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Influence of an amphoteric retanning agent on the properties of leather. Part II

Olga Ballús, Ramón Palop[1], Llorenç Noguera[1], Ricardo Micó[1]

[1]Laboratorio de Curtidos. Cromogenia Units S.A.
Zona Franca. Sector E. Calle nº 50, 08040-Barcelona, España

Laboratorio de Curtidos, Cromogenia Units SA; Zona Franca. Sector E. Calle nº 50, 08040-Barcelona, España;
Teléfono (+34) 932643462, e-mail: oballus@cromogenia.com

Abstract

A comparative study of three retanning agents was conducted by using the optimized process studied in the first part of this work, where the best results were obtained with the amphoteric retanning agent AFF applied during the dyeing-fatliquoring stages.
The selected retanning agents were:

Amphoteric retanning agent based on protein PROT
Anionic retanning agent based on pure dihydroxydiphenyl sulfone SULF
Amphoteric retanning agent based on pure dihydroxydiphenyl sulfone AFF

This work design will be used to assess the influence of each of the two characteristics (sulfone base and amphoteric nature) on the properties of the leather.
Physical-chemical and organoleptic parameters were assessed which allowed deducing that the amphoteric retanning agent AFF provides the leather with specific properties different from those of the other two agents.
Data analysis was performed with the program Statgraphics Plus (5) to find the optimal areas.
The methodology used originates from a Simplex-Centroid (6) design as an experimental plan, adjusted to a linear model.

Keywords: Retanning, Amphoteric, Physical Resistance, Color

1. Introduction

There is an incessant demand for improving the properties of leather in general, particularly of those relating to grain fullness and firmness [(1.2)] With this purpose in mind, new retanning agents have been and are being developed which, in addition to the above characteristics, offer the right feel to each article as well as deep colors.
Retanning agents must penetrate the hide and be selectively deposited in the empty areas. The most critical parameters when designing these products are: composition, molecular weight (with polymers), and leather affinity.
It is well known that water soluble polymers based on dihydroxydiphenyl sulfones are highly indicated to achieve these properties, and their use is being increased to this end.
In polymers, excessively high molecular weights will hinder penetration, increase hardness, and lead to grain problems. In turn, excessively low molecular weights will lead to insufficient fullness selectivity.[(3)]
A polymer with excessive affinity would result in rough grain. Excessively low affinity would make obtaining a selective filling much more difficult. Well-balanced amphoteric products are highly indicated to obtain good affinity, deep and leveled dyeing, and a smooth grain.
The following two-part project was conducted:
Study of a new amphoteric retanning agent, AFF, based on a dihydroxydiphenyl sulfone structure, as compared to a reference without retanning. Assessment of the properties it provides to the leather when applied at four different stages of the process: rechroming (before and after chrome), dyeing, and fatliquoring.
In Part 1 of the study,[(4)] the application of retanning agent AFF at the dyeing stage was shown to provide the skin with the best physical-chemical and organoleptic properties.
Part 2 of the study includes a comparative study of all three retanning agents by using the process optimized in Part 1.
With this design we shall attempt to assess the influence of each characteristic (sulfone base and amphoteric nature) on the properties of the skin.

2. Materials and method

2.1. Substrate

Wet-blue, 1,1 mm-thick Spanish cattle hides were used.

2.2. Products

a) Amphoteric retanning agent based on protein PROT

b) Anionic retanning agent based on pure dihydroxydiphenyl sulfone SULF

c) Amphoteric retanning agent based on pure dihydroxydiphenyl sulfone AFF

2.3. Method

The skins were split along the backbone. The left halves were taken as references —no retanning agent— while the right halves underwent the same process but with the inclusion of the retanning products and mixtures thereof at the quantities defined in Table 1, and underwent the standard process described in Fig. 1. Each variable was made in duplicate.

All processes were performed in pilot plant drums with automatically controlled speed and temperature.

The effect of each retanning agent and mixtures thereof was assessed by comparing the left half with its corresponding right half, and calculated with Equation 1 below:

$$\%\ \text{of property variation} = \frac{\text{Right half value} - \text{left half value} \times 100}{\text{Left half value}} \quad (1)$$

A Simplex-Centroid design[6] adjusted to a linear model was used as experimental plan.

The retanning formulation for all seven experiments conducted, the tested retanning agents and combinations thereof, and the sampling diagram for property determination are shown in Fig. 1, Table 1 and Fig. 2, respectively.

The Statgraphic Plus program[4.5] was used for statistical analysis of results with the purpose of finding the optimal areas of each property.

The objective is to obtain a representation likely to relate the results of the seven variables shown in Table 1 and likely to predict the results that would be obtained by a ternary formulation of the retanning agents (PROT, SULF and AFF) at a maximum concentration of 10% of active matter on wet-blue weight.

A graph depicting the ternary sample is used. One retanning agent at a concentration of 10% is represented at each vertex of the triangle. This means that there is no mixing at these points —which indicate the value of the property as compared to the retanning-free reference.

The three sides of the triangle are the areas where two retanning agents coexist, while all three retanning agents coexist inside the triangle. The center of the triangle corresponds to test 5, and has 3.33% of each retanning agent.

The assessed properties were:

-DEGREE OF SOFTNESS = SOF (IUP-36)

-THICKNESS= THI (IUP-4)

-TEAR LOAD= (Mean of the parallel and perpendicular values) = TLO (IUP-8)

-TENSILE STRENGTH= (Mean of the parallel and perpendicular values) = TST (IUP-36)

-COLOR DEPTH = CDE (Colorimeter)

-COLOR LEVELING = CLE (Colorimeter)

-GRAIN FINENESS = GFI (Organoleptic and microscope)

-GRAIN BURST = GBU (IUP-9)

DOSE ON SHAVED W.B. WEIGHT

SOAKING

200% Water at 35ºC
0.2% Nonionic surfactant
0.2% Oxalic acid
Run 2 hours. Night in bath, running 2 min every hour. Following day pH = 3.8. Drain bath and wash 10 min

RECHROMING

100% Water at 35ºC
5% Chrome salt 33º Sch — *Run 15 min*
2% Sodium formate — *Run 60 min………pH=4.2*

NEUTRALIZATION

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

DYEING-FATLIQUORING

50% Water at 35ºC
LEFT HALVES – REFERENCE
RIGHT HALVES - RETANNING AGENT — *Run 60 min*
2% Dye dispersant
2.0% Dyestuff — *Run 45 min*
100% Water at 65ºC
5.0% Sulfated neatsfoot oil
5.0% Sulpho chlorinated paraffin — *Run 60 min*
2.0% Formic acid — *Run 60 min. pH =3.7*
Drain bath and wash 10 min

MECHANICAL OPERATIONS

Lay down on beam for 12 hours. Dry toggling with air at 50ºC. Condition at 22ºC and 62% R.H. for 2 hours (12% R.H. measured on skin). Stake.

Fig. 1. Application process

Test	**PROT (%)**	**SULF (%)**	**AFF (%)**
1	**0**	**5**	**5**
2	**5**	**5**	**0**
3	**0**	**0**	**10**
4	**10**	**0**	**0**
5	**3.3**	**3.3**	**3.3**
6	**0**	**10**	**0**
7	**5**	**0**	**5**

Table 1. Simplex Centroid Design. Variables applied.

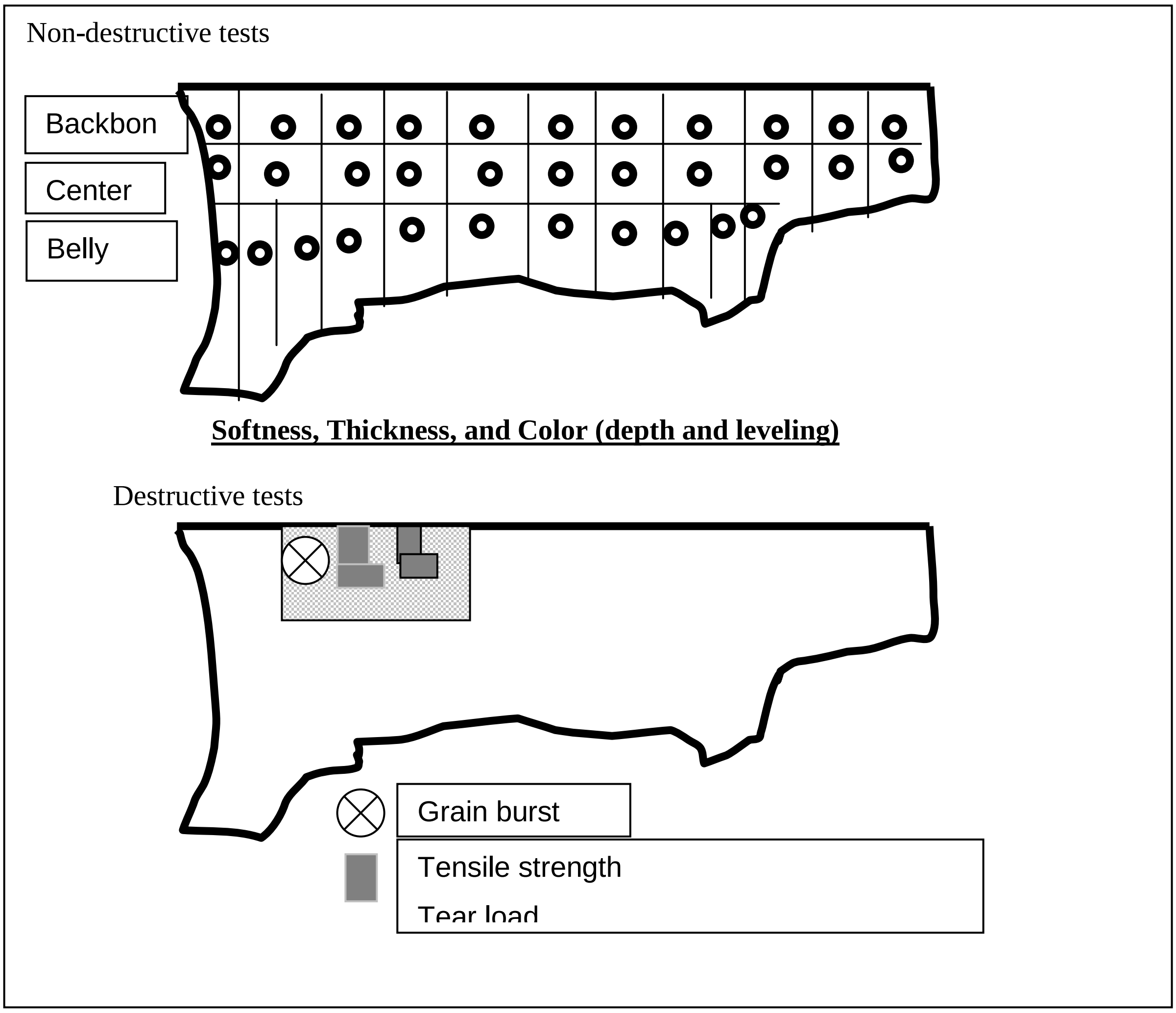

Fig. 3. Property assessment diagram

3. Results and discussion

Test	PROT (%)	SULF (%)	AFF (%)	SOF %Δ	THI %Δ	TLO %Δ	TST %Δ	CDE %Δ	CLE %Δ	GBU %Δ	GFI %Δ
1	0	5	5	4	15	-7	-11	-11	45	0	30
2	5	5	0	2	9	4	-10	-7	33	0	15
3	0	0	10	4	16	-10	-8	-8	46	2	40
4	10	0	0	-8	2	13	-7	-1	30	1	9
5	3.3	3.3	3.3	0	12	0	-10	-9	36	0	28
6	0	10	0	4	14	-1	-12	-15	40	-2	22
7	5	0	5	2	8	1	-9	-7	36	2	29

Table 2. Assessment results

3.1. Degree of softness

The degree of softness was measured with the Softness Tester as per Standard IUP-36. Eleven values were determined in each skin area, totaling 33 measurements.

A linear equation was adjusted to predict the % of variation in the degree of softness (SOF) of the values of the right halves corresponding to retanning agents PROT, SULF and AFF vs. the left halves (reference without retanning agent), and R^2 = 81.31% was obtained.

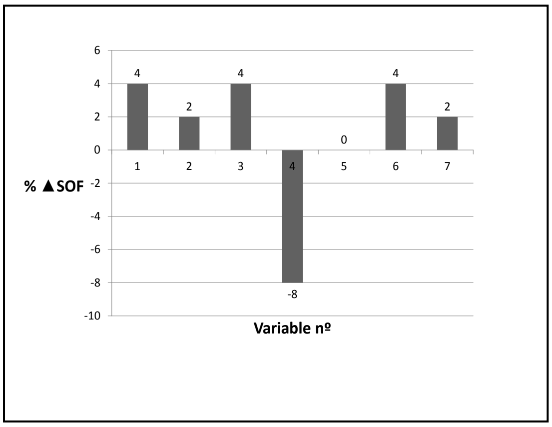

Fig. 4. Variation in the degree of softness

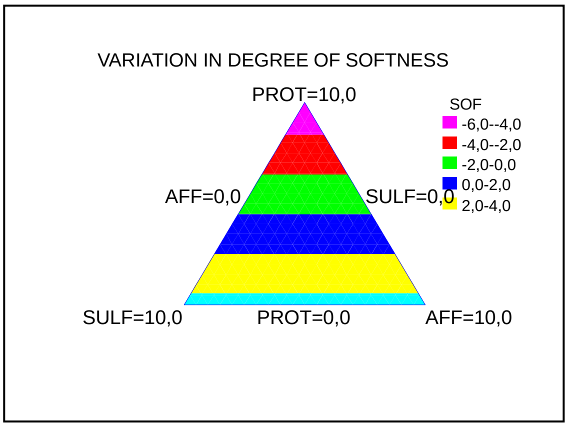

Fig. 5. Optimization of the degree of softness

The results of the variation in the degree of softness are shown in Fig. 4. PROT (nº 4) decreases softness by 8%, while SULF (nº 6) and AFF (nº 3) increase it by 4%.
The optimal areas for the degree of softness are shown in Fig. 5. The 10% PROT vertex depicts negative values that increase as the SULF and AFF ratios are increased.

3.2. Thickness
Thickness was measured as per Standard IUP-4. Eleven values of each skin area were determined, totaling 33 measurements, with R^2= 97.84%.

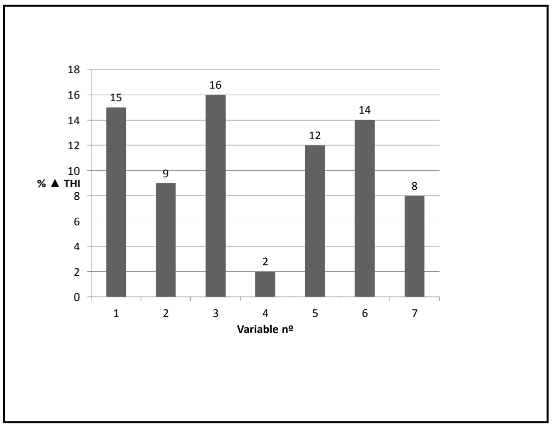

Fig. 6. Variation in thickness

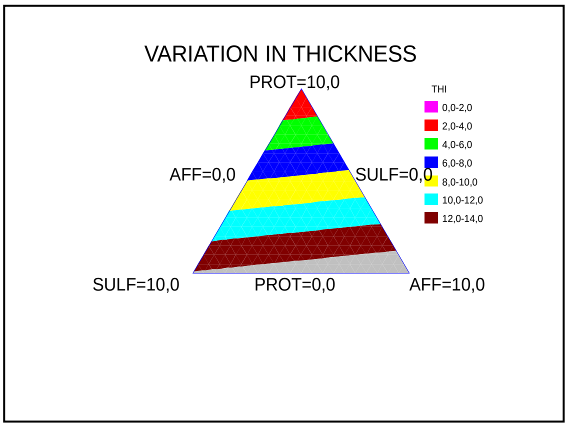

Fig. 7. Optimization of thickness

Thickness variation in absolute values is shown in Fig. 6. Variable 3 (AFF) increases thickness by 16%. Variable 6 (SULF) increases thickness by 14%, while variable 4 (PROT) does so negligibly (2%).
Optimal areas for thickness are shown in Fig. 7. More fullness is found in the vertex with 10% AFF. Thickness values range from 8 to 12% in the low areas of the triangle (AFF and SULF mixtures). These values decrease significantly as PROT is approached.
The significantly increased thickness obtained with AFF and SULF is to be emphasized.

3.3. Tear load.
Assessments were performed as per IUP-8. In this case, R^2= 98.93%.

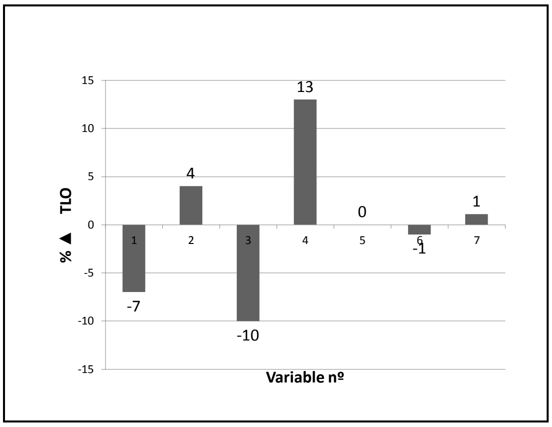

Fig. 8. Variation in tear load

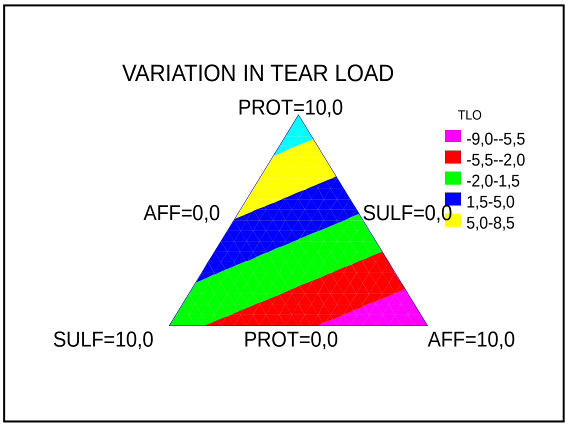

Fig. 9. Optimization of tear load

As shown in Fig. 8, tear load is improved by variable 4 PROT (13%), decreased by variable 3 AFF (10%), and left practically unchanged by variable 6 SULF.

As shown in Fig. 9, the highest values are found in the PROT vertex, and these values are decreased as areas with AFF predominance are reached.

Significant mean values are shown.

3.4. Tensile strength

As per IUP-36. In this case, R^2=88.06%.

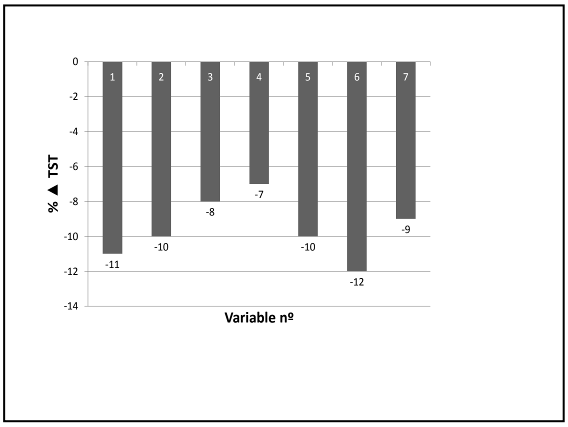

Fig. 10. Variation in tensile strength

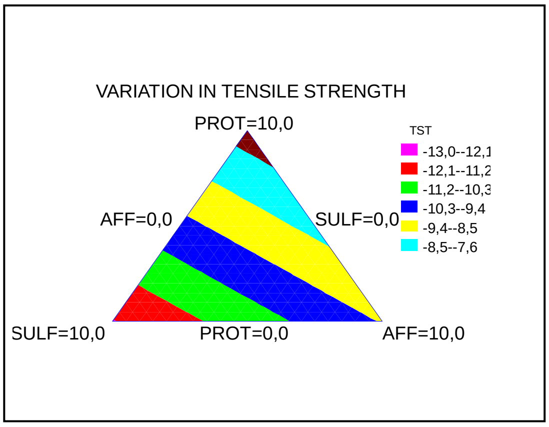

Fig. 11. Optimization of tensile strength

As shown in Fig. 10, tensile strength is decreased by 7%, 8% and 12% by variables 4 PROT, 3 AFF and 6 SULF, respectively.

As shown in Fig. 11, the highest values are found at the PROT vertex. These values decrease as the areas with SULF and AFF predominance are reached.

Significant mean values are shown.

3.5. Color depth

As with degree of softness and thickness, color depth L* was measured at 33 points. In this case, R^2 = 94.06%.

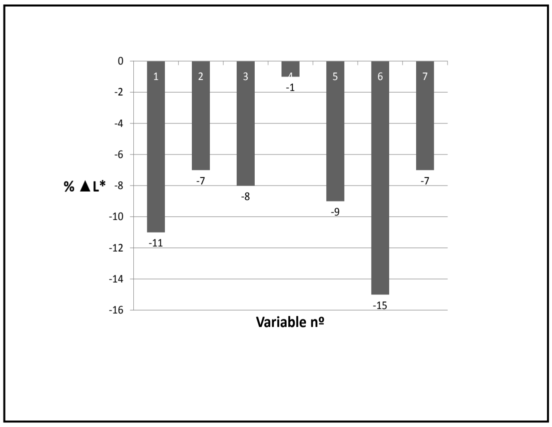

Fig. 12. Variation in color depth

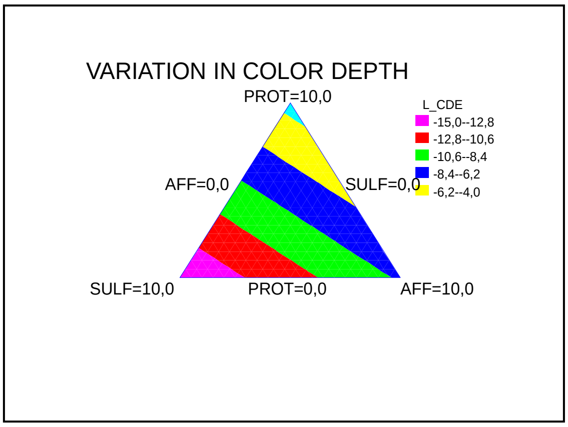

Fig. 13. Optimization of color depth

Fig. 12 shows variation in absolute values. Color depth is decreased by 15%, 8% and 1% by variables 6 SULF, 3 AFF and 4 PROT, respectively.
As shown in Fig. 13, a smaller decrease of color depth is shown in the PROT vertex. This is increased as the AFF vertex is approached, even more so when the SULF area is approached.

Significant mean values are shown.

3.6. Color leveling
This was assessed by measuring total color (E*) at the physical test area and by assessing the difference (Δ E*) with the 10-point values at different areas of the leather.
The values shown in Table 2 correspond to the mean of the measurements of these 10 values of Δ E*. In this case, R^2 = 93.10%.

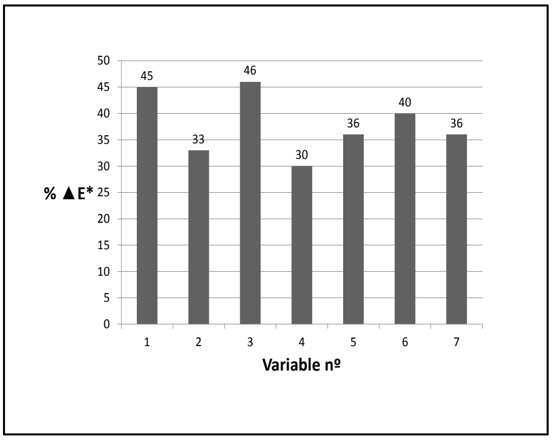

Fig. 14. Variation in color leveling

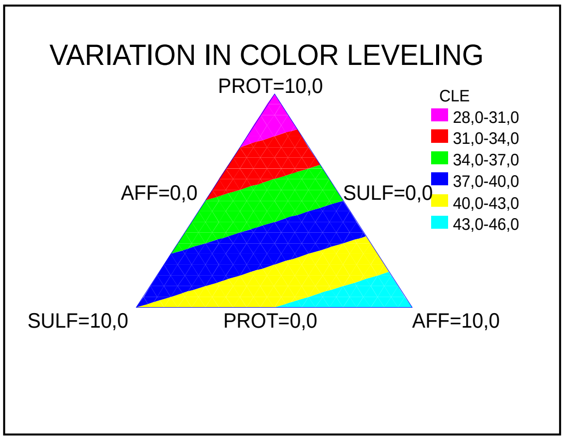

Fig. 15. Optimization of color leveling

As shown in Fig. 14, leveling is improved by 46%, 40% and 30% by variables 3 AFF, 6 SULF and 4 PROT, respectively.
As shown in Fig. 15, maximum color leveling is found in the AFF vertex. Leveling is slightly decreased as the SULF vertex is approached, and becomes less visible as the PROT vertex is approached.

The greatly improved color leveling obtained with all three retanning agents, particularly AFF, is to be emphasized.

3.7. Grain burst
As per IUP-9. In this case, R^2=95.61%.

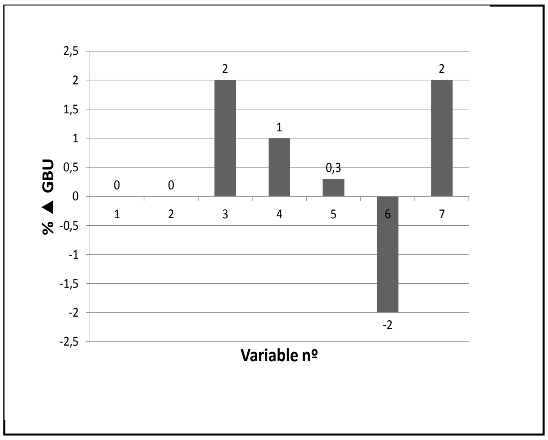

Fig. 16. Variation in grain burst

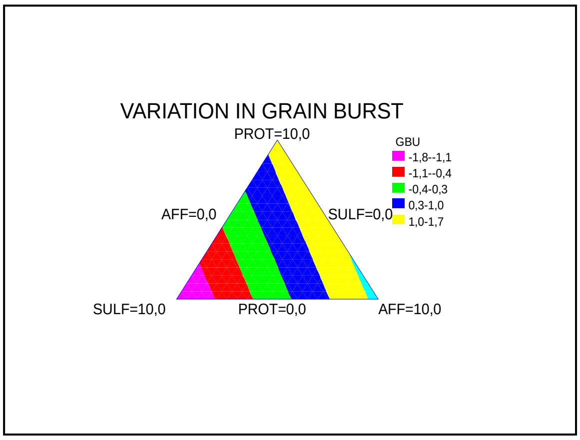

Fig. 17. Optimization of grain burst

As shown in Fig. 16, grain burst is slightly increased by variables 3 AFF and 4 PROT, and slightly decreased by variable 6 SULF. As shown in Fig. 17, higher values are obtained at the AFF vertex and lower values are obtained at the SULF area.

Importantly, very small, little significant variations were obtained with all three retanning agents.

3.8. Grain fineness

A scale to assess grain fineness was defined with a 5-point scale (from low to high) addressing grain uniformity, size, and embossing.

Reference skin without retanning agent (Value 2; left) and skin treated with AFF (Value 5; right) are shown in Photo 1 and 2 below.

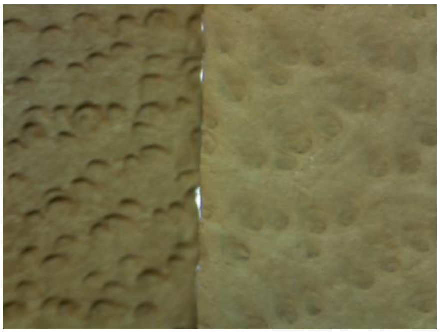

Photo 1. Digital microscope 60x

Photo 2. Microscope 10x

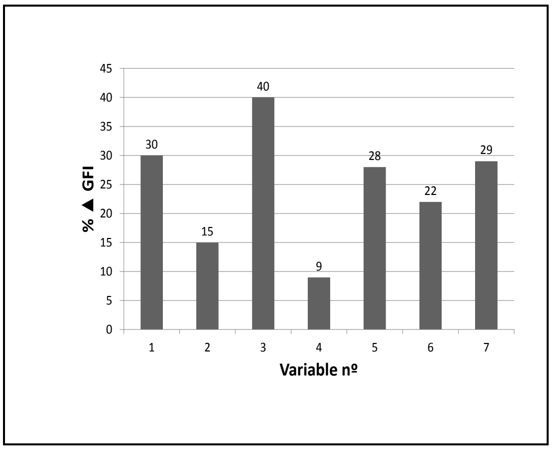

Fig. 18. Variation in grain fineness

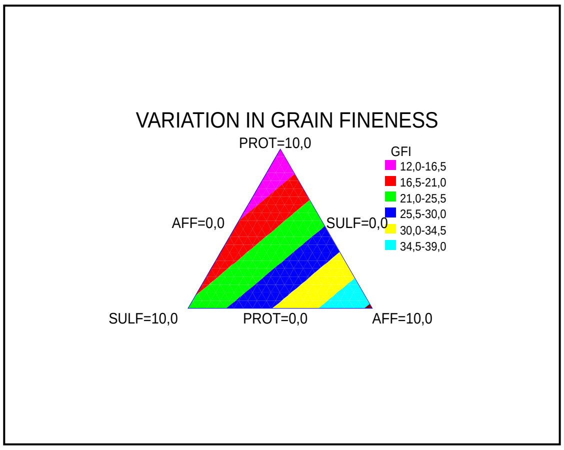

Fig. 19. Optimization of grain fineness

As shown in Fig. 18, fineness is improved by 40%, 22% and 9% with variables 3 AFF, 6 SULF and 4 PROT, respectively.

As shown in Fig. 19, maximum grain fineness is found at the AFF vertex, and is slightly decreased as the SULF vertex is approached. The worst result is obtained at the PROT vertex.

The excellent improvement of color leveling obtained with all three retanning agents, particularly with AFF, is to be emphasized.

4. Conclusions

Amphoteric retanning agent AFF imparts very good fullness without hardening the leather.

When a dihydroxydiphenyl sulfone SULF base is added with reagent groups that give it an amphoteric nature AFF, color depth is increased and color leveling is improved.

When a dihydroxydiphenyl sulfone SULF base is added with reagent groups that give it an amphoteric nature AFF, grain fineness is dramatically increased.

The best results in physical resistance are obtained with amphoteric protein PROT.

5. References

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