

INFLUENCE OF NEUTRALIZATION AND FATLIQUORING PROCESSES ON THE CHARACTERISTICS OF GOATSKINS

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ABSTRACT

The effect of neutralization at three different pH values (4, 5, 6) and that of the fatliquoring agent applied at three different offers (0, 5 and 10 %) on the physical properties of skins was assessed.

A standard process was applied to the left halves of goatskins from Nigeria, whereas the right halves were subjected to the corresponding variables. The variation in the results of each studied property was evaluated.

The statistical analysis of the results obtained in the experimental plan, which was based on a 3² factorial design for two variables at three levels, was carried out by means of the Analysis of Variance (ANOVA), through the Statgraphics Plus Program. The best results of softness and physical resistances were obtained with the highest fatliquoring agent offer (10 %), whereas a 0 % offer was required to obtain the highest colour intensity and grain firmness. The influence of the neutralization pH was not significant on most of the studied properties.

ABSTRACTO

El efecto de neutralizar a tres diferentes valores de pH (4,5 y 6) y el de suministrar el agente engrasante a tres diferentes ofertas (0, 5 y 10%) sobre las propiedades de pieles fue evaluado. Un proceso estándar fue efectuado sobre medias pieles izquierdas caprinas de Nigeria, mientras que las medias pieles derechas fueron sometidas a las correspondientes variables. La variación en los resultados de cada propiedad estudiada fue evaluada. El análisis estadístico de los resultados obtenidos en el plan experimental, el cual se basó en un diseño 3² factorial para dos variables a tres niveles, se ejecutó por medio de Análisis de Varianza (ANOVA), a través del programa Statgraphics Plus. Los mejores

resultados de blandura y resistencias físicas se obtuvieron con la máxima oferta del agente engrasante (10%), mientras que a 0% de oferta se obtuvo máxima intensidad de color y firmeza de flor. La influencia del pH de neutralización no resultó significativa sobre la mayoría de las propiedades estudiadas.

INTRODUCTION

The effect of the different chemical processes on the physical resistances of leather has been considerably studied.

Abuelhassan et al¹ found that the reduction of liming time from 67 to 24 hours gave rise to a decrease in both tensile strength and grain resistance in the lastometer.

Kanagy² found values of tear resistance which were 30 % higher for chrome tanned leather than those for chrome tanned and vegetable retanned leather; other works^{3,4} showed that the higher the leather softness, the better the tensile strength.

As regards the softness effect, studies^{3,5} on drying conditions, humidity and stretching method were carried out; all drying methods that employ a high tension increase the area yield at the expense of a decrease in physical properties.

To study the effect of different chemical processes on physical and organoleptic properties of goatskins from Nigeria, the authors performed this work which was divided in four Parts.

In Part I⁶, the effect of the offer of both vegetable retanning agent and fatliquoring agent on the following properties was assessed: tensile strength, elongation at break and tear resistance for test samples cut in parallel or perpendicularly to the backbone. Likewise other properties such as softness, colour intensity, grain resistance and grain firmness were also evaluated.

In this previous work⁶, it was concluded that the highest tensile strength values corresponded to a 0 % offer of the vegetable retanning agent and to a 10 % offer of the fatliquoring

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agent, whereas the highest values of tear resistance were obtained with a 6 % offer of the vegetable retanning agent and to a fatliquoring agent offer of 10 %. However, the best grain firmness values corresponded to an offer of 0 % of the fatliquoring agent and 6 % of the vegetable retanning agent.

In Part II, the effect of three levels of neutralization (pH=4, 5 and 6) and their interactions with three different offers (0 %, 5% y 10%) of fatliquoring agent on the above mentioned properties will be studied.

EXPERIMENTAL

Materials and Procedure

Wet-blue goatskins from Nigeria of 1 mm thickness and 720 g/skin weight were used. The skins were divided along the backbone. The left halves were subjected to a standard process in which the neutralization pH was maintained at 3.7 and a 6 % offer of fatliquoring agent (FATLQ) was applied. The same process was applied to the right sides but the neutralization pH was studied at three levels (4.0, 5.0 and 6.0)

MECHANICAL OPERATIONS

LEFT HALVES (CONTROL)

Offers on wet-blue weight shaved to 1mm

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 60 min. pH=3.7;
Run-off and Wash 10 min

Dyeing - Fatliquoring

60% Water at 30°C
2% Vegetable retanning agent (B)
Drum 45 min
3.0% Dye
Drum 45 min
100% Water at 60°C
6.0 % Sulphited fish oil (C)
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 1mm

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 60 min. pH=3.7;
Run-off and Wash 10 min

Neutralization

100 % water at 30 °C +
a) 2 % sodium formate. Drum 60 min pH = 4
b) 2 % sodium formate.
1.5 % Sodium bicarbonate. Drum 60 min. pH = 5
c) 2 % sodium formate
2.5 % sodium bicarbonate. Drum 60 min. pH = 6
Run-off and Wash 10 min

Dyeing - Fatliquoring

60% Water at 30°C
2 % Vegetable retanning agent (B)
Drum 45 min
3.0% Dye
Drum 45 min
100% Water at 60°C
0 % - 5 % - 10 % Sulphited fish oil (C)
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

as well as the offer of the fatliquoring agent (0 %, 5 % and 10 %). The offers are based on wet-blue weight shaved to 1 mm. The processes are shown in figure 1. The chemicals used in this work were: A: Ethoxylated Fatty Alcohol (CELESAL DL); B: Vegetable Retanning Agent (RETANAL TRT) (mimosa) and C: Sulphited Fish Oil (FOSFOL AUT).

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

The experiments were programmed in accordance with a 3² factorial design for two variables at three levels. Table 1 shows the nine experiments required by this experimental design.

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 in thirty three points of each half skin by 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. Figure 2 shows the sampling diagram for the assessment of both destructive properties (physical resistances and grain firmness) and non-destructive properties (softness and colour).

The statistical analysis of the results obtained in the experimental plan was carried out by means of the Analysis of Variance (ANOVA), through the Statgraphics Plus Program⁷. The ANOVA partitions the variability into separate pieces for each of the effects, by comparing the mean square against an estimate of the experimental error obtained through the three degrees of freedom of the residual sum of squares because no replications were done. The significance of the effects was given by the Snedecor-F parameter with one and three degrees of freedom.

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:

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

For the discussion of results, three graph types, provided by the Statgraphics Plus Program, were used: i) Main Effects; ii) Variable Interaction and iii) Estimated Response Surface. Although the comments derived from these plots were included in the text, only the "Estimated Response Surface" graphs are shown in this paper for the sake of simplicity.

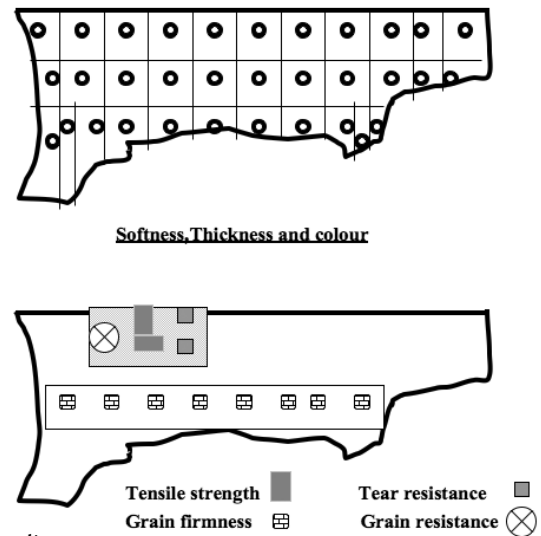


Figure 2. Sampling

TABLE I
Processes of the Experimental Plan

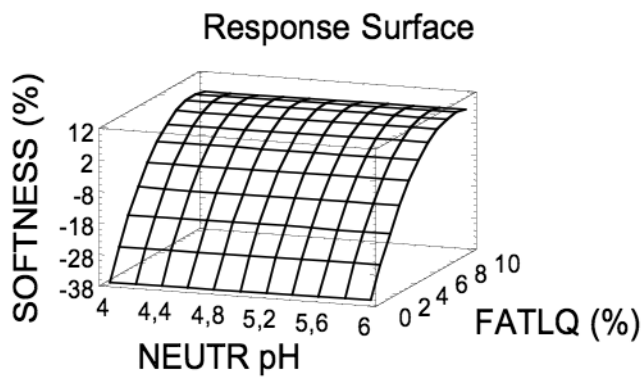
Right Half Processes	Neutralization level(pH)	Fatliquoring Agent (%)
1	4	0
2	5	0
3	6	0
4	4	5
5	5	5
6	6	5
7	4	10
8	5	10
9	6	10

RESULTS AND DISCUSSION

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

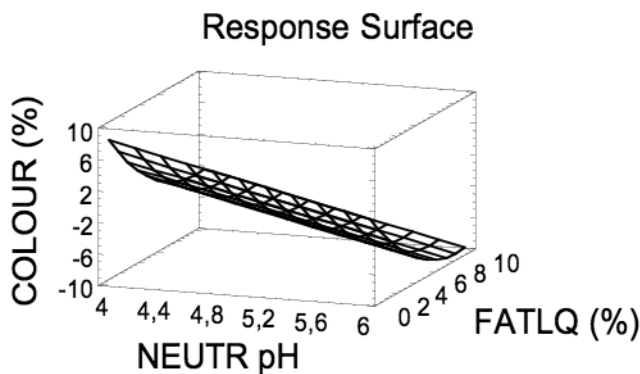
The values of property variation (Δ in %) were used for the statistical analysis of the results, which was carried out with the Statgraphics Plus Program. All the possible linear, quadratic effects and interactions were included in the mathematical model. The non significant variables were excluded from the model to obtain the optimum regression equations. 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 V shows the coefficients of the optimum regression equations, significance levels of the variables and the determination coefficient for all the physical and organoleptic properties over which the studied variables exerted an influence.



NEUTR pH: Neutralization pH; FATLQ: Fatliquoring Agent

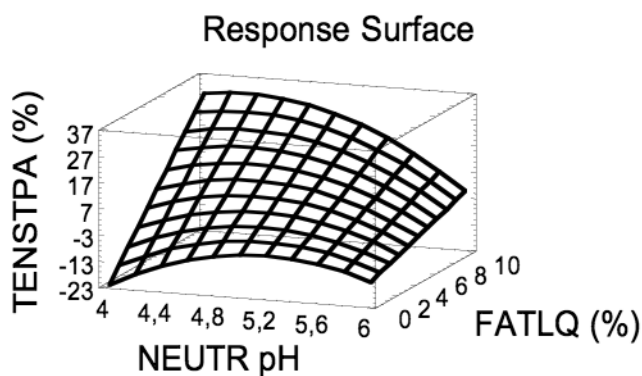
Figure 3. Response surface for softness as a function of neutralisation pH and fatliquoring agent offer



NEUTR pH: Neutralization pH; FATLQ: Fatliquoring Agent

COLOUR: Colour Intensity

Figure 4. Response surface for colour intensity as a function of neutralisation pH and fatliquoring agent offer



NEUTR pH: Neutralization pH; FATLQ: Fatliquoring Agent

TENSTPA: Tensile strength for parallel test samples

Figure 5. Response surface for tensile strength for parallel test samples as a function of neutralisation pH and fatliquoring agent offer

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.

Softness

Eleven determinations in each area of the half skin were carried out, which resulted in a total of thirty three determinations.

Formula 1 was applied to compare the right half values with those of the left halves (control).

As shown in table V the determination coefficient (R^2) for this property was 92.9 %. This Table also reveals that the influence exerted by the neutralization pH was not significant. The fatliquoring agent offer exerted an influence which was significant at the level of 0.1%.

Softness remained practically constant for any neutralization pH and increased from -37 % to +7 % when the fatliquoring agent offer varied from 0 % to 10 %.

Figure 3 shows that the highest softness values corresponded to a fatliquoring agent offer of approximately 10 %; however, it remained practically constant at any neutralization pH.

Colour intensity

Values of the right halves were compared with those of the left halves by means of formula 1. A determination coefficient (R^2) value of 88.1 % was obtained as shown in Table V. The neutralization pH exerted an influence which was significant at the level of 5 %, whereas that of the fatliquoring agent was significant at the 1 % significance level.

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

The colour intensity decreased from 0 % to - 8 % when the neutralization pH varied from 4.0 to 6.0. Likewise, this property also decreased from + 5 % to - 6 % for increasing offers of the fatliquoring agent.

The highest colour intensity corresponded to a neutralization pH of 4.0 and to a fatliquoring agent offer of 0 % as observed in figure 4.

Tensile strength and percentage of elongation at break

a) Tensile strength

a-1) Parallel test samples

Table V shows that the determination coefficient (R^2) obtained for this property was 92.5 %. This Table also reveals that the influence exerted by the neutralization pH was not significant, whereas that exerted by the fatliquoring agent offer was significant at 1 % significance level.

The tensile strength for parallel test samples increased from + 4 % to + 10 % when the neutralization pH varied from 4.0 to 5.0. However, tensile strength decreased when neutralization

TABLE II

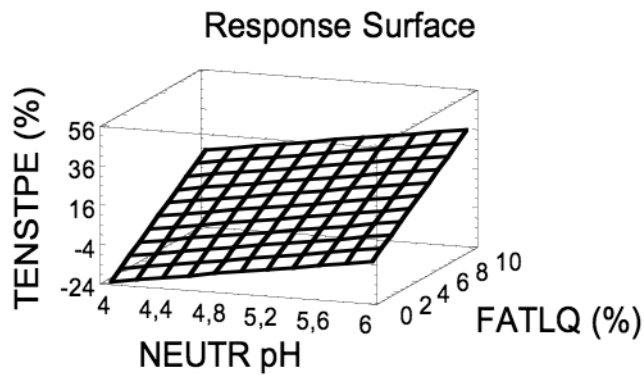
Average of the measured values, standard deviation and property variation for treatments 1 - 3

Property	Units	Treatment 1			Treatment 2			Treatment 3		
		Right half (variable)	Left half (control)	Δ (%) (formula 1)	Right half (variable)	Left half (control)	Δ (%) (formula 1)	Right half (variable)	Left half (control)	Δ (%) (formula 1)
Softness										
	mm	3.9±0.22	5.9±0.34	-33.9	4.0±0.23	6.0±0.37	-33.3	3.5±0.19	6.2±0.33	-43.5
Colour Intensity										
	L*	71.0±3.34	65.0±3.12	9.2	64.8±3.18	62.0±3.10	4.5	61.0±2.75	61.0±2.81	0.0
Tensile Strength										
Parallel	N/mm ²	23.2±0.88	28.7±1.03	-19.2	26.1±1.04	29.0±1.10	-10.0	25.3±0.89	27.4±0.93	-7.7
Perpend.	N/mm ²	12.9±0.48	20.2±0.81	-36.1	19.0±0.74	21.7±0.78	-12.4	20.1±0.72	19.8±0.75	1.5
Elong. at break										
Parallel	%	17.0±1.16	25.0±1.65	-32.0	19.8±1.29	26.4±1.69	-25.0	19.3±1.37	24.8±1.69	-22.2
Perpend.	%	56.0±3.64	74.7±4.86	-25.0	56.2±3.77	75.0±5.18	-25.1	68.0±4.83	73.2±5.20	-7.1
Tear resistance										
Parallel	N	40.3±1.41	47.0±1.69	-14.3	49.2±1.87	47.8±2.06	2.9	42.2±1.56	48.0±1.63	-12.1
Perpend.	N	34.8±1.15	58.0±2.20	-40.0	36.6±1.28	57.2±2.06	-36.0	43.0±1.63	59.0±2.01	-27.1
Grain Resistance										
	mm	6.96±0.13	8.70±0.19	-20.0	6.08±0.13	8.20±0.15	-25.9	6.58±0.12	7.90±0.12	-16.7
Grain firmness										
	(0-10)	6.46±0.29	6.00±0.25	7.7	7.24±0.33	6.80±0.32	6.5	5.35±0.25	5.20±0.23	2.9

TABLE III

Average of the measured values, standard deviation and property variation for treatments 4 - 6

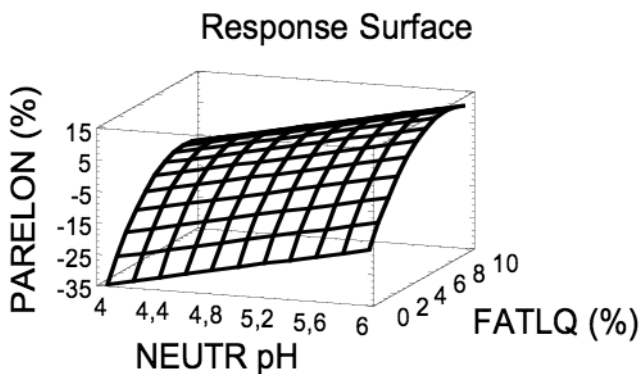
Property	Units	Treatment 4			Treatment 5			Treatment 6		
		Right half (variable)	Left half (control)	Δ (%) (formula 1)	Right half (variable)	Left half (control)	Δ (%) (formula 1)	Right half (variable)	Left half (control)	Δ (%) (formula 1)
Softness										
	mm	6.1±0.35	6.6±0.40	-7.6	5.8±0.32	5.8±0.34	0.0	6.5±0.35	6.2±0.34	4.8
Colour Intensity										
	L*	60.3±2.89	59.0±2.77	2.2	58.5±2.93	63.0±3.28	-7.1	59.7±2.75	64.0±3.07	-6.7
Tensile Strength										
Parallel	N/mm ²	28.3±1.16	27.5±1.16	2.9	26.0±0.96	25.0±0.93	4.0	22.8±0.89	26.4±0.92	-13.6
Perpend.	N/mm ²	21.5±0.88	20.1±0.70	7.0	19.8±0.75	19.0±0.74	4.2	25.0±0.88	20.5±0.76	22.0
Elong. at break										
Parallel	%	23.0±1.54	25.6±1.79	-10.2	25.9±1.79	27.3±1.77	-5.1	28.8±1.90	25.3±1.75	13.8
Perpend.	%	71.8±4.74	76.4±5.20	-6.0	70.8±4.67	74.3±4.76	-4.7	54.7±3.83	72.8±4.88	-24.9
Tear resistance										
Parallel	N	46.7±1.96	46.5±2.09	0.4	51.3±2.00	45.0±1.67	14.0	43.1±1.59	49.0±1.91	-12.0
Perpend.	N	63.5±2.73	57.8±2.31	9.9	49.5±1.73	56.6±2.15	-12.5	56.5±2.15	58.9±2.41	-4.1
Grain Resistance										
	mm	6.58±0.14	8.90±0.20	-26.1	7.54±0.14	7.60±0.14	-0.8	9.49±0.15	9.10±0.18	4.3
Grain firmness										
	(0-10)	6.70±0.28	6.70±0.29	0.0	7.00±0.34	7.00±0.34	0.0	6.28±0.27	5.90±0.28	6.4



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent

TENSTPE: tensile strength for perpendicular test samples

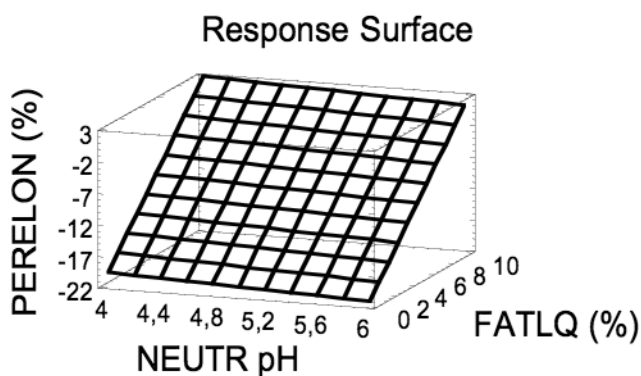
Figure 6. Response surface for tensile strength for perpendicular test samples as a function of neutralisation pH and fatliquoring agent offer



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent

PARELON: elongation at break for parallel test samples

Figure 7. Response surface for elongation at break for parallel test samples as a function of neutralisation pH and fatliquoring agent offer



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent

PERELON: elongation at break for perpendicular test samples

Figure 8. Response surface for elongation at break for perpendicular test samples as a function of neutralisation pH and fatliquoring agent offer

pH approached to 6.0. By contrast, this property strongly increased from - 8 % to + 26 % when the fatliquoring agent offer varied from 0 % to 10 %.

An interaction between both variables, which was significant at 10 % level, was found for this property. For a fatliquoring agent offer of 0 %, tensile strength values increased from - 23 % to -7 % when the neutralization pH varied from 4.0 to 5.0 and decreased to - 13 % for a neutralization pH of 6, whereas for a fatliquoring agent offer of 10 %, the tensile strength decreased from + 31 % to + 1 % when the neutralization pH varied from 4.0 to 6.0.

The highest tensile strength values corresponded to a neutralization pH of approximately 5.0 and to a fatliquoring agent offer of 10 % as observed in figure 5.

a-2) Perpendicular test samples

Table V shows that a determination coefficient value (R^2) of 78.6 % was obtained. The influence exerted by the fatliquoring agent offer on this property was highly significant (significance level of 1 %), whereas that exerted by the neutralization pH was significant at the 10 % level.

The tensile strength values for perpendicular test samples increased from -4 % to +16 % when the neutralization pH varied from 4.0 to 6.0; however, this increase was more marked, from -14 % to + 26 %, for increasing offers of the fatliquoring agent.

Figure 6 reveals that the highest values of tensile strength corresponded to a neutralization pH of 6.0 and to a fatliquoring agent offer of 10 %.

b) Percentage of elongation at break

b-1) Parallel test samples

The determination coefficient (R^2) value obtained was 94.9 % as shown in Table V. The influence exerted by both variables neutralization pH and fatliquoring agent offer was very significant with significance levels of 1% and 0.1 %, respectively.

The elongation at break increased from -9 % to +8 % when the neutralization pH varied from 4.0 to 6.0. Likewise, this property strongly increased from - 26 % to + 5 % when the fatliquoring agent offer varied from 0 % to 8 %. For a fatliquoring agent offer of 10 %, it decreased up to + 3 %.

The highest elongation at break values corresponded to a fatliquoring agent offer of 8 % and to a neutralization pH of 6.0 as shown in figure 7.

b-2) Perpendicular test samples

Table V shows that the determination coefficient (R^2) value obtained was 57.9 %. The influence exerted by the neutralization pH was not significant, whereas that exerted by the fatliquoring agent offer was significant at the significance level of 5 %.

The elongation at break for perpendicular test samples

TABLE IV

Average of the measured values, standard deviation and property variation for treatments 7 - 9

Property	Units	Treatment 7			Treatment 8			Treatment 9		
		Right half (variable)	Left half (control)	Δ (%) (formula 1)	Right half (variable)	Left half (control)	Δ (%) (formula 1)	Right half (variable)	Left half (control)	Δ (%) (formula 1)
Softness										
	mm	6.8±0.41	6.6±0.38	3.0	7.8±0.44	6.8±0.36	14.7	6.2±0.36	6.1±0.34	1.6
Colour Intensity										
	L*	58.6±2.75	60.0±3.06	-2.3	56.5±2.77	62.0±3.04	-8.9	57.0±2.62	61.0±3.05	-6.6
Tensile Strength										
Parallel	N/mm ²	36.2±1.30	28.3±1.10	27.9	34.8±1.46	26.0±1.04	33.8	28.2±1.13	27.9±1.00	1.1
Perpend.	N/mm ²	23.7±0.88	21.2±0.89	11.8	29.5±1.18	21.1±0.76	39.8	23.5±0.92	19.6±0.76	19.9
Elong. at break										
Parallel	%	24.7±1.73	26.9±1.91	-8.2	29.9±2.03	28.3±1.87	5.7	32.1±2.12	29.4±2.06	9.2
Perpend.	%	81.7±5.56	75.6±5.29	8.1	76.2±5.41	78.0±5.30	-2.3	79.8±5.51	76.2±5.03	4.7
Tear resistance										
Parallel	N	45.2±1.72	44.2±1.81	2.3	56.4±2.20	45.6±1.73	23.7	52.8±2.11	42.8±1.80	23.4
Perpend.	N	63.7±2.74	54.0±2.43	18.0	85.9±3.35	56.2±2.08	52.8	62.0±2.39	60.1±2.16	3.2
Grain Resistance										
	mm	8.97±0.19	8.50±0.16	5.5	8.33±0.12	7.70±0.13	8.2	8.71±0.17	8.80±0.18	-1.0
Grain firmness										
	(0-10)	6.42±0.31	6.30±0.28	1.9	7.23±0.33	7.02±0.32	3.0	5.66±0.24	5.90±0.27	-4.1

TABLE V

Regression Coefficients, Determination Coefficients and Significance Levels of the Variables for the Physical and Organoleptic Properties

Effect	Softness	Colour	Tensile Strength		Elongation at Break		Tear Resistance		Grain Resistance	Grain Firmness
			Parallel	Perpend.	Parallel	Perpend.	Parallel	Perpend.		
Constant	- 38.07	23.23	- 296.22	- 63.92	- 69.07	- 16.76	- 397.28	- 20.24	- 43.27	9.08
Neutralization										
pH.: V ₁	0.23	- 3.73 ^c	111.28	10.12 ^d	8.53 ^b	- 0.73	157.65	- 2.65	4.53	- 0.73
Fatl.										
Ag.: V ₂	10.05 ^a	- 2.32 ^b	12.90 ^b	3.95 ^b	7.50 ^a	2.26 ^c	2.43 ^c	5.90 ^b	2.51 ^c	- 0.54 ^d
V ₁ ²	-	-	- 10.70 ^d	-	-	-	- 15.58 ^c	-	-	-
V ₁ x V ₂	-	-	- 1.92 ^d	-	-	-	-	-	-	-
V ₂ ²	- 0.57 ^c	0.13	-	-	- 0.46 ^c	-	-	-	-	-
R ²	92.9	88.1	92.5	78.6	94.9	57.9	80.6	76.6	68.3	41.4
R ² adj.	88.6	80.9	84.9	71.5	91.9	43.9	69.0	68.8	57.7	21.9

Significance levels: ^a0.1 %; ^b1 %; ^c5 %, ^d10

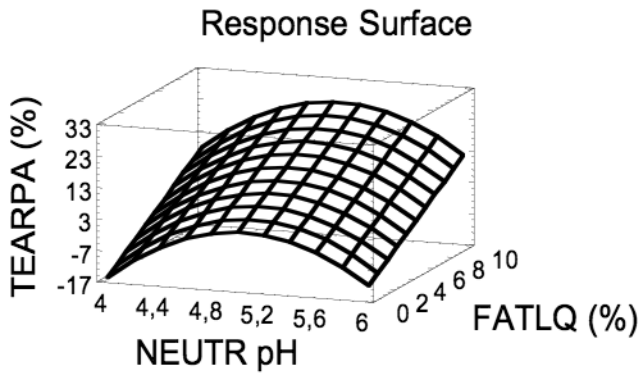
remained practically constant when the neutralization pH varied from 4.0 to 6.0. However, it strongly increased from -20 % to +2 % for increasing offers of the fatliquoring agent.

Figure 8 shows that the highest elongation at break values corresponded to a fatliquoring agent offer of 10 % and it remained practically constant at any neutralization pH.

Tear Resistance

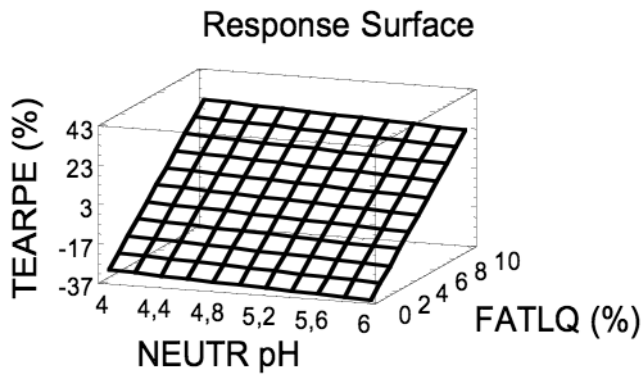
a) Parallel test samples

The determination coefficient (R²) value obtained was 80.6 % as observed in Table V. The fatliquoring agent offer was the variable that exerted a significant influence on this property (significance level of 5 %). The influence exerted by the neutralization pH was not significant.



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent
TEARPA: Tear resistance for parallel test samples

Figure 9. Response surface for tear resistance for parallel test samples as a function of neutralisation pH and fatliquoring agent offer



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent
TEARPE: Tear resistance for perpendicular test samples

Figure 10. Response surface for tear resistance for perpendicular test samples as a function of neutralisation pH and fatliquoring agent offer

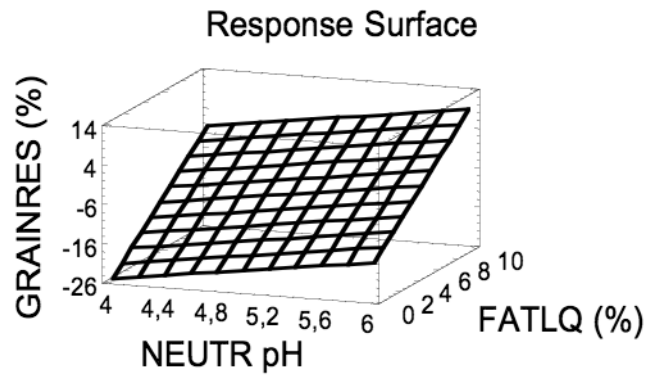
A maximum tear resistance (+14 %) was obtained at a neutralization pH of 5.2. Tear resistance also increased from +2 % to +26 % when the fatliquoring agent offer increased from 0 % to 10 %.

Figure 9 shows that the highest tear resistance corresponded to a neutralization pH value of 5.2 approximately and to a fatliquoring agent offer of 10 %.

b) Perpendicular test samples

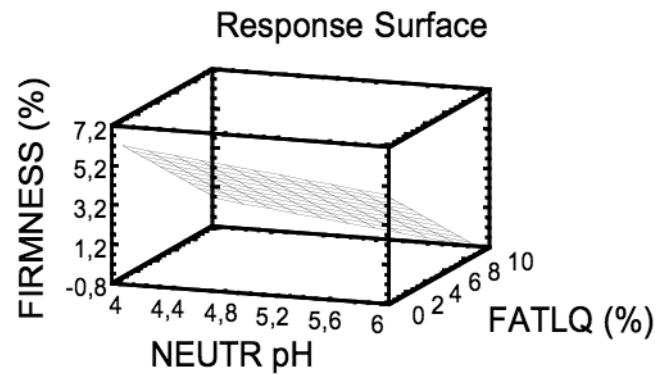
Table V shows that a determination coefficient value (R^2) of 76.6 % was obtained. The variation of the neutralization pH from 4.0 to 6.0 had no influence on the tear resistance for perpendicular test samples. However, the influence exerted by the fatliquoring agent offer on this property was highly significant (significance level of 1 %).

Tear resistance slightly decreased from -1 % to -6 % when the neutralization pH varied from 4.0 to 6.0. This property strongly



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent
GRAINRES: Grain resistance

Figure 11. Response surface for grain resistance as a function of neutralisation pH and fatliquoring agent offer



NEUTR pH: Neutralization pH; **FATLQ:** Fatliquoring Agent
FIRMNESS: Grain firmness

Figure 12. Response surface for grain firmness as a function of neutralisation pH and fatliquoring agent offer

increased from - 33 % to +26 % when the fatliquoring agent offer increased from 0 % to 10 %

Figure 10 shows that the highest tear resistance values for perpendicular test samples corresponded to a fatliquoring agent offer of 10 % and to a neutralization pH value of 4.0, although the difference in the pH interval from 4.0 to 6.0 was very small.

Grain resistance

A R^2 (determination coefficient) value of 68,3 % was obtained, as shown in Table V. The influence exerted by the neutralization pH was not significant. The variation of the fatliquoring agent offer from 0 % to 10 % exerted an influence on the grain resistance which is significant at the 5 % significance level.

Grain resistance considerably increased from - 20 % to + 5 % when the fatliquoring agent offer increased from 0% to 10%. This increase was less marked from -13 % to -3 % when the neutralization pH varied from 4.0 to 6.0.

Figure 11 reveals that the highest grain resistance values corresponded to a 10 % fatliquoring agent offer and to a neutralization pH of 6.0.

Grain firmness

The determination coefficient (R^2) value obtained was 41.4 % as observed in Table V. This Table also shows that the influence exerted by the neutralization pH was not significant, whereas that of the fatliquoring agent offer was significant at the 10 % significance level.

Grain firmness decreased from + 5.4 % to - 0.1 % when the fatliquoring agent offer increased from 0.0 % to 10 %, whereas grain firmness decreased from + 3.4 % to + 2 % when the neutralization pH varied from 4.0 to 6.0.

The highest grain firmness values corresponded to a 0% offer of the fatliquoring agent and to a neutralization pH of 4.0, although the difference in the pH interval from 4.0 to 6.0 was very small, as observed in figure 12.

A comparison between softness and grain firmness values reveals that the higher the softness, the lower the grain firmness. It seems evident that an increase in softness improves the physical resistances and impairs the grain firmness. Offers of 10 % and 0 % of the fatliquoring agent were required to obtain the best softness and grain firmness values, respectively; whereas both properties remained practically constant for any neutralization pH between 4.0 and 6.0.

CONCLUSIONS

The interaction between neutralization pH and fatliquoring agent offer allows us to draw the following conclusions:

The influence of the neutralization pH variation from 4.0 to 6.0 was not significant on most of the studied properties. It was significant on colour intensity (5 % significance level), tensile strength for perpendicular to the backbone test samples (10 % significance level) and elongation at break for parallel to the backbone test samples (1% significance level).

The fatliquoring agent variation from 0 % to 10 % exerted an influence which was significant on all the studied properties at different levels: significance level of 0.1 % for softness and elongation at break for parallel test samples; significance level of 1 % for colour intensity, tensile strength for parallel/perpendicular test samples and tear resistance for perpendicular test samples; significance level of 5 % for elongation at break for perpendicular test samples, tear resistance for parallel test samples and grain resistance and significance level of 10 % for grain firmness.

The highest physical resistances values, including softness, were obtained with a 10 % fatliquoring agent offer, whereas a 0 % offer was required for the best colour intensity and grain firmness to be obtained.

The variation of the neutralization pH from 4.0 to 6.0 did not provide any difference on: softness, elongation at break for perpendicular test samples and grain firmness. A neutralization pH of 4.0 was necessary to obtain the best results of colour intensity and tear resistance for perpendicular test samples, whereas the best results of tensile strength for perpendicular test samples, elongation at break for parallel test samples and grain resistance were obtained at a neutralization pH of 6.0. An intermediate pH of 5.0 provided the best results of tear resistance and tensile strength both for parallel test samples.

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