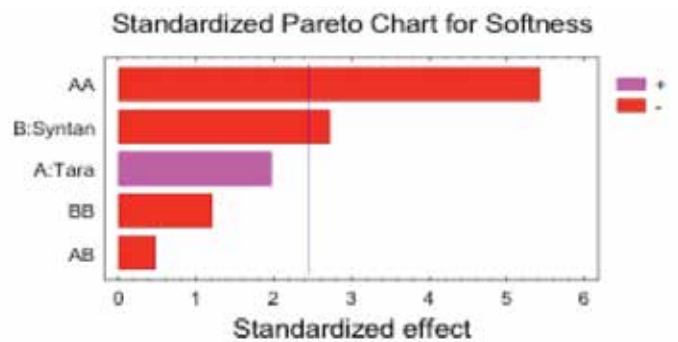


Figure 7. Pareto chart for Softness test.

As can be seen in the Pareto chart, the amount of tara has a quadratic response and the amount of syntan are statistically significant. That is, the higher the amount of synthetic and higher the amount of tara, the lower the Softness is.

Excluding the values that are not statistically significant (P-value >0.05), the regression equation, the optimization table, and the response surface plot are obtained below, in Table IX and Figure 8. respectively.

The equation of the fitted model is:
 Softness = 1.76 – 0.10*Syntan – 0.21*Tara²

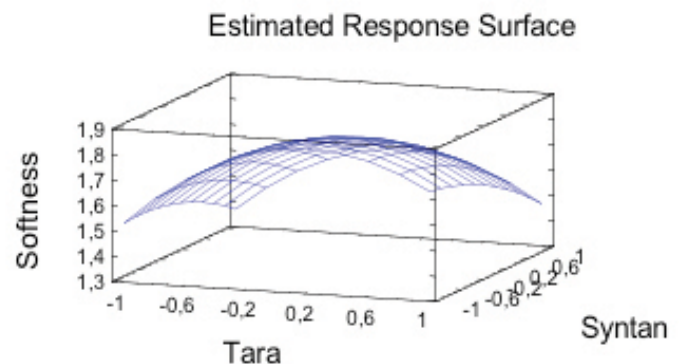


Figure 8. Response surface for Softness test.

TABLE IX
Optimize response for Softness test.

Factor	Low	High	Optimum
Tara	-1.41421	1.41421	0.0
Syantn	-1.41421	1.41421	-1.41421

Table IX shows the combination of factor levels, which maximizes Softness over the indicated region. **Again, the optimal formulation used 9% tara and 2% syntan.**

Light fastness was another property studied in this experimental design. Figure 9. shows the results obtained.

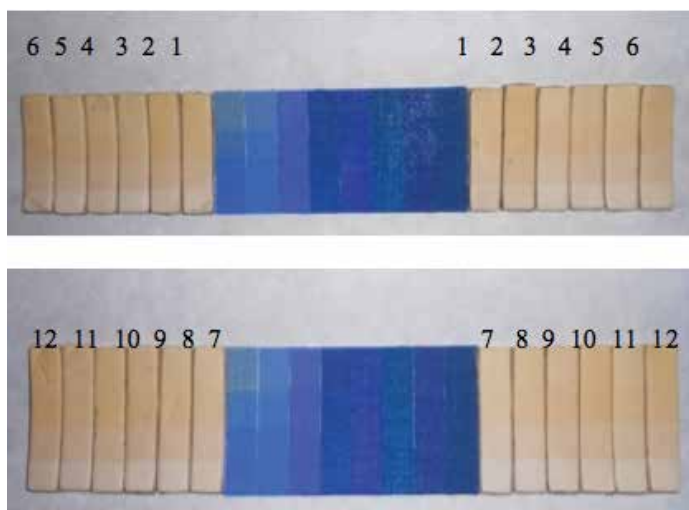


Figure 9. Light fastness test.

As can be seen, there is a color change in all of the samples; nevertheless, the differences between them are not significant.

The key result of the statistical program pointed to trial number 5 as the one that gave optimal performance for each of the tested leather properties. This resultant optimized formulation is shown in Table IX. It is an innovative recipe, which is based on tara to produce wet-white, and metal free leather articles.

The fibrous structure of a leather sample resulting from the optimized formulation is shown in Figure 9. It was obtained by using the scanning electron microscope Jeol JSM 6400.

Figure 9. shows a compact fibrous structure, and the uniform penetration/fixation of the products, which were used in this pre-tanning process. In contrast, Figure 10. that corresponds to a SEM image of a conventional vegetable leather, shows a more open and spongy fibers

TABLE X
Optimized pre-tanning formulation.

%	PRODUCT	TIME	OBSERVATIONS
50	WATER + SALT 20°C	15'	6 °Be
X	9% Milled and sieved Tara (50 – 40 µm) 2% Naphthalene Sulphonic syntan 4% Pyrophosphate		
2	Sulphited oil	Over night	Cut
0.8	Formic acid	2h	pH=3.75
			Drain

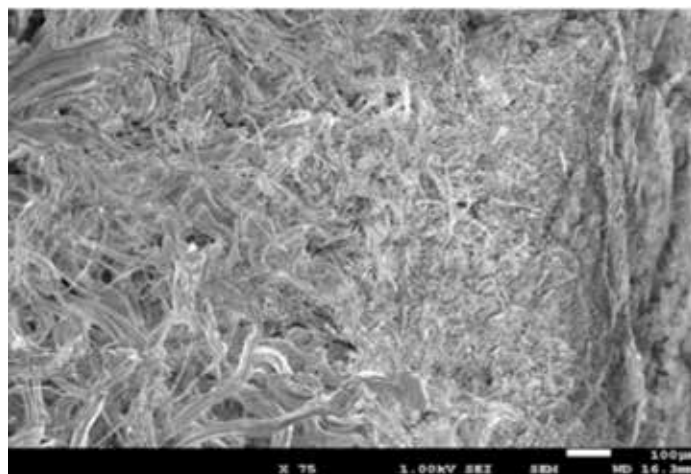


Figure 10. Scanning electron microscopy.

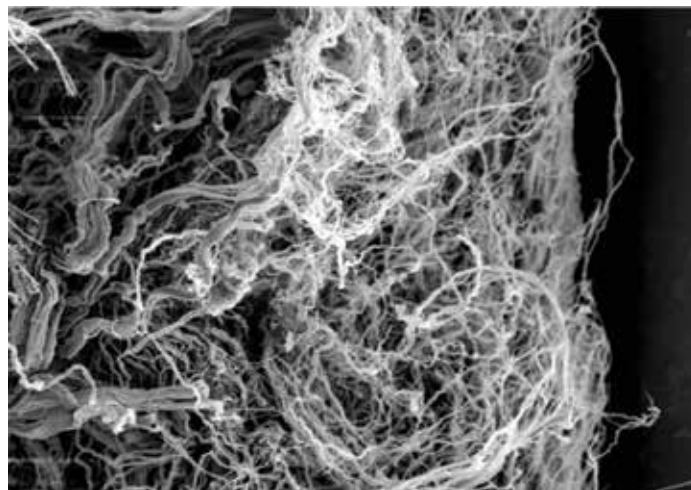


Figure 11. Scanning electron microscopy of conventional vegetable leather.

Table XI shows the results of chemical analyses, which were done on float samples of the final bath for the innovative modified tara, and the reference gluteraldehyde pre-tanning processes.

The analytical results from the new pre-tanning recipe using modified Tara show a clear reduction in values as compared with those derived from the control or reference wet-white leathers using gluteraldehyde. Specifically, there is a 21% reduction in COD, which highlights the improvement using a natural product versus a chemically synthesized product. The analytical result also show a decrease in the level of suspended matter and in the electrical conductivity [soluble salts] of the spent float in favor of the new process.

Finally, the amount of remaining tannins in the spent float of the final bath for the innovative modified tara process was determined as shown in Table XII.

The data show that a trivial amount of 0.8% tannin was detected in the final bath. This result meant that the modified tara tannins penetrated thoroughly in the leather cross section, and exhausted fully therein.

CONCLUSIONS

In our previous publication [Part I], the physical modification process of tara did not give an extract with high tannin content like obtained with the alternate aqueous extraction method. (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara),¹ But, as this current study showed, the physical modification of tara improved the penetration/

fixation of its tannins into the leather, reduced the suspended matter and chemical oxygen demand in the spent floats.

The best physical modification of tara was obtained by milling, sieving and using the particle size fraction of 50-40 microns (see Low carbon products to design innovative leather processes. Part II: determination of the optimal physical modification of tara).²

The statistical analyses from Statgraphics have included by design our intentional goal to maximize the offer to leather of modified tara, and to simultaneously minimize that of synthetic chemicals. The results of this experimental study defined the following optimal offers to leather in/for our innovative and eco-friendly recipe:

- A maximum 9% of milled and sieved Tara (50 – 40 µm).
- A maximum 2% of naphthalene sulphonic synthetic dispersing agent.

This new pre-tanning formulation using a 9% offer of tara is expected to give tanners a sustainable product, and further lower the offer of synthetic auxiliary products to a maximum of 2%. Additionally, a clear improvement in environmental safeguards was obtained by decreasing COD, suspended matter and the electrical conductivity (soluble salts) in the final spent floats of this innovative recipe.

TABLE XII
Results of tannin determination
of final floats.

Determination	Tara WW	Units
Solids	16.6	%
Ashes at 500°	7.5	
Soluble solids	9.1	%
Total solids	9.3	%
No tannins	8.3	%
Tannins	0.8	%
Insoluble	0.7	%
Water	90.2	%
pH	3.8	
Density	9.7	°Bé

TABLE XI
Chemical determination of final floats.

Determination	Tara WW	Conventional WW	Units
pH	3.8	4.3	
Suspended matter (M.E.S.)	7976	9097	mg/L
Chemical Oxygen Demands	25560	32550	mgO ₂ /L
Organic Nitrogen Ammonia	390	362	mgN/L
Conductivity	69855	78315	µS/cm

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