INFLUENCE OF AN AMPHOTERIC RETANNING AGENT ON THE PROPERTIES OF LEATHER. PART I

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SUMMARY:
This study consists of three parts:
1. Study of a new retanning amphoteric AFF agent as compared to an reference without product. Study of the properties provided to the leather when applied at four different stages of the process: rechroming (before and after chromium), retanning-dyeing, and fatliquoring.
2. Comparative study of the AFF agent versus three types of the most frequently used retanning agents.
3. Optimization of the mixture of four types of retanning agents, depending on the different articles to be made.
This work corresponds to the first part, where different properties such as softness, thickness, color intensity, color levelness, grain fineness, physical resistances and grain firmness, are assessed on lambskin and cattle hide.
In descending order of effectiveness, the product was most effective at rechroming after chrome salt addition and dyeing, then at rechroming before chrome salt addition, then after fatliquoring.
The work includes graphics and photographs detailing the above ratings.
Keywords: Retanning, Amphoteric, Physical Resistance, Color.

INTRODUCTION

The retanning process has the following priority objectives (1.2):
a) To fill the most inconsistent, defective, empty parts of the leather in order to homogenize its physical and organoleptic properties.
b) To improve the penetration and distribution of dyestuffs and fatliquoring agents used in the process.
Many retanning agents of varying nature are currently available, including, but not limited to:
1- Condensation of phenolic compounds
2- Vegetable agents
3- Acrylic acid derivatives
4- Urea derivatives
5- Dicyandiamide derivatives
6- Styrene maleic derivatives
7- Proteins and derivatives thereof
Nº 1 through nº 6 above have a more or less marked anionic character, while nº 7 has an amphoteric character on account of its amine-reactive and carboxyl-reactive groups.
Practical studies(3) show that anionic retanning agents generally meet the above objectives. In turn, however, a strongly decreased intensity and shine of dyeings is obtained.
Protein derivatives have an intermediate behavior, that is, they do not fill as much as anionic compounds but the intensity and shine of dyeings is much less decreased.
The present work consists of three parts:
1- Study of a new amphoteric retanning agent AFF and of the properties provided to the leather when applied at four different stages of the process (rechroming before and after chromium, retanning, and fatliquoring) as compared to a reference without product.
2- Comparative study of AFF versus three types of the most frequently used retanning agents.
3- Optimization of the four types of retanning agent as related to the different articles to be made.

2. EXPERIMENTAL PART

2.1. Materials

2.1.1. Substrate

1 mm-thickness, 720 g/skin mean weight, wet blue "lacaune" lambskins were used. This substrate was selected for being an empty skin with dyeing difficulties.
The skins were divided along the line of the backbone. Left halves were taken as reference (no retanning agent) and right halves underwent the same process with AFF retanning agent.
In a second part of the experiment, wb (1.5 mm) cattle hide was used. Rectangular samples

symmetric with respect to the backbone were cut in the butt zone, and the same methodology as with the lambskin was used.

2.1.2. Product

likely to enhance the quality of leather have been and are being developed.
Retanning agents must penetrate the leather and be selectively deposited in the empty areas. When designing these products, the most critical parameters are the composition, the molecular weight (in the case of polymers), and the affinity with the leather.
It is well known that polymers based on water-soluble dihydroxy diphenyl sulfones are most indicated to achieve these properties, and their use is thus being increased.
With polymers, an excessive molecular weight would hinder penetration into the leather, thereby increasing its hardness and leading to grain problems. Conversely, if the molecular weight is too low, the filler could fail to be selective enough.
A polymer with excessive affinity would result in harsh grain. Conversely, selective filler would be much harder to obtain. Well-balanced amphoteric products are very indicated to achieve good affinity as well as intense, leveled dyeing with a smooth grain.
The AFF retanning agent is a dihydroxy diphenyl sulfone-based polymer with amphoteric characteristics, and is designed to improve the quality of the leather.

2.2. Method

All tests were performed in duplicate and results are expressed as mean values.
In process nº 1, the product was applied at rechroming before chromium addition. In process nº 2, it was applied at rechroming after chromium addition. In process nº 3, it was applied at retanning-dyeing. And in process nº 4, it was applied at fatliquoring..

DOSE ON W.B. SHAVED WEIGHT
SOAKING
200% Water at 35º C
0.2% Non-ionic surfactant
0.2% Oxalic acid
Run 2 hours. Overnight bath, running 2 min every hour. Following day pH =3.8 . Run off and wash for 10 min

RECHROMING

100% Water at 35ºC	
LEFT SIDES—REFERENCE	*Run 30 min……pH=3.64*
*RIGHT SIDES **2.5 % (a.m) AFF RETANNING AGENT***	*Run 30 min……pH=5.24*
5% Chromium salt 33º Sch	*Run 30 min*
X% Sodium formate	*Adjust pH to 4.3*

NEUTRALIZATION

150% Water at 30º C	
2% Sodium formate	*Run 15 min*
0.5% Sodium bicarbonate	*Run 60 min…..pH=5.5.*
	Run off and wash for 10 min

DYEING-FATLIQUORING

50% Water at 35º C	
2% Dye dispersing agent	
2% Dyestuff	*Run 60 min*
100% Water at 65º C	
5% Sulphated neatsfoot oil	
5% Sulpho Chlorinated Paraffin	*Run 60 min*
2% Formic acid	*Run 60 min… pH=3.7.*
	Run off and wash for 10 min

MECHANICAL OPERATIONS
Allow to rest for 12 hours on beam. Dry toggling at 50ºC. Condition at 22ºC and 62% R.H. for 2 hours (12% R.H. measured on lambskin). Stake

Process nº1

DOSE ON W.B. SHAVED WEIGHT
SOAKING
200% Water at 35º C
0.2% Non-ionic surfactant
0.2% Oxalic acid
Run 2 hours. Overnight bath, running 2 min every hour. Following day pH =3.8 . Run off and wash for 10 min

RECHROMING
100% Water at 35ºC
5% Chromium salt 33º Sch — *Run 15 min*
2% Sodium formate — *Run 30 min…..pH=4.1*
*LEFT SIDES—**REF.*** — *Run 60 min…..pH=4.2*
*RIGHT SIDES **2.5'% (a.m) AFF RETANNING AGENT*** — *Run 60 min…..pH=4.32.*
Run off and wash for 10 min

NEUTRALIZATION
150% Water at 30º C
2% Sodium formate — *Run 15 min*
0.5% Sodium bicarbonate — *Run 60min…..pH=5.5.*
Run off and wash for 10 min

DYEING-FATLIQUORING
50% Water at 35º C
2% Dye dispersing agent
2% Dyestuff — *Run 60 min*
100% Water at 65º C
5% Sulphated neatsfoot oil
5% Sulpho Chlorinated Paraffin — *Run 60 min*
2% Formic acid — *Run 60 min - pH=3.7.*
Run off and wash for 10 min

MECHANICAL OPERATIONS
Allow to rest for 12 hours on beam. Dry toggling at 50ºC. Condition at 22ºC and 62% R.H. for 2 hours (12% R.H. measured on lambskin). Stake

Process nº2

DOSE ON W.B. SHAVED WEIGHT
SOAKING
200% Water at 35ºC
0.2% Non-ionic surfactant
0.2% Oxalic acid
Run 2 hours. Overnight bath, running 2 min every hour. Following day pH = 3.8.
Run off and wash for 10 min

RECHROMING
100% Water at 35ºC
5% Chromium salt 33º Sch — *Run 15 min*
1.5% Sodium formate — *Run 30 min……..pH=4.2*

NEUTRALIZACION
100% Water at 30ºC
2.0% Sodium formate — *Run 15 min*
1.0% Sodium bicarbonate — *Run 60 min……..pH=5.5.*
Run off and wash for 10 min

DYEING-FATLIQUORING
50% Water at 35ºC

LEFT SIDES – REFERENCE
RIGHT SIDES 2.5% (a.m) AFF RETANNING AGENT *Run 60 min*
2% Dye dispersing agent
2.0% Dyestuff *Run 45 min*
100% Water at 65ºC
5.0% Sulphated neatsfoot oil
5.0% Sulpho Chlorinated Paraffin *Run 60 min*
2.0% Formic acid *Run 60 min. pH =3.7*
Run off and wash for 10 min

MECHANICAL OPERATIONS
Allow to rest for 12 hours on beam. Dry toggling at 50ºC. Condition at 22ºC and 62% R.H. for 2 hours (12% R.H. measured on lambskin). Stake

Process nº 3

DOSE ON W.B. SHAVED WEIGHT
SOAKING
200% Water at 35ºC
0.2% Non-ionic surfactant
0.2% Oxalic acid
Run 2 hours. Overnight bath, running 2 min every hour. Following day pH = 3.8.
Run off and wash for 10 min
RECHROMING
100% Water at 35ºC
5% Chromium salt 33º Sch *Run 15 min*
1.5% Sodium formate *Run 30 min……pH=4.2*
NEUTRALIZACION
100% Water at 30ºC
2.0% Sodium formate *Run 15 min*
1.0% Sodium bicarbonate *Run 60 min……pH=5.5*
Run off and wash for 10 min
DYEING-FATLIQUORING
50% Water at 35ºC
2% Dye dispersing agent
2.0% Dyestuff *Run 45 min*
100% Water at 65ºC
5.0% Sulphated neatsfoot oil
5.0% Sulpho Chlorinated Paraffin *Run 60 min*

LEFT SIDES – REFERENCE
RIGHT SIDES 2.5% (a.m) AFF RETANNING AGENT *Run 60 min*
2.0% Formic acid *Run 60 min. pH = 3.7.*
Run off and wash for 10 min

MECHANICAL OPERATIONS
Allow to rest for 12 hours on beam. Dry toggling at 50ºC. Condition at 22ºC and 62% R.H. for 2 hours (12% R.H. measured on lambskin). Stake

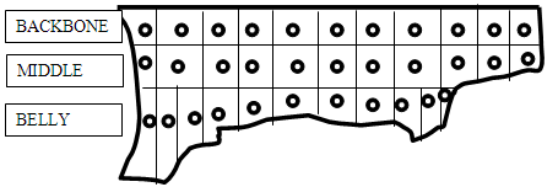
Process nº 4

All processes were performed in pilot plant drums with automatic speed and temperature control.

The following properties were assessed:
-DEGREE OF SOFTNESS = BLA (IUP-36)
-THICKNESS =(IUP-4)
-COLOR INTENSITY = COL (Colorimeter)
-COLOR LEVELNESS = IGCO (Colorimeter)

-GRAIN FINENESS (Pore photograph)
-TENSILE STRENGTH (Mean of the parallel and perpendicular values) = RTR (IUP-6)
-TEAR LOAD (Mean of the parallel and perpendicular values) = RDE (IUP-8)
-ELONGATION (Mean of the parallel and perpendicular values) = ELO (IUP-36)
-GRAIN BURST = RFL (IUP-9)
-GRAIN FIRMNESS = FFL (SATRA PM-36)

Non-destructive tests



Softness, thickness and color (intensity and levelness)

Destructive tests

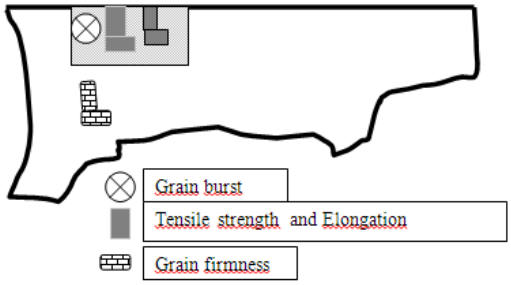


Fig. nº 1. Assessments and sampling in lambskin

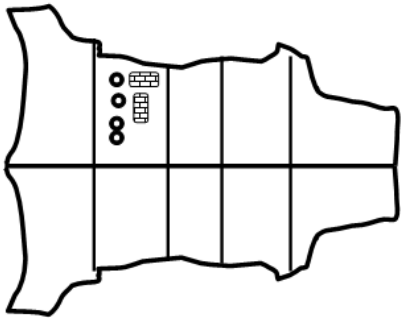


Fig. nº 2. Cattle hide sampling

The data represent variations (% □) of the values of each variable vs. the reference retanning agent, by means of the following formula::

$$\Delta\ \%\text{VARIABLE} = \frac{\text{Right half value (variable)} - \text{Left half value (reference)} \times 100}{\text{Left half value (reference)}}$$

2.3 Results and discussion

2.3.1. Degree of softness

A) Lambskin

The variations in the degree of softness of the AFF-treated half vs. the untreated half (% Δ) and in the three leather areas (backbone, middle and belly) are shown in Figure 3. Since 11 assessments are performed per area and the test was performed in duplicate, each datum expressed in the graph corresponds to the mean of 22 measurements.

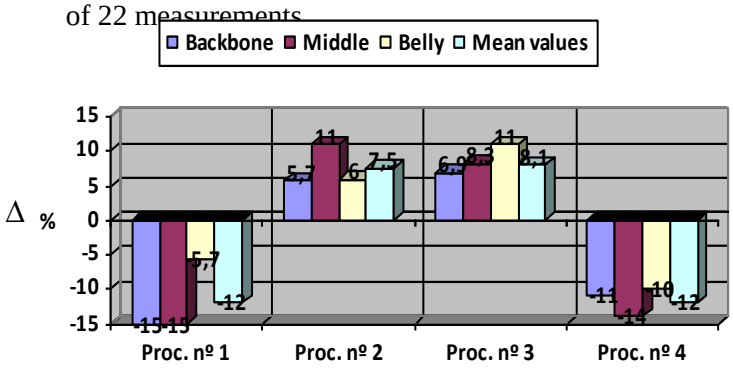


Figure 3. Variations in the degree of softness according to the process applied in lambskin

In process nº 1, AFF hardens by a mean of 12%, to a lower extent (5%) in the belly zone.
In process nº 2, AFF softens by a mean of 7.5%, to a similar extent in the backbone and belly areas (5.7 and 6%) and to a greater extent in the middle zone (11%)
In process nº 3, AFF softens by a mean of 8.1% (6.9, 8.3 and 11% in the backbone, middle and belly areas, respectively).
In process nº 4, AFF hardens by a mean of 12%, to a similar extent in all three areas.

B) Cattle hide

Five measurements per piece were performed (mean values shown).

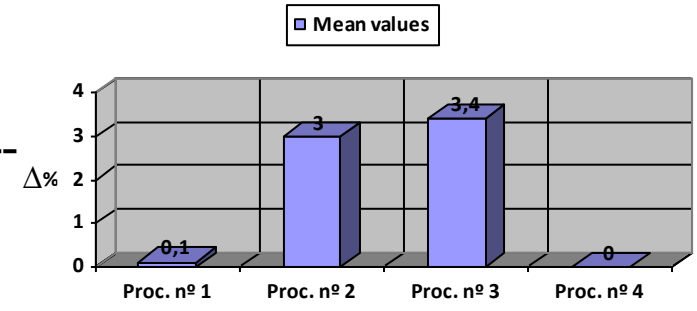


Fig.4. Variations in the degree of softness according to the process applied in cattle hide

Cattle leather shows a similar tendency as compared to lambskin leather, with smaller differences being obtained.
Processes nº 1 and 4 barely show any variation, while processes nº 2 and 3 increase the degree of softness.

2.3.2. Thickness variations

A) Lambskin

The assessment was similar to the previous one. The thickness variations vs. non-retanned reference, also in all three areas with the same number of measurements, are shown in Fig. 5.

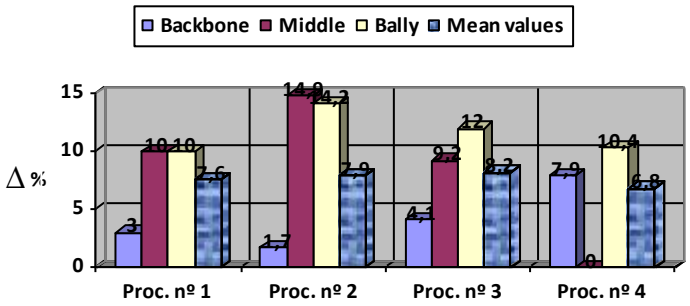


Fig. nº 5. Thickness variations according to the process applied in lambskin

In process nº 1, mean thickness is increased by 7.6%, to a greater extent in the middle and belly areas (10%).
In process nº 2, mean thickness is increased by 7.9%, to a greater extent in the middle and belly areas (14.9 and 14.2%, respectively).
In process nº 3, mean thickness is increased by 8.2% (4.1%, 9.2% and 12% in the backbone, middle and belly areas, respectively).
In process nº 4, mean thickness is increased by 6.8%, but does so irregularly.

B) Cattle hide

Five measurements per piece were performed (mean values shown).

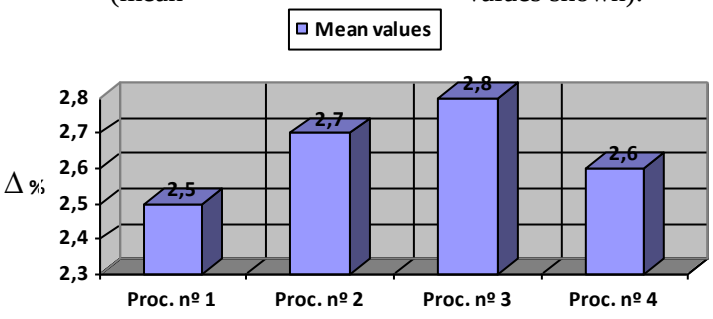


Fig.6. Thickness variations according to the process applied in cattle hide

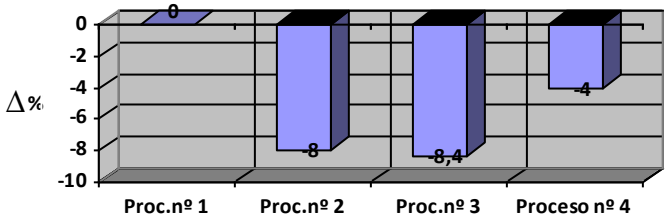
Thickness variations in cattle hide are very small, and follow the same tendency as with the degree of softness.

2.3.3. Color intensity

A) Lambskin

Brightness (L*) was measured with a colorimeter. Variations vs. reference are shown in Figure 7.

Figure 7. Color intensity variation according to the process applied in lambskin



Intensity is unchanged in process nº 1.
Intensity is decreased by 8.6% in process nº 2.
Intensity is decreased by 8.4% in process nº 3.
Intensity is decreased by 4% in process nº 4.

B) Cattle hide

Five measurements per piece were performed (mean values shown).

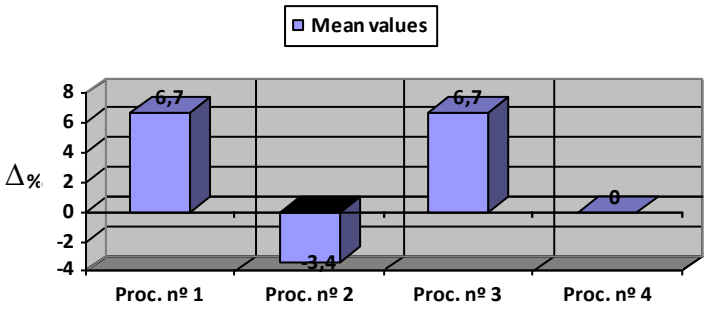


Fig. 8. Color intensity variations according to the process applied in cattle hide

In cattle hide, color intensity is increased by 6.7% in processes nº 1 and 3, slightly decreased in process nº 2, and remains unchanged in process nº 4.
The dyeing behavior of cattle hide differs from that of lambskin. This can be attributed to the different treatment undergone by the two skin types until tanning.
Importantly, this retanning agent fails to significantly decrease dyeing intensity, and even increases it (vs. untreated hide)

2.3.4. Color levelness

A) Lambskin

Total color (E*) was measured on a reference point (physical tests) and on 10 different skin assessment points. ΔE* vs. these points is

represented in the graphs below (the lower the values, the better the levelness of dyeing).

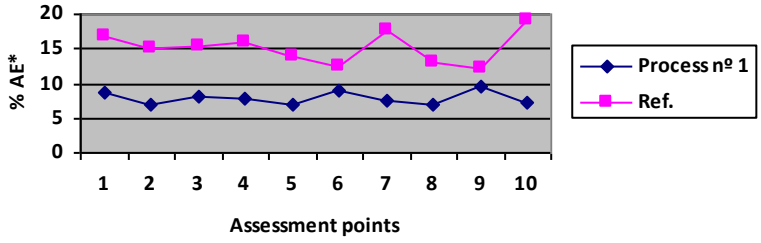


Figure 9. Color dispersion in process nº 1.

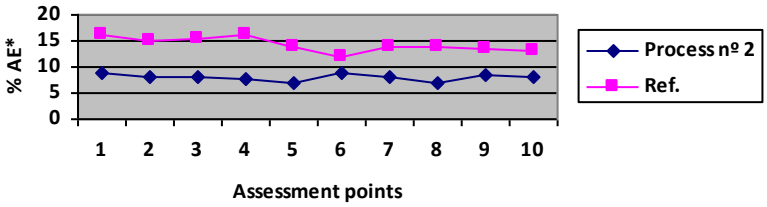


Fig.10.Color dispersion in process nº 2.

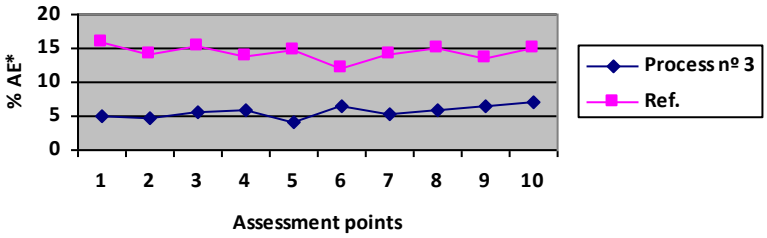


Fig.11Color dispersion in process nº 3.

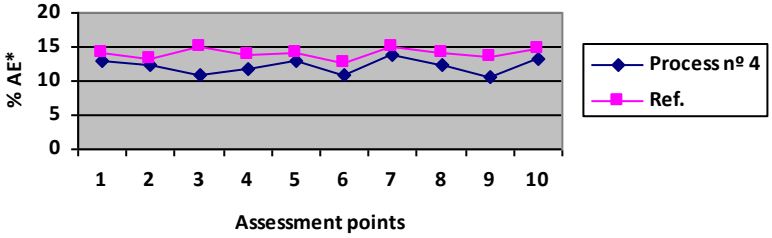


Fig.12. Color dispersion in process nº 4.

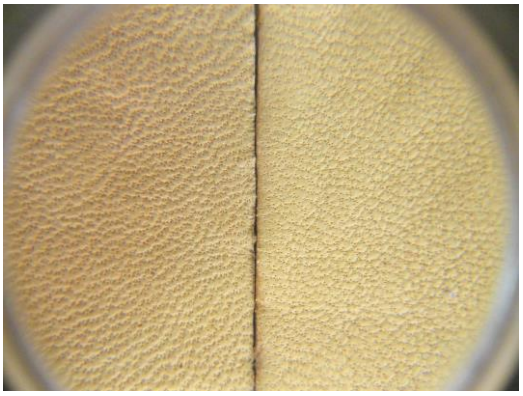
In all four processes, ΔE* values are lower than the matching reference, i.e. their color levelness is better.
In processes nº 1 and 2 (rechroming), ΔE* values range between 5 and 10.
In process nº 4, negligible differences between process and reference are found, and hence this is the process with less influence on the levelness of dyeing.

2.3.5. Grain fineness.

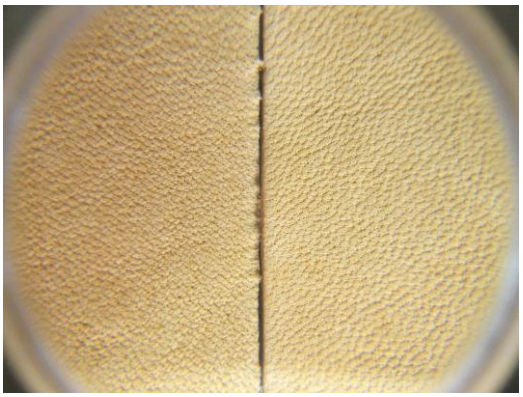
A) Lambskin

A scale was defined to assess "grain fineness", with values of 0 to 5 (in ascending order) and considering grain uniformity, size and relief.

Photograph nº 1 shows the AFF-treated lambskin on the right (Value 5) and the product-free reference on the left (Value 2).
Photograph nº 2 shows the AFF-treated lambskin on the right (Value 2) and the product-free reference on the left (Value 2)



Photograph nº 1



Photograph nº 2

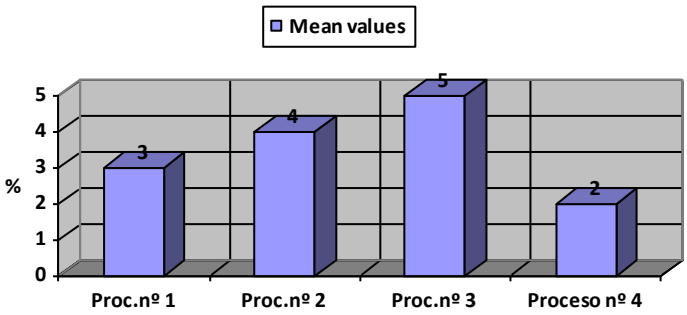
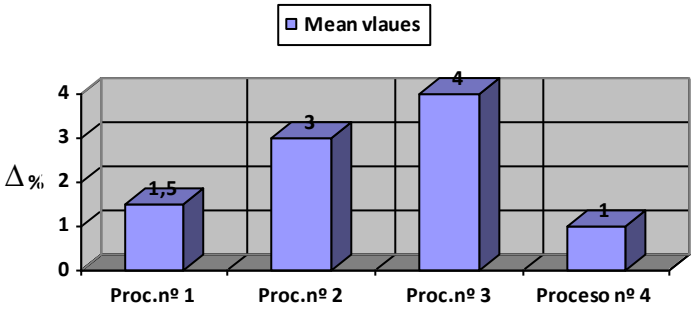


Fig.9. Grain fineness according to the process applied in lambskin

The highest grain fineness vs. reference (value 5, photograph nº 1) is obtained with process nº 3. The lowest grain fineness vs. reference (value 2, photograph nº 2) is obtained with process nº 4.

B) Cattle hide

Same tendencies as with lambskin, with smaller differences obtained.



2.3.6 Physical resistances (lambskin)

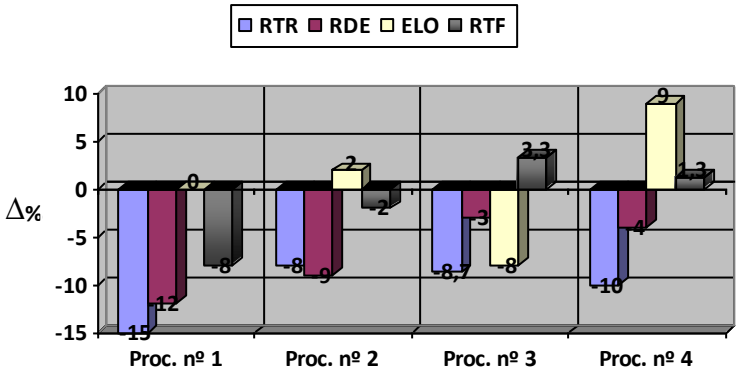


Figure 8. Physical resistance variations according to the process applied in lambskin

The values of physical resistance variations in processes nº 2 and 3 are within the margin of error of the assessment method (RTR = ±8%; RDE = ±5%; ELO = ±12%; RTF = ±5%). Somewhat higher variations are obtained in processes nº 1 and nº 4.

Physical resistances were not assessed in cattle hide because butt pieces —not meeting the sampling requirements for physical tests— were used.

2.3.7. Grain firmness

A) Lambskin

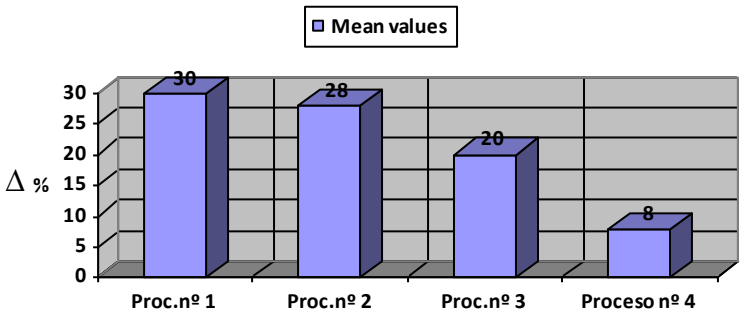


Figure 9. Grain firmness variations according to the process applied in lambskin

Maximum grain firmness was obtained with process nº 1 (30%), followed by processes nº 2, 3 and 4.

B) Cattle hide

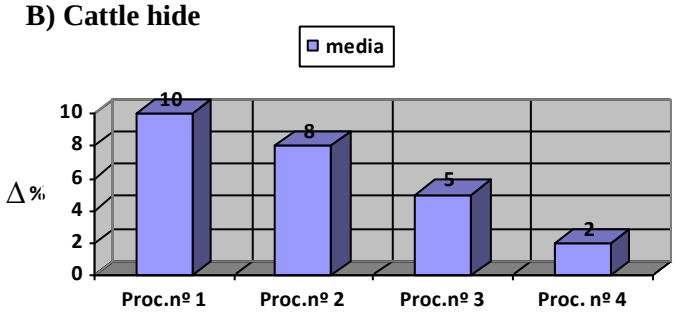


Figure 10. Grain firmness variations according to the process applied in cattle hide

The increase in grain firmness follows the same sequence as in lambskin, although to a lesser extent.

3. CONCLUSIONS

3.1. Processes nº 2 and 3 slightly increase softness and grain fineness and minimally decrease physical resistances.

3.2. Color levelness is improved in all processes, with exceptional values obtained in process nº 3. Intensity is significantly increased in processes nº 2 and nº 3.

3.3. Grain firmness is improved in all processes, more significantly so in processes nº 1, 2 and 3.

3.4. The best properties are obtained in processes nº 2 and nº 3 (average of all values obtained in this study).

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Product used:
AFF RETANNING = RETANAL AFF (Cromogenia Units, S.A.)