Factors That Influence the Physical Properties of Goatskins: Polymeric Derivatives and Optimization of the Process

by
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Abstract

The first series of tests evaluated the influence of a polymeric derivative, applied in the retanning process, on the physical properties of goatskin at ten levels of concentration (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10%).

The second series of tests applied an optimized process that included the most favourable conditions for each variable obtained in the three earlier parts of the study.

The addition of the polymeric derivative improved all the physical properties and only decreased the strength of the grain from a 4 % concentration onwards in contrast to all the variables studied previously.

The application of an optimized process considerably improved all the properties, especially those related to physical resistance.

Resumen

La primera serie de pruebas evaluó la influencia de un derivado polimérico, aplicada en el proceso de recurtido, en las propiedades físicas de la piel de cabra en diez niveles de la concentración (1, 2, 3, 4, 5, 6, 7, 8, 9 y 10%). La segunda serie de pruebas aplicó un proceso optimizado que incluyó las condiciones más favorables para cada variable obtenida en las tres partes anteriores del estudio.

La adición del derivado polimérico mejoró todas las propiedades físicas y disminuyó solamente la resistencia de la flor en una concentración de 4% en adelante en contraste con todas las variables estudiadas previamente. La aplicación de un proceso optimizado mejoró considerablemente todas las propiedades, especialmente aquellas relacionadas con la resistencia física.

Introduction

Parts I[1], II[2], III[3] of this work had assessed the influence of different variables such us: the vegetable retanning process, fatliquoring process, neutralization pH and the offer of a sulphated fatty alcohol on the following properties: tensile strength and tear resistance for test samples cut perpendicular and parallel to the backbone, softness, colour intensity, grain resistance and grain firmness.

These works confirmed that, as far as tensile strength was concerned, the best results were obtained with the following conditions: a 0% offer of the vegetable retanning agent; a neutralization pH of 5,5; a 10% offer of the fatliquoring agent and an offer of the sulphated fatty alcohol of 2,5%.However, it was also confirmed that the higher the physical resistances, the lower the grain firmness.

In this work, we seek to ascertain whether the application of a polymeric derivative in the retanning process could balance the aforementioned properties.

Experimental

Materials and Procedure

The same material as in Parts I, II and III, wet-blue goatskins from Nigeria of 1mm thickness and 720 g/skin weight, was used in this work. However, the processes applied were different. Here again, the skins were divided along the backbone.

In the first series of trials, ten wet-blue goatskins were used in a matched pair test. The left halves, used as "control" halves, were subjected to a standard process, which was already applied in the previous Parts[1,2,3]. The right halves of the ten goatskins, used as "test" halves, were subjected to a process in which the offer of a polymeric derivative (Retanal AGS-10) added in the retanning process was 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10%, respectively. "Test" and "control" halves were run simultaneously side by side. Figure 1 shows the applied processes.

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In a second trial, one wet-blue goatskin was used in a matched pair test. The left half of the goatskin was subjected to the standard process, whereas an "optimized" process based on the best conditions encountered in the previous Parts to obtain good physical properties without adversely affecting the organoleptic properties, was applied to the right half of the same goatskin. Right and left halves were run simultaneously. Figure 2 shows the applied processes. The most outstanding conditions applied to the right half were: 4 % of a polymeric derivative (F, Retanal AGS-10) applied in the retanning process; 4 % of a vegetable retanning agent (C, mimosa) applied in the dyeing-fatliquoring process; 2 % of a sulphated fatty alcohol (E, Deterpiel CT-20) applied in the dyeing-fatliquoring process and 8.0 % of a sulphited fish oil (D, Fosfol AUT) applied in the dyeing-

Left Halves (Control)

Offers on wet-blue weight shaved to 1.1 mm

Soaking

500% Water at 35°C
0.2% Ethoxylated Fatty Alcohol (A)
0.2% Oxalic Acid
Drum 2 hours. In bath overnight, drumming 2 min each hour. Next day pH =3.8.

Run-off and Wash 10 min

Retanning

100% Water at 35°C
4,0% Chromium Salt 33°Sch
Drum 60 min
2,0% Sodium Formate
Drum 30 min.
2% Buffering- Neutralizing Agent (B)
Drum 30 min
pH=4,6;

Run-off and Wash 10 min

Dyeing - Fatliquoring

60% Water at 30°C
2% Vegetable retanning agent (RESVEG) (C)
Drum 45 min
3,0% Dye
Drum45 min
100% Water at 60°C
6,0 % Sulphited fish oil (D)
Drum 60 min
1,5% Formic Acid
Drum 30 min
1,5% Formic Acid
Drum 30 min. Adjust pH = 3,9.

Run-off and Wash 10 min

Right Halves (Variables)

Offers on wet-blue weight shaved to 1.1 mm

Soaking

500% Water at 35°C
0,2% Ethoxylated Fatty Alcohol (A)
0,2% Oxalic Acid
Drum 2 hours. In bath overnight, drumming 2 min each hour. Next day pH =3,8.

Run-off and Wash 10 min

Retanning

100% Water at 35°C
4,0% Chromium Salt 33°Sch
Drum 60 min
2,0% Sodium Formate
Drum 30 min.
2% Buffering- Neutralizing Agent (B)
Drum 30 min
0-10 % polymeric derivative (F)
pH=4,6;

Run-off and Wash 10 min

Dyeing - Fatliquoring

60% Water at 30°C
2% Vegetable retanning agent (RESVEG) (C)
Drum 45 min
3,0% Dye
Drum45 min
100% Water at 60°C
6,0 % Sulphated fatty alcohol (E)
Drum 30 min
6 % sulphited fish oil (D)
Drum 60 min
1,5% Formic Acid
Drum 30 min
1,5% Formic Acid
Drum 30 min. Adjust pH = 3,9.

Run-off and Wash 10 min

Mechanical Operations

Twelve hours of horse resting. Toggle drying at 50°C. Two hours of conditioning in a chamber at 22°C and 62% RH. (RH in hide: 12%). Staking.

Figure 1: Applied Processes

fatliquoring process. The offers are based on wet-blue weight shaved to 1.1 mm. Other chemicals used in this work were: A: Ethoxylated Fatty Alcohol (CELESAL DL); B: Neutralizing agent (Neutragent NT).

All the treatments were carried out in pilot drums equipped with automatic controls of speed and temperature.

LEFT HALVES (CONTROL)

Offers on wet-blue weight shaved to 1.0 mm

Soaking

500% Water at 35°C
0,2% Ethoxylated Fatty Alcohol (A)
0,2% Oxalic Acid
Drum 2 hours. In bath overnight, drumming 2 min each hour. Next day pH =3,8.

Run-off and Wash 10 min

Retanning

100% Water at 35°C
4,0% Chromium Salt 33°Sch
Drum 60 min
2,0% Sodium Formate
Drum 30 min.
2,0 % Buffering- Neutralizing Agent (B)
Drum 30 min
pH=4,6;

Run-off and Wash 10 min

Dyeing - Fatliquoring

60% Water at 30°C
2% Vegetable retanning agent (RESVEG) (C)
Drum 45 min
3,0% Dye
Drum45 min
100% Water at 60°C
6,0 % Sulphited fish oil (D)
Drum 60 min
1,5% Formic Acid
Drum 30 min
1,5% Formic Acid
Drum 30 min. Adjust pH = 3,9.

Run-off and Wash 10 min

RIGHT HALVES (VARIABLES)

Offers on wet-blue weight shaved to 1.0 mm

Soaking

500% Water at 35°C
0,2% Ethoxylated Fatty Alcohol (A)
0,2% Oxalic Acid
Drum 2 hours. In bath overnight, drumming 2 min each hour. Next day pH =3,8.

Run-off and Wash 10 min

Retanning

100% Water at 35°C
4,0% Chromium Salt 33°Sch
Drum 60 min

2,0 % Buffering- Neutralizing Agent (B)
Drum 60 min
4 % polymeric derivative (F)
pH=3,9

Run-off and Wash 10 min

Neutralization

100 % Water at 30°C
2,0% Sodium Formate
Drum 15 min
0,5 % sodium bicarbonate
Drum 60 min. pH = 5.5
Run-off and Wash 10 min

Dyeing - Fatliquoring

60% Water at 30°C
4,0 % Vegetable retanning agent (RESVEG) (C)
Drum 45 min
3,0% Dye
Drum45 min
100% Water at 60°C
2,0 % Sulphated fatty alcohol (E)
Drum 30 min
8,0 % sulphited fish oil (D)
Drum 60 min
1,5% Formic Acid
Drum 30 min
1,5% Formic Acid
Drum 30 min. Adjust pH = 3,9.

Run-off and Wash 10 min

MECHANICAL OPERATIONS

Twelve hours of horse resting. Toggle drying at 50°C. Two hours of conditioning in a chamber at 22°C and 62% RH. (RH in hide: 12%). Staking.

Figure 2: Optimized process vs standard process

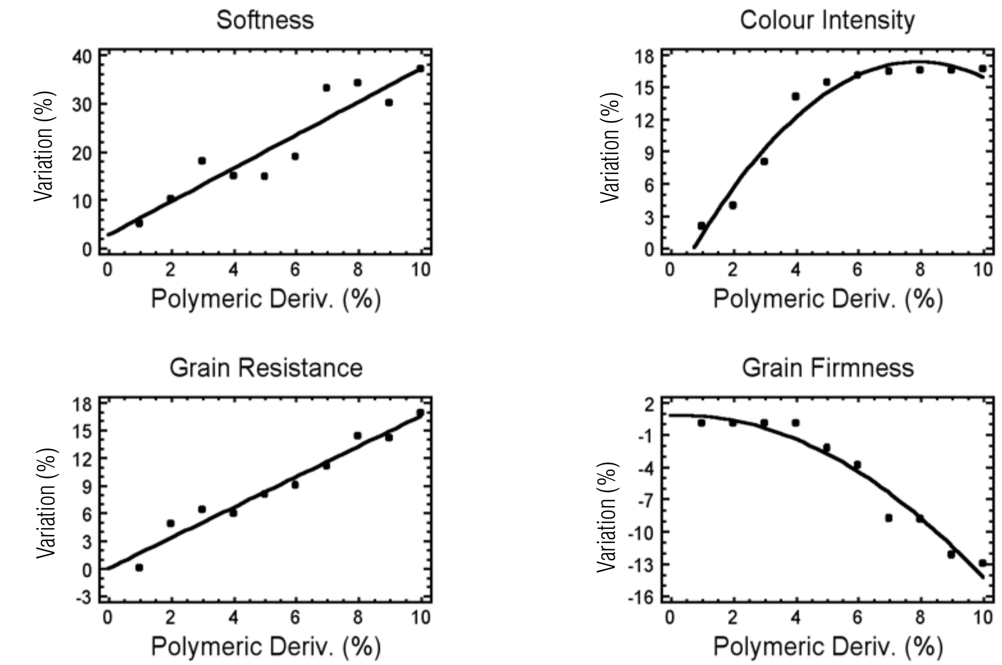

Figure 3: Polynomial regression relating the variation of the organoleptic properties as a function of the polymeric derivative offer.

TABLE I
Average of the measured values and variation for softness, colour intensity and tensile strength

POLYMERIC DERIVATIVE OFFER (%)	Softness (mm)			Color Intensity (L*)			Tensile Strength (parallel) N/mm²			Tensile Strength (perpendicular.) N/mm²		
	Right half (variable)	Left half (control)	Δ (%)	Right half (variable)	Left half (control)	Δ (%)	Right half (variable)	Left half (control)	Δ (%)	Right half (variable)	Left half (control)	Δ (%)
1	7.21	6.87	5.0	68.6	70.0	-2.0	28.5	26.4	8.0	22.4	21.3	5.2
2	7.06	6.42	10.0	65.7	68.4	-3.9	28.3	25.9	9.3	23.7	22.4	5.8
3	7.05	5.98	17.9	63.5	69.0	-8.0	29.5	26.8	10.1	22.2	20.8	6.7
4	6.93	6.03	14.9	61.2	71.2	-14.0	33.9	29.4	15.3	24.8	22.5	10.2
5	6.62	5.77	14.7	58.3	68.9	-15.4	29.9	24.9	20.1	25.0	21.8	14.7
6	8.37	7.04	18.9	60.3	71.8	-16.0	31.9	26.3	21.3	25.8	22.4	15.2
7	9.29	6.99	32.9	58.0	69.4	-16.4	31.0	25.8	20.2	24.7	21.5	14.9
8	9.23	6.89	34.0	60.0	71.9	-16.5	33.5	27.4	22.3	29.1	25.3	15.0
9	8.48	6.53	29.9	58.0	69.5	-16.5	33.5	26.9	24.5	30.4	26.0	16.9
10	8.19	5.98	37.0	58.4	70.0	-16.6	33.4	25.7	30.0	27.8	23.2	19.8

Once processed, the skins underwent assessment of the following properties: softness, measured with the Softness Tester in accordance with the IUP-36 Standard; colour intensity, measured using a reflexion spectrophotometer; grain resistance determined in accordance with the IUP-9 Standard and grain firmness determined by using the break/pipiness scale apparatus in accordance with the SATRA PM-36 method. Tensile strength and percentage of elongation at break, determined in accordance with the IUP-6 Standard, and tear resistance, determined in accordance with the IUP-8 Standard, were evaluated for test samples cut perpendicular and parallel to the backbone.

The effect of the studied variables on each property was assessed by comparing the right half value with the corresponding left half (standard process) value. The variation was calculated by applying formula 1:

$$\text{Property Variation } (\Delta, \%) = \frac{\text{Right half value} - \text{Left half value}}{\text{Left half value}} \times 100 \quad (1)$$

TABLE II
Average of the measured values and variation for tear resistance, grain resistance and grain firmness

POLYMERIC DERIVATIVE OFFER (%)	Tear Resistance (parallel) (N)			Tear Resistance (perpendicular) (N)			Grain Resistance (mm)			Grain Firmness (0-10)		
	Right half (variable)	Left half (control)	Δ (%)	Right half (variable)	Left half (control)	Δ (%)	Right half (variable)	Left half (control)	Δ (%)	Right half (variable)	Left half (control)	Δ (%)
1	51.7	51.2	1.0	57.8	55.0	5.1	8.0	8.0	0.0	4.3	4.3	0.0
2	54.5	50.5	7.9	62.6	56.4	11.0	8.7	8.3	4.8	4.5	4.5	0.0
3	54.1	49.3	9.7	65.3	54.4	20.0	8.5	8.0	6.3	4.0	4.0	0.0
4	63.0	52.5	20.0	67.4	55.7	21.0	9.0	8.5	5.9	5.4	5.4	0.0
5	58.6	48.4	21.1	72.2	56.4	28.0	9.5	8.8	8.0	4.2	4.3	-2.3
6	62.7	49.0	28.0	69.7	53.6	30.0	8.5	7.8	9.0	4.9	5.1	-3.9
7	68.5	52.3	31.0	80.7	57.2	41.1	9.0	8.1	11.1	3.1	3.4	-8.8
8	73.6	49.4	49.0	81.3	54.2	50.0	8.8	7.7	14.3	5.1	5.6	-8.9
9	75.0	49.7	50.9	87.2	55.2	58.0	8.9	7.8	14.1	4.3	4.9	-12.2
10	78.0	50.3	55.1	90.2	56.4	59.9	10.4	8.9	16.8	4.7	5.4	-13.0

TABLE III
Regression Coefficients, Determination Coefficients, Model Significance, Standard Deviation of the residuals and Significance Levels of the Variable for the Physical and Organoleptic Properties

	Softness	Color	Tensile Strength		Tear Resistance		Grain Resistance	Grain Resistance
			Parallel	Perpend.	Parallel	Perpend.		
Constant	2.65	-3.88	5.4	3.6	-6.77	-2.07	-0.07	0.73
V_1:Polymer derivative	3.43[a]	5.34[a]	2.31[a]	1.61[a]	6.21[a]	6.27	1.65[a]	0.10
V_1^2	---	-0.34[a]	---	---	---	---	---	-0.16[c]
R^2 Determination Coefficient (%)	87.38	96.31	93.71	91.13	96.80	98.00	95.68	95.53
Model Significance (%)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Standard deviation	4.19	1.24	1.92	1.61	3.62	2.88	1.13	1.27

Significance levels: [a]0.1 %; [b]1 %; [c]5 %, [d]10 %

RESULTS AND DISCUSSION

A) First series of trials: application of a polymeric derivative

Tables I and II show the averages of the measured values and the variation between the different treatments with respect to the corresponding controls for each property determined by applying the formula 1.

The values of property variation (Δ in %) were used for the statistical analysis of the results, which was carried out with the Statgraphics Plus Program[4]. All the treatments were adjusted to a second order polynomial regression. All the possible linear and quadratic effects were included in the mathematical model. Given that some of these effects (linear and/or quadratic) were non-significant, they were excluded from the model in order to obtain the optimum regression equations[5]. The regression equation coefficients were estimated by means of the least squares procedure whereas the significance levels of each variable as well as the determination coefficient (R^2) of the model were calculated by the variance analysis (ANOVA).

Table III shows the coefficients of the optimum regression equations, the determination coefficients, the model significance, the standard deviation of the residuals and the significance levels of the variables for all the physical and organoleptic properties over which the studied variable exerted an influence.

It should be pointed out that in the discussion below comments are referred to the variation in % of the considered property with respect to the standard process.

TABLE IV
Absolute values and variation of all the properties obtained in the "optimized" process with respect to the standard process.

Property	Control Process	Optimized Process	Variation Δ , (%)
Softness (mm)	6.02	7.16	19.0
Color Intensity	67.00	68.54	2.3
Tens. Strength (parallel) (N/mm^2)	26.40	31.68	20.0
Tens. Stength (perpendicul.) (N/mm^2)	21.20	24.16	14.0
Tear Resistance (parallel) (N)	50.10	62.62	25.0
Tear Resistance (perpendicular) (N)	55.30	70.78	28.0
Grain resistance (mm)	8.07	9.03	12.0
Grain Firmness (0-10)	4.50	4.37	-3.0

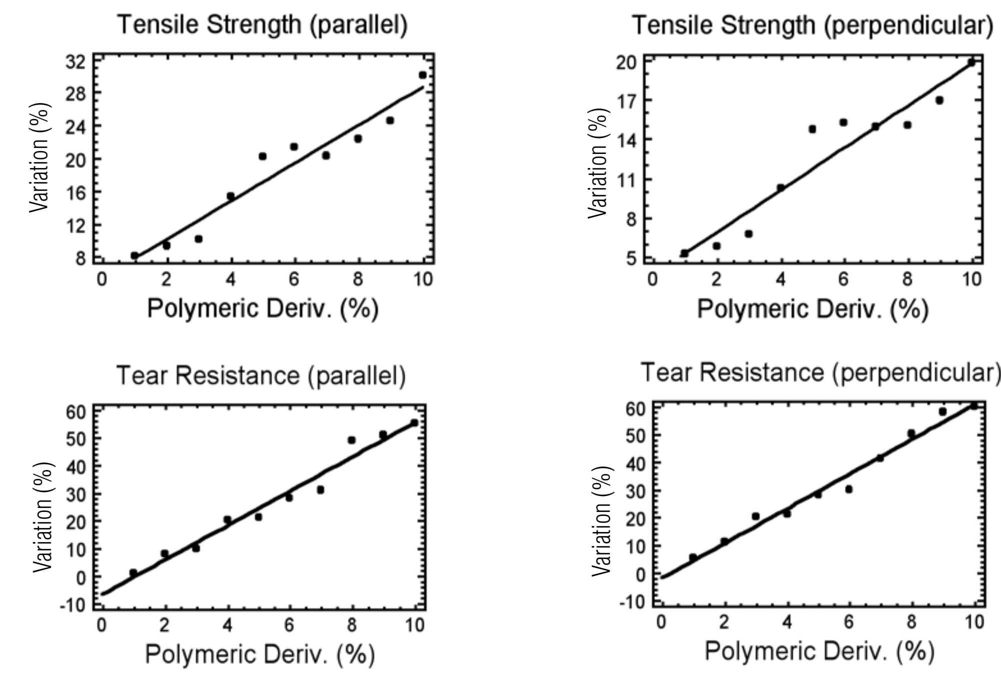

Figure 4: Polynomial regression relating the variation of the physical properties as a function of the polymeric derivative offer..

Figures 3 and 4 show the polynomial regression relating the variation of the studied properties as a function of the polymeric derivative offer.

Softness

Table I and Figure 3 show that the higher the polymeric derivative offer, the higher the softness. For a 10 % offer of the polymeric derivative, this increase reached 37 % with respect to the corresponding control.

Table III shows that the determination coefficient (R^2) obtained for this property was 87.38 %. This table also shows that the influence exerted by the polymeric derivative offer was significant at the 0.1 % level.

Color intensity and color levelness

Given that high luminosity (L*) values correspond to values of lower intensity; we have changed the sign in the graph, so that "color" denomination correspond to intensity.

Color intensity increased with the polymeric derivative offer up to an offer of 4 % (increase of 14 % with respect to the corresponding control) as observed in Table I and Figure 3. However, this property stabilized for offers higher than 4 %.

The determination coefficient (R^2) for colour intensity was 96.31 % as shown in Table III. It can be also observed that the influence exerted by the polymeric derivative offer was significant at the 0.1 % level. Moreover, the quadratic effect of this variable was also highly significant (0.1 %).

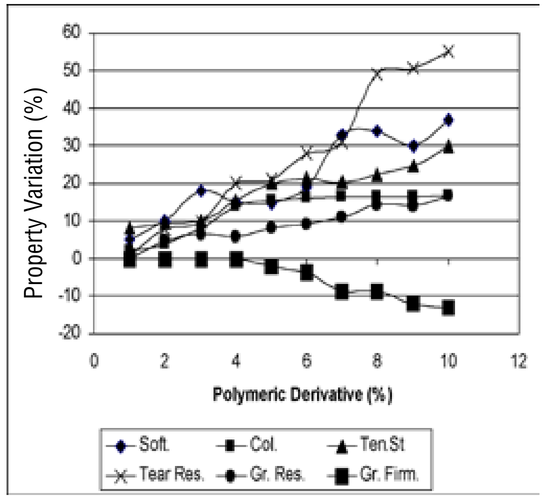

Figure 5: Variation of all the properties as a function of the polymeric derivative offer.

Color levelness was also improved for this polymeric derivative offer (4 %).

Tensile strength
Tensile strength for both parallel and perpendicular to the backbone test samples showed an increase of 30 % and 20 %, respectively, with respect to the corresponding control (Table I and Figure 4) for a polymeric derivative offer of 10 %.

Table III shows that the determination coefficient (R^2) obtained for tensile strength for parallel/perpendicular to the backbone test samples was 93.71 % and 91.13 %, respectively. This Table also shows that the influence exerted by the polymeric derivative offer was significant at the 0.1 % level in both cases (parallel/perpendicular test samples).

Tear resistance
Table II and Figure 4 show that tear resistance increased with the polymeric derivative offer and that this increase reached, with a polymeric derivative offer of 10 %, a maximum of 55 % and a 60 % with respect to the corresponding control, for parallel and perpendicular to the backbone test samples, respectively.

The determination coefficient (R^2) for parallel/perpendicular to the backbone test samples was 96.80 % and 98.00 %, respectively, as shown in Table III. The influence exerted by the polymeric derivative offer was significant at the 0.1 % level in both cases (parallel/perpendicular test samples).

Grain resistance
Likewise, the higher the polymeric derivative offer, the higher the grain firmness. For a 10 % offer of the polymeric derivative, this increase reached 16 % with respect to the corresponding control, as observed in Table II and Figure 3.

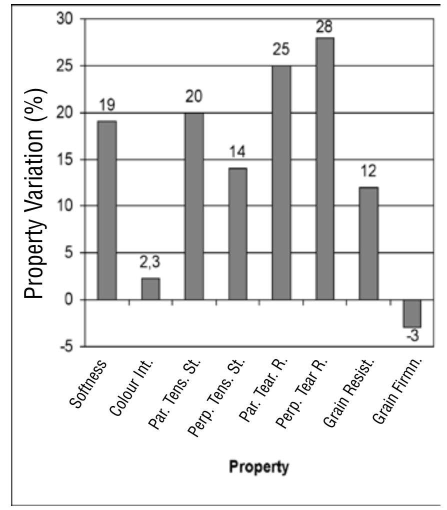

Figure 6: Variation of all the properties obtained in the "optimized" process with respect to the standard process.

The determination coefficient (R^2) for this property was 95.68 % as observed in Table III. This Table also shows the influence exerted by the polymeric derivative offer was significant at the 0.1 % level.

Grain firmness
Table II and Figure 4 show that grain firmness remained constant up to a polymeric derivative offer of 4 %. However, this property decreased for higher offers, reaching a maximum decrease of 13 % with respect to the corresponding control for a polymeric derivative offer of 10 %.

In this case, the determination coefficient (R^2) obtained was 95.53 % (Table III). The influence exerted by the polymeric derivative offer on this property was not significant; however, the quadratic effect of this variable was significant at the 5 % level.

Summary of property variation
Figure 5 shows the variation curves of all the properties with respect to the corresponding controls as a function of the polymeric derivative offer. Although most of the properties (softness, tensile strength and tear resistance for parallel and perpendicular to the backbone test samples and grain resistance) increased for greater polymeric derivative offers, the optimum offer of polymeric derivative to be used is 4 % given that grain firmness decreased considerably for higher offers. For this offer of polymeric derivative (4 %), the following increases were obtained: softness (15 %), colour intensity (14 %), parallel/perpendicular tensile strength (15 %) and (10 %), respectively, tear resistance for both parallel and perpendicular to the backbone test samples (20 %) and grain resistance (6 %). Grain firmness remained practically constant up to this offer.

B) Second trial: application of an "optimized" process
Table IV and Figure 6 show the results obtained by applying the "optimized" process, which is shown in figure 2. The following increases were obtained with respect to the standard process:

softness (19 %), colour intensity (2.3 %), tensile strength for parallel to the backbone test samples (20 %), tensile strength for perpendicular to the backbone test samples (14 %), tear resistance for parallel/perpendicular to the backbone test samples (25 %) and (28 %), respectively and grain resistance (12 %). Grain firmness decreased by 3 %.

CONCLUSIONS

* The polymeric derivative offer exerted an influence on all the studied properties which was highly significant (0.1 % level). Only in the case of grain firmness, this variable was not significant. However, its quadratic effect was significant at the 5 % level.
* The application of a polymeric derivative in the retanning operation improved all the studied variables. An offer of 4 % of the polymeric derivative (on wet-blue weight shaved to 1.1 mm) yielded the best results.
* The application of an "optimized" process based on the most favorable conditions encountered in the previous Parts 1, 2, 3 showed an improvement in all the physical resistances. Only a slight decrease of 3 % with respect to the standard process was observed in grain firmness. However, a larger scale trial needs to be run to confirm these results.

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