Low Carbon Products to Design Innovative Leather Processes. Part IV: Manufacture of Automotive Leather Using Tara

by

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Abstract

In three previous studies, it has been used the fruit of the tara tree (Cæsalpinia Spinosa) as a pre-tanning agent[1]. This new tailored tara product will be able to facilitate the penetration of the tannin molecules through the leather section, avoiding or reducing the use of aldehydes, syntans, common vegetable tannins and other mineral salts.

The aim of this part of the study is to manufacture final articles meeting the parameters set by different regulations, and assess if this modified tara can be marketed and used in the industry to replace some less sustainable products.

Introduction

The fruit of tara tree and its derivatives have high interest in a number of industries and, thus, a great worldwide economical potential for commerce. The properties of pods and seeds result in a sustainable and quality raw material for several applications.

The weight of the fruit of tara is composed by: 60-64% of pods, 34-38% of seeds and 2% of non-valuable residues. It is important to point out that tara powder is composed of 45- 50% tannins; tara gum can be obtained from 24% of the weight of the seeds.

Tara powder is obtained by simply mechanically milling and sifting the gross powder after threshing the pods and separate the seeds. The tara powder is a fine (100 to 200 mesh) yellowish "sawdust." Further than the leather industry, it is used, as well, in the chemical industry to obtain tara extract, also used in the leather industry and to other applications. The leather industry appreciates the tara powder as a source of vegetable tannins to obtain light colors, with good light fastness, and full and soft leather articles, with a firm and smooth grain. Tara is easily soluble in water and do not contain color substances like other vegetable tannins.

Tara powder can be used to tan all kind of hides and skins and to re-tan chrome tanned leathers to improve the grain tightening. The main application is in the manufacture of leather for car seats. The general specifications for commercial tara powder for tanning application are:

Tannin content	min. 48%
Water content	max. 13%
pH (at 6,9ºBè)	3 – 4.

In our previous publication, the physical modification process of tara not gave 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]

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. (see Low carbon products to design innovative leather processes. Part III: optimization of an eco-friendly formulation using tara).[3] 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. Another product we used in this innovative formulation is sodium acid pyrophosphate. It is a sequestering agent of iron, and further helped distribute the products in the leather cross section.

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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 safeguards the environment was obtained by decreasing COD, suspended matter and the electrical conductivity (soluble salts) in the final spent floats of this innovative recipe.

Materials and Methodolgy

The aim of this part of the work is to obtain an optimized innovative formulation based on tara for wet-white or metal free article and able to produce automotive leather. By using the new modified product (milled and sieved tara) and a synthetic based on naphthalene sulphonic syntan we will obtain a better penetration and distribution of the tara in leather section. Another product to consider is the sodium acid pyrophosphate that, besides of being a good sequestering of iron, it helps in the distribution of chemicals. This mix is called compact product.

In order to carry out a study of the feasibility of the new formulation, a comparison with a conventional formulation using glutaraldehyde was performed. The formulations of pre-tannage for each process, the new and the conventional, can be seen in Table I and II.a

After pretannage, leathers were re-tanned, dyed and fatliquored, following the formulations shown in Table III and IV. The leathers pre-tanned with modified tara were re-tanned using the formulation of Table III. The leathers pre-tanned with glutaraldehyde were re-tanned using the formulation of Table IV.

Table I
Pre-tanning formulation using tara.

%	PRODUCT	TIME	OBSERVATIONS
50	Water + Salt 20ºC	15'	6 ºBé
X	**Compact product***		
2	Sulphited oil	Over night	Cut
0.8	Formic acid	2h	pH=3.75
			Drain

*The compact product corresponds to the mix of milled and sieved tara (modified tara), naphthalene sulphonic syntan and sodium acid pyrophosphate.

A final bath after pre-tanning and after re-tanning was taken and assessed to compare both processes. For the purpose of assessing the pollution in wastewaters, the following parameters were analyzed: Conductivity (μ/cm), Suspended solids (mg/L), COD (mg/L), N Kjeldahl (mg/L).

In order to determine the quality of the leathers and compare both systems, we carried out the physical tests set up by the IULTCS, which allowed us to assess the capacity of the leathers to withhold the wear and tear of automotive upholstery. The following official methods were used to this end:

IUP 6 Measurement of tensile strength and percentage elongation (in accordance with EN ISO 3376).

IUP 8 Measurement of tear load (in accordance with EN ISO 3377-2).

IUP 36 Measurement of leather softness (in accordance with EN ISO 17235:2002).

Results and Discussion

The aim of this part of the study is to assess whether the leathers processed with this new system present advantages over the conventional one. In addition, we will check that the leathers meet the demands required for automotive upholstery.

Table V shows the comparison of pollution in wastewaters between the pre-tannage using modified tara and the pre-tannage using glutaraldehyde.

The values show a clear decrease in almost every determination for the new pre-tanning process with modified Tara. In the case of COD there is a reduction of about 21%, which highlights the improvement using a natural product against the use of a

Table II
Pre-tanning formulation using glutaraldehyde.

%	PRODUCT	TIME	OBSERVATIONS
50	Water + Salt 20ºC	15'	6 ºBé
2.5	**Glutaraldehyde 50%, exempt from free formaldehyde**	3h30'	pH=4.2-4.4
5	Sulfonic synthetic	5h	pH= 4.0-4.2
300	Water	20'	Drain Horse up. Sammy

Table III

Re-tanning, dyeing and fatliquoring for automotive leather using modified tara.

OPERATION	°C	%	PRODUCT	TIME	OBSERVATIONS
Wash	20	200	Water		
		0,5	Oxalic Acid	20’	
					Drain and wash
Neutralizing	25	60	Water		
		1	Sodium Formate	60’	pH= 4.2-4.4
		0.5	Sodium Bicarbonate	60’	pH final= 4.7
Re-tanning		5	**Compact Product ***		
		2	Naphthalene sulphonic syntan	30’	
		3	Sulphited synthetic oil		
		3	Lecithin	30’	
Main Re-tanning	30	50	Water	5’	
		3	Naphthalene sulphonic syntan		
		5	**Modified Tara**	60’	
		1	Dye		
		4	Naphthalene sulphonic syntan		
		6	**Modified Tara**	2 h	
	50	50	Water	5’	
Fatliquoring		2	Sulphited synthetic oil		
		2	Lecithin		
		2	Sulphated oil	2 h	
					Over night
					R-10’ stop 45’
		1	Formic Acid	60’	pH = 3.6-3.8

Table III continued on following page.

Table III continued.

					Drain
	45	150	Water At 45 °C		
		2	Sulphited synthetic oil		
		2	Lecithin		
		4	Sulphated oil	60’	
		1	Formic Acid	30’	pH final = 3.50
	30	200	Water At 30		Drain and wash

*The compact product refers to the combination of modified tara, synthetic naphthalene sulphonic and sodium acid pyrophosphate.

Table IV

Re-tanning, dyeing and fatliquoring for automotive leather using conventional tara.

OPERATION	°C	%	PRODUCT	TIME	OBSERVATIONS
Wash	30	200	Water	10'	Drain
Neutralizing	30	200	Water		
		1	Sodium formate		
		0,5	Sodium bicarbonate	20'	pH= 5.0
Re-tanning		10	Phenol syntan	30'	
		5	Tara	30'	
		2	Resin syntan	40'	
		10	Phenol syntan	30'	
		5	Tara	30'	
		1	Dye	3h	
				Night	
		1	Formic acid (1:10)	60'	pH= 3.8 Drain
Washing	50	200	Water		

Table IV continued on following page.

Table IV continued.

Fatliquoring	50	200	Water		
		4	Combination of Synthetic and natural oil		
		8	Low fog oil	60'	
		1,5	Formic acid (1:10)	30'	pH= 3.8
					Drain
Wash	40	200	Water	10'	Drain
					Rest horse-up

chemically synthesized product. The suspended solids also show a decrement in the value, as well a decrease in the conductivity. In addition, a determination of tannins has been made for the new process with modified tara, in order to determine the tannin exhaustion on final baths. The results can be seen in Table VI.

As can be see, there is a small value on tannin (0.8%), which makes us notice the great penetration of the tannins into the leather structure.

Table VII shows the comparison of pollution in wastewaters between the re-tanning process using modified tara and the conventional re-tanning process.

Table V
Pollution in wastewaters of pre-tannage.

Determination	Tara WW	Conventional WW	Units
pH	3.8	4.3	
Suspended solids	7976	9097	mg/L
Chemical Oxygen Demands	25560	32550	mgO_2/L
Organic Nitrogen Ammonia	390	362	mgN/L
Conductivity	69855	78315	µS/cm

Once again, for these processes, there is a big difference in almost every determination. The use of naphthalene sulphonic syntan as auxiliary in the new re-tanning process, as well the use of the modified tara is a difference maker in terms of better penetration of the products into the leather and therefore a decrease in COD and suspended solids in the wastewater.

Table VIII shows the physical tests carried out on the tanned leathers.

Table VI
Tannins determination in new pre-tanning final float.

Determination	Tara WW	Units
Solids	16.6	%
Ashes a 500º	7.5	
pH Analytic Solution	4.0	%
Soluble solids	9.1	%
Total solids	9.3	%
No tannins	8.3	%
Tannins	0.8	%
Insoluble	0.7	%
Water	90.2	%
pH Solution 100%	3.8	
Density	9.7	ºBé

Table VII
Pollution in wastewaters of re-tanning.

Determination	Tara	Conventional	Units
pH	3.7	3.5	
Suspended solids	2245	2641	mg/L
Chemical Oxygen Demands	29852	35120	mgO_2/L
Organic Nitrogen Ammonia	314.5	370	mgN/L
Conductivity	15667	14702	µS/cm

The leathers have a very good appearance, with a uniform dye and acceptable smoothness; also the results from physical tests are within the parameters established for each item. As can be seen in Table 8 the leathers processed using the modified tara present similar results to those obtained using the conventional system.

Conclusions

The physical modification process does not allow for an extract with high tannin content as it was with the aqueous extraction (see Low carbon products to design innovative leather processes. Part I: determination of the optimal chemical modification of tara),[1] but it improves the penetration of the extract into the leather and reduces the suspended matter and chemical oxygen demand of the residual floats.

The best physical modification is obtained by milling and sieving at 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]

By using the new pre-tanning formulation using modified tara, we can use a sustainable product and we can reduce the use of synthetic products. The new pre-tanning and re-tanning processes based on modified tara produce perfectly free-chromium leathers meeting all requirements for automotive upholstery. In addition, the new system is an environmentally friendly process due to the fact that reduces by 17-21% in COD in contrast with the glutaraldehyde system and reduces by 12-15% in suspended solids.

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Table VIII
Automotive upholstery physical tests.

Determination	Tara	Conventional	Minimum Recommendations	Unit	Method
Tensile Strength					IUP-6 / ISO 3376
Strength	259,90	249.90	100	N	
Elongation at break	46,70	44,40	35-60	%	
Tear Resistance	107,10	61,90	40	N/mm	IUP -8/ ISO3377
Softness test	3	3		mm	IUP -36/ EN ISO 17235

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