Effect of Fatliquoring on Grain and Corium Quality of Leather Assessed by Ball Bursting and Tearing Tests

by

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Abstract

Leather quality depends largely on the physical, mechanical and organoleptic characteristics of the finished leather from which the final articles are manufactured. Tearing strength and ball burst tests are especially relevant for leather goods that will be subjected to significant tearing and bursting stresses during use.

The influence of different fatliquors on tearing and ball burst tests is studied using wet-blue leathers from Ireland as starting material. Leathers were retanned and dyed following a conventional process and then, they were fatliquored with nine different fatliquoring agents provided by Trumpler Española. A 7% of active matter (on shaved weight) was applied. After a final washing, a sample of the treated leathers was kept in "crust" state (without finishing), and the rest received a light finishing process following a conventional recipe.

To estimate differences between sides, the central parts of them were fatliquored with the same combination used as reference (sulphited triglycerides of rapeseed oil/fatty polymer). The characteristic components of the fatliquoring agents used were a) Soy lecithin, b) Sulphited triglycerides of rapeseed oil, c) Acrylic polymer (waterproofing agent), d) Fatty Polymers (sarcosinates), e) Sulphated triglycerides of rapeseed oil, f) Phosphoric Ester, g) C_{14} Paraffin, h) Sulphonated paraffin, and i) Sulphited fish oil.

Based on the experimental results, treatments with similar effects on tearing and ball burst test behavior were grouped, clustering the fatliquors with similar effects on these characteristics when compared with the results of the non-fatliquored leather. The effect of finishing has also been studied.

Introduction

The quality of leather depends largely on the physical and mechanical characteristics of the finished leather from which the final articles are manufactured.[1] Leather finds wide application as a quality material for shoes, clothing, upholstery, luggage, bags, etc. The ability to withstand tearing forces is one of the most significant mechanical properties required for leather products, particularly those used in footwear and upholstery. It is generally accepted that leather shows a satisfactory tearing resistance; however, there are circumstances when susceptibility to tearing is a problem especially when tearing is combined with humidity and temperature as occurs during lasting operation of shoe making. The small cracks that can be caused in the grain layer are detrimental to the appearance, wear and life of the shoe. Tearing strength and grain crack load has to be considered as parameters, which can condition the final application of leather. The initiation and subsequent propagation of cracks in tearing and ball burst test of leather is also studied in many materials that will be subjected to these kinds of stresses during use, in order to assure a satisfactory performance.

Cracks in the grain surface of finished leather are undesirable for aesthetic values as well as the durability and service expectancy of leather products. To assess the initiation of cracks in the grain surface of leather, the lastometer ball burst test simulates conditions experienced during the lasting operation in footwear manufacture. However, the lastometer test is not a true fracture toughness test as it mainly identifies the strength and distension of the grain and does not address the initiation and subsequent propagation of cracks as is normally the case in fracture toughness tests. Nevertheless, if lastometer progresses up to leather bursting, the energy spent up to bursting includes the contribution of the energy spent in the formation of the crack induced in leather up to the end of the test.

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The mobility between macromolecules or fibers may considerably influence the tear and burst properties of leather. The introduction of filler may influence leather behavior by modifying the secondary forces between macromolecules and fibers.[2] The effect of fatliquoring on leather compressibility and softness that also depends on fiber mobility was studied and the application of cluster analysis enabled to group fatliquors with similar effects on these parameters.[3]

The study of the behavior of leather subjected to tear and ball burst tests is important because is a common mode of mechanical failure in service.[4] The greater ability of the corium layer's fiber structure to impede propagating tears by means of tear tip blunting and fiber pull out can be modified by fatliquoring. Fatliquors, that are added to leather for similar reasons as plasticizers to polymers (the improvement of their flow properties),[5] enhances fiber mobility due to the reduction of the friction between fibers[4] and prevents fiber adhesion by filling the spaces between the network structure, resulting in a greater fiber mobility.[4]

Crack Increase in Tearing and Energy

Rivlin and Thomas have developed the relationship between tearing strength and structure of polymeric materials. They apply the critical stress and the Griffith's criteria[6] for the study of tearing in rubber. A cut will spread increasing crack if the energy stored elastically by deformation is greater than the increase in surface free energy due to the formation of the new surface linked to the crack increase. The increase in surface free energy per unit area is characteristic of the material and can be considered as the energy expended irreversibly per unit increase in the length of the tear and per unit thickness of the sheet.

By suitable choice of the shape and dimensions of the test-piece, the relationship between the surface free energy ***TE*** with the increase in length of the tear ***dc*** in a sheet of thickness ***h*** and the work ***dW*** done by the tearing force is ***TE.h.dc = dW***. The equation can be applied to continuous tearing, and ***TE*** will, presumably, be a function of the rate.[7] Thomas tested[8] the validity of the surface free energy in tearing under a variety of conditions and polymers.

It is reasonable to assume that the energy consumed in pulling fibers from the entangled mass of fibers can be modified by the addition of plasticizers or fatliquors. The situation is analogous to synthetic fiber composites where the degree of fiber pull out from the matrix is regarded as an important factor controlling the strength of the composites.[1]

Bursting Behavior, Grain Crack and Energy

The ball burst test causes a multidimensional increase of the sample that is stretched in all directions by the application of tensile, bending and shearing stresses forcing the network of fibers to move between them.[9] At the tip of the round ball the maximum stress is concentrated and causes grain crack that progresses up to final failure of leather. The test reflects the behavior of the grain and corium layers of leather.

The energy measured under the load–extension curve gather together the influence of elastic stored energy, the energy lost by fiber migration that results in bagginess and the energy spent in the formation of the surface of crack that progresses up to bursting. Besides the parameters given by the test (load and distension of grain crack and bursting) it seems interesting to consider the energy required to complete the test, how is modified by fatliquoring and finishing and how it is related with the surface free energy determined in tearing.

Objectives

This study concerns with the influence of different fatliquoring agents and finishing on the behavior of the grain and corium layers of leather when subjected to tearing and ball burst tests and their relationship, according to the fatliquors, and finishing. Treatments with similar effects will be grouped by the application of cluster analysis.

MATERIALS

The experimental work was carried out at the pilot plant of Trumpler Española SA. Five wet-blue sides from Ireland, shaved to a thickness of 1.2-1.4 mm, were used. After washing, rechroming and neutralization, leathers were retanned and dyed following a conventional process and, then, they were fatliquored with nine fatliquoring agents of different chemical composition. In order to compare the effect of the different fatliquoring agents, a fatliquoring mixture (used as control) was applied on each side. In this way, differences attributable to differences in substrate may be compensated.

Sides were cut perpendicularly to the backbone in three samples (zones) of similar size. Thus, three zones (upper, central, lower) were separated from each side as shown in Figure 1. The "control" fatliquoring mixture was applied to the central zone of the five sides and the upper and lower zones were fatliquored with different fatliquoring agents, facilitating the comparison of the effect of these products. The central areas have also allowed characterizing the differences in tearing and ball burst behavior that can be attributed to the fact of being different sides (leathers). The lower zone of the last side was not fatliquored. This sample acted as a "blank" test, which was used to estimate the effect of the fatliquoring process on the parameters of tearing and ball burst test.

The fatliquoring process was carried out by applying 7% of active matter on shaved weight. A final fixation with chromium was applied in those fatliquoring agents that required it. After a final washing, tearing and ball burst tests were determined on a sample separated from each of the treated leathers once dried. To evaluate the effect of the finishing operation on the studied properties, a light finishing process was applied to each of the treated leathers as shown in Figure 1.

The characteristic components of the fatliquoring agents used were as follows:

- Soy lecithin ***LES***
- Sulphited triglycerides of rapeseed oil ***TCSi***
- Acrylic polymer (including polysiloxanes) ***ACR***
- Fatty Polymers (including sarcosinates) ***PGR***
- Sulphated triglycerides of rapeseed oil ***TCSa***
- Phosphoric Ester ***ESF***
- C_{14} Paraffin ***C14***
- Sulphonated paraffin ***PSn***
- Sulphited fish oil ***PSi***

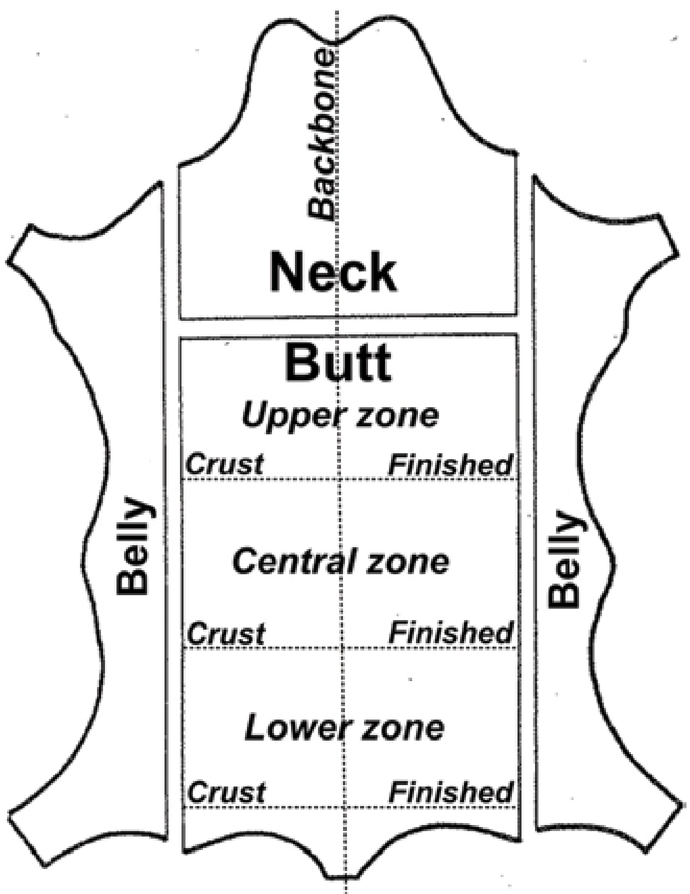

Figure 1. Upper, central and lower zones of a cow hide butt, used to apply different fatliquoring agents. Zones were cut in half and the half right finished. Differences between hides were estimated by comparing the central zones of the five sides fatliquored with the same "control" fatliquoring mixture.

A combination of sulphited triglycerides of rapeseed oil and fatty polymer (***TCSi/PGR***) was the standard fatliquoring agent (reference), which was applied to the central zone of each one of the five sides.

METHODS

Tear behavior: Leather samples cut as a rectangle 50 mm long and 25 mm wide using a press knife, which cuts out the specimen with a slot that enables its fixation in jaws for tearing. Three samples in perpendicular and in parallel directions were cut and fixed on jaws that are separated at a constant speed causing the leather to tear completely. The test is performed according to the ISO 3377-2:2002 (IULTCS/IUP 8) standard (10). The load extension plot is similar to that shown in Figure 2. The following results are obtained:

- ***ThT*** (mm): Thickness of the sample measured according to the ISO2589:2002 (IULTCS/IUP 4) standard.
- ***C*** (mm): Length of the crack growth during tear test.
- ***TL*** (N): Tear Load (cfr. Fmax in Figure 2), the maximum reached load.
- ***TS*** (N/mm): Tear Strength given by the ratio ***TL*** / ***ThT***.
- ***TW*** (mJ): Tear Work; the area under the load/extension curve during the crack growth.
- ***TE*** (mJ/mm^2 or N/mm): Surface free energy in tearing given by ***TW*** / (***C*** × ***ThT***)

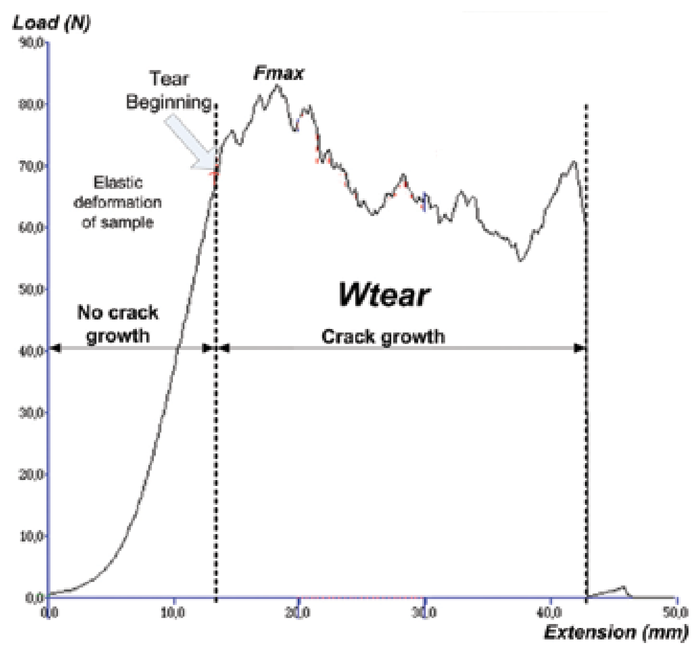

Figure 2. Tear plot of leather sample given by the dynamometer MT-LQ according to the ISO 3377-2:2002 (IUP 8) standard. Tear load is the maximum Fmax load reached, and the area below the curve during crack growth is the work of tear Wtear.

Ball burst behavior: The test is mainly focused on assessing the performance of the leather in the upper side using a Lastometer (developed by SATRA). The leather is progressively deformed until the first crack on the grain layer appears, acquiring thus a conic shape inducing a combination of multidirectional stretching with bending and shearing stresses on the sample. The test is not stopped until the total leather burst is reached. The trial is performed according to the ISO 3379:1976 (IULTCS/IUP 9 standard (11). The load extension plot is similar to that shown in Figure 3 and the following results are obtained:

- ***ThL*** (mm): Thickness of the sample measured according to the ISO2589:2002 (IUP 4) standard.
- ***GL*** (N): Grain Load (at which grain cracks).
- ***GD*** (mm): Grain Distension (at which grain cracks).
- ***BL*** (N): Bursting Load (at which leather bursts).
- ***BD*** (mm): Bursting Distension (at which leather bursts).
- ***BW*** (mJ): Work of bursting (area under the curve up to bursting).

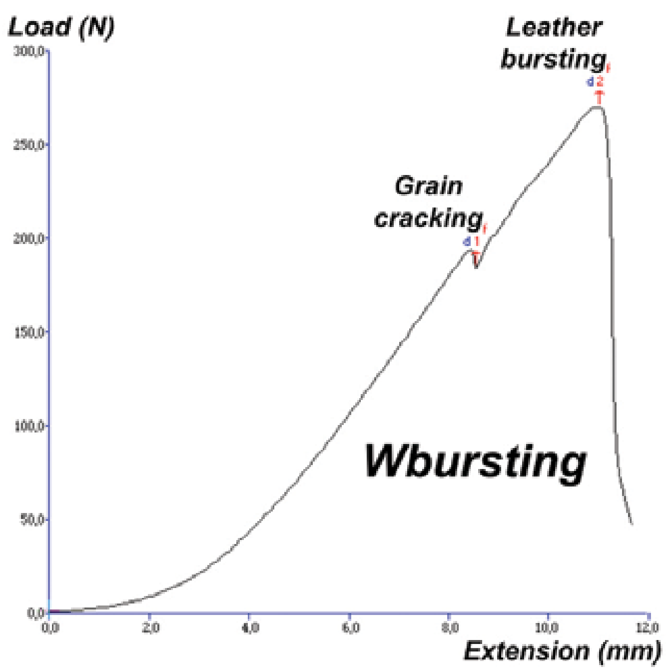

Figure 3. Load/Extension plot of a leather sample given by the dynamometer MT-LQ according to the ISO 3379:1976 (IUP 9) standard. The lastometer enables to identify the load and distension where grain cracks, the bursting load and distension, and the work of bursting by measuring the area under the curve up to bursting.

Tear and ball burst test parameters have been measured when leathers were in "crust", before finishing, estimating the effect of the different fatliquoring components, and also after finishing, assessing the influence of this treatment on tear and ball burst test behavior.

RESULTS AND DISCUSSION

Table I shows the mean values of the results of the tear test: Thickness ***ThT***, length of the crack growth ***C***, the tear load and strength ***TL*** and ***TS***, the work of tear ***TW*** and the surface free energy in tearing ***TE*** according to the experimental plan, grouped by sides and fatliquoring agents applied to leather. The central area of each side was fatliquored with a mixture of TCSi / PGR used as reference for comparison purposes. The lower area of side 5 was not fatliquored, and is identified by NO. The results of each treatment were measured in "crust" C and after finishing F.

Tear behavior can be characterized by tear load ***TL***, tear strength ***TS***, work of tear ***TW*** and the surface free energy in tearing ***TE***. The multiple correlation analysis between the four tear parameters based on the experimental results (204 experiments) yielded highly significant correlation coefficients higher than 0.90. Then it could be interesting to select the parameters most related with the step (crust/finished) and fatliquors. To this end, the analysis of variance relating fatliquor and step was applied to ***TL***, ***TS***, ***TW*** and ***TE***, resulting that the surface free energy ***TE*** was the parameter most significantly related to fatliquor and step. Being that tearing strength ***TS*** is the parameter given by the standard, it will be also analyzed.

Table II shows the mean values of the results of the ball burst test: Thickness ***ThL***, parameters of the grain crack (load ***GL*** and distension ***GD***), leather bursting (load ***BL*** and distension ***BD***) and the work up to leather bursting given by the area under the plot up to bursting (***BW***) according to the experimental plan, grouped by sides and fatliquoring agents applied to leather.

The Lastometer evaluates the characteristics of the grain layer providing the load and distension at which a grain crack appears. Consequently, both parameters ***GL*** and ***GD*** will be analyzed. There are also three additional parameters related with the bursting behavior of leather that are highly significant correlated: bursting load ***BL***, bursting distension ***BD*** and work of bursting ***BW***. The analysis of variance applied to the three parameters of bursting (load, distension and work) revealed that bursting load ***BL*** and work of bursting ***BW*** were the parameters most related with fatliquors and step. Consequently, these parameters will be studied to characterize the bursting behavior of leather.

TABLE I

Mean values of the tear test: thickness of the samples ***ThT***, length of the crack growth ***C***, tear load and strength ***TL*** and ***TS***, work of tear ***TW*** and surface free energy in tearing ***TE*** according to the experimental plan, grouped by sides and fatliquoring agents applied to the fatliquored leathers in "crust" (before) C and after finishing F. If a final fixation with chromium was needed, Cr has been added to the treatment. *[Tables use European comma convention for decimal points. – Editor]*

Fatliquor agent	Step	*ThT* (mm)	*C* (mm)	*TL* (N)	*TS* (N/mm)	*TW* (mJ)	*TE* (N/mm)
Side 1:							
Soy lecithin: ***LES***	C	1,252	24,74	92,85	73,99	2005,54	65,54
	F	1,245	26,92	134,66	108,04	3171,59	95,09
Reference: ***TCSi/PGR***	C	1,225	28,44	64,68	52,85	1545,22	44,10
	F	1,302	30,15	107,19	81,88	2703,42	70,28
Sulphited triglycerides of rapeseed oil: ***TCSi***	C	1,198	28,95	66,10	55,35	1594,69	45,60
	F	1,237	31,12	126,45	102,05	3427,76	89,34
Side 2:							
Acrylic polymer: ***ACR***	C	1,215	28,56	62,25	51,23	1418,85	40,90
	F	1,228	27,79	72,52	58,76	1641,67	47,94
Acrylic polymer + Cr fixation: ***ACR Cr***	C	1,215	27,24	70,29	58,12	1593,67	48,20
	F	1,113	28,79	88,37	79,40	2045,30	63,90
Reference: ***TCSi/PGR***	C	1,110	28,40	66,36	59,77	1565,81	49,59
	F	1,245	32,54	105,79	84,90	2783,73	69,01
Fatty polymer: ***PGR***	C	1,373	27,38	120,02	87,58	2730,28	73,53
	F	1,332	30,26	127,44	95,70	2987,58	74,21
Fatty polymer + Cr fixation: ***PGR Cr***	C	1,255	30,79	72,75	57,86	1790,56	46,12
	F	1,313	31,10	123,11	93,70	2932,49	72,13
Side 3:							
Sulphated triglycerid. of rapeseed oil: ***TCSa***	C	1,237	30,59	67,07	54,13	1691,10	44,67
	F	1,385	33,03	103,52	74,63	2833,41	62,07
Reference ***TCSi/PGR***	C	1,118	30,55	59,17	52,87	1468,94	43,03
	F	1,242	27,30	94,49	75,63	2152,36	65,51
Phosphoric Ester: ***ESF***	C	1,215	28,25	99,05	81,20	2354,73	68,22
	F	1,352	32,43	171,26	126,09	4545,09	102,95

Table I continued on following page.

Table I continued.

Side 4:							
C_{14} Paraffin: ***C14***	C	1,148	27,97	56,76	49,44	1313,04	40,62
	F	1,185	32,85	85,84	72,47	2233,55	57,37
Reference ***TCSi/PGR***	C	1,223	31,67	70,79	57,85	1887,85	48,70
	F	1,275	33,14	102,05	80,01	2729,85	64,95
Sulphonated Paraffin: ***PSn***	C	1,183	31,05	76,10	64,26	1937,49	52,87
	F	1,203	28,53	111,08	92,42	2621,62	76,82
Side 5:							
Sulphited fish oil: ***Psi***	C	1,153	25,18	75,40	65,34	1670,42	57,89
	F	1,270	26,50	125,21	98,54	2938,44	87,43
Reference ***TCSi/PGR***	C	1,125	27,66	53,90	47,72	1240,78	39,74
	F	1,260	31,45	85,25	67,56	2262,62	57,26
Not fatliquored: ***NO***	C	1,228	25,43	40,95	33,64	787,46	25,30
	F	1,212	26,17	63,49	52,40	1241,31	39,77

TABLE II

Mean values of the ball burst test: thickness of the samples ***ThL***, grain load ***GL***, grain distension ***GD***, bursting load ***BL***, bursting distension ***BD*** and work of bursting ***BW*** according to the experimental plan, grouped by sides and fatliquoring agents applied to the fatliquored leathers in “crust” (before) C and after finishing F. If a final fixation with chromium was needed, Cr has been added to the treatment.

Fatliquor agent	**Step**	***ThL* (mm)**	***GL* (N)**	***GD* (mm)**	***BL* (N)**	***BD* (mm)**	***BW* (mJ)**
Side 1:							
Soy lecithin: ***LES***	C	1,343	192,93	8,83	249,98	10,79	1070,15
	F	1,453	362,98	10,75	689,83	16,48	4353,53
Reference: ***TCSi/PGR***	C	1,293	189,32	7,66	239,72	8,57	701,45
	F	1,320	212,35	7,92	346,47	10,33	1280,62
Sulphited triglycerides of rapeseed oil: ***TCSi***	C	1,273	197,48	8,83	290,07	11,45	1276,70
	F	1,310	280,20	9,24	435,34	11,92	1765,19
Side 2:							
Acrylic polymer: ***ACR***	C	1,240	303,41	9,71	360,49	10,79	1322,47
	F	1,233	357,99	9,98	395,65	10,67	1418,51

Table II continued on following page.

Table II continued.

Acrylic polymer + Cr fixation: ***ACR Cr***	C	1,283	249,84	8,77	292,52	9,55	900,01
	F	1,240	318,29	10,54	354,24	11,33	1341,93
Reference: ***TCSi/PGR***	C	1,190	263,00	8,58	323,35	9,77	1137,24
	F	1,367	363,91	9,07	434,61	10,33	1572,00
Fatty polymer: ***PGR***	C	1,330	181,90	8,14	224,05	9,41	705,72
	F	1,350	495,71	10,43	517,99	10,71	1902,90
Fatty polymer + Cr fixation: ***PGR Cr***	C	1,507	327,53	7,71	414,71	9,15	1327,22
	F	1,520	470,87	10,88	515,26	11,17	1977,03
Side 3:							
Sulphated triglycerid. of rapeseed oil: ***TCSa***	C	1,250	171,96	7,45	202,96	8,24	572,57
	F	1,433	251,52	9,20	367,32	11,25	1470,75
Reference ***TCSi/PGR***	C	1,243	186,92	8,26	281,52	10,81	1104,52
	F	1,280	215,11	8,98	321,53	11,42	1274,75
Phosphoric Ester: ***ESF***	C	1,300	236,95	8,81	370,78	11,66	1608,06
	F	1,477	529,71	10,01	838,59	13,05	3803,85
Side 4:							
C_{14} Paraffin: ***C14***	C	1,247	323,77	9,28	373,09	10,11	1206,66
	F	1,310	397,99	10,22	481,10	11,47	1884,94
Reference ***TCSi/PGR***	C	1,293	281,70	9,32	321,99	10,15	1100,09
	F	1,333	285,43	9,56	368,96	11,24	1463,37
Sulphonated Paraffin: ***PSn***	C	1,287	277,41	8,66	442,69	11,18	1692,04
	F	1,287	229,90	7,61	478,90	12,10	2142,08
Side 5:							
Sulphited fish oil: ***Psi***	C	1,223	178,12	8,11	262,41	10,75	1053,95
	F	1,407	222,74	8,25	419,89	12,98	2146,62
Reference ***TCSi/PGR***	C	1,243	167,22	7,13	219,50	8,49	687,08
	F	1,320	211,22	8,55	325,21	11,28	1360,43
Not fatliquored: ***NO***	C	1,183	121,43	5,40	179,13	6,65	406,12
	F	1,223	220,86	6,74	269,54	7,48	696,74

Summarizing, the effect of fatliquoring and step on the tear behavior, grain quality and bursting characteristics of leather will concern two parameters given by each property:

- Tear behavior: tear strength ***TS*** and surface free energy of tearing ***TE***
- Grain quality: grain crack load ***GL*** and distension ***GD***
- Bursting behavior: bursting load ***BL*** and work of bursting ***BW***.

The effect of fatliquoring and step (crust or finished) on these characteristics will be evaluated by comparing the results with those of the non-fatliquored samples.

It is known that a variation in an experimental result can be attributed both to the effect of fatliquoring and to the effect of the side, i.e., the heterogeneity of the sample (differences between sides). The heterogeneity of the sample was identified by comparing the results of the central part of the different sides fatliquored with the same product. Then differences between the central parts of sides ***i*** and ***j*** will reflect the heterogeneity in a property ***X*** between the characteristics of both substrates ($Xref_i - Xref_j$). The effect of the fatliquor can be obtained by the addition of two components: first, the difference between the fatliquored part to the central part ($X_i - Xref_i$) of the same side and, second, the difference between the central part of side 5 to the non-fatliquored (lower) part of this side ($Xref_5 - Xnf_5$). Then the variation induced on a property by a fatliquoring agent in percentage vs. the non-fatliquored sample will be calculated as follows:

$$X(\%) = 100 \times [(X_i - Xref_i) + (Xref_5 - Xnf_5)] / Xnf_5$$

Being X_i the value of the characteristic analyzed on the fatliquored side ***i***, $Xref_i$ the result given by the central part of the same side fatliquored by the reference fatliquor, $Xref_5$ the value of the central part of side 5 fatliquored with the reference fatliquor and Xnf_5 the result of the property given by the lower part of side 5 (not fatliquored).

Then variations in tear behavior, grain quality and bursting characteristics induced by the different fatliquors in percentage vs. those of the non-fatliquored samples can be calculated. Samples in "crust" (before finishing) have been referred to the results of the non-fatliquored "crust" sample, and those of the finished samples, to the results of the finished non-fatliquored sample. Table III shows the variations (in percentage) induced by the different fatliquors on the characteristics of leather in "crust" (C) and after finishing (F).

Relationship between variations in grain, bursting and tearing behavior of fatliquored leather with respect to the non-fatliquored one:

The regression analysis between the different parameters pointed out the existence of two very significant linear relationships between tear strength ΔTS and surface free energy of tearing ΔTE (r = 0.99) and between bursting load ΔBL and work of bursting ΔBW (r = 0.92). This means that either tear strength or tear surface free energy indistinctively can characterize the tear behavior, and that either load of bursting or work of bursting can characterize the bursting behavior of leather. As regards the parameters of grain quality, the application of the multiple regression analysis revealed that grain distension ΔGD significantly increases with both grain load ΔGL and work of bursting ΔBW and decreases with bursting load ΔBL. The use of highly correlated data in predictive models can lead to the "messy data problem" that invalidates the resulting models (12). To overcome this situation, the effect of fatliquoring and finishing on tear behavior, grain quality and bursting characteristics has been restricted to the analysis of the variations induced in surface free energy ΔTE that reflects the evolution of tear load along the whole test and the grain load ΔGL and bursting load ΔBL that can be easily measured.

The application of the factorial analysis to the three considered parameters (ΔTE, ΔGL, ΔBL) leads to identify two independent factors that explain more than 90% of variability observed in the 24 experimental results. The two orthogonal factors that account for the 90.93% of the variability using normalized results are explained by the following equations:

1st Factor = $0.128 \times \Delta TE + \mathbf{0.936} \times \Delta GL + \mathbf{0.896} \times \Delta BL$ (61.83% variability)

2nd Factor = $\mathbf{0.989} \times \Delta TE + 0.028 \times \Delta GL + 0.235 \times \Delta BL$ (29.10% variability)

The "communalities" of the two factors explain the 99% of the variation in ΔTE, the 88% of the variation in ΔGL and the 86% of the variation in ΔBL.

The 1st Factor clearly increases with increasing grain load ΔGL and bursting load ΔBL and to a lesser extent with the increase in surface free energy of tearing ΔTE. High values are given by treatments improving grain quality and bursting behavior of leather. This factor reflects the quality level of the grain and corium layers of leather. The 2nd Factor grows with increasing surface free energy of tearing ΔTE and to a lesser extent with the increase in bursting load ΔBL. High values are related with a strong improvement in tear behavior and better bursting characteristics that mainly depends on the quality of the corium layer.

O'Leary and Attenburrow[1] explain the greater ability of the corium layer's fiber structure to impede propagating tears through the fibers embedded and attached to the entangled mass of the feltwork of thicker bundles of fibers constituting the corium.

TABLE III

Variation (in percentage) induced in tear strength ***TS***, surface free energy of tearing ***TE***, grain crack load ***GL*** and distension ***GD***, bursting load ***BL*** and work of bursting ***BW*** caused by different fatliquoring agents measured in crust state C and after finishing F. If final fixation with chromium has been needed, Cr is added to the treatment.

Fatliquoring agent	Step	*ΔTS(%)*	*ΔTE(%)*	*ΔGL(%)*	*ΔGD(%)*	*ΔBL(%)*	*ΔBW(%)*
Side 1:							
Soy lecithin: ***LES***	C	105,08	142,32	40,68	53,75	28,27	159,97
	F	79,22	109,06	63,84	68,87	148,04	536,30
Sulphited triglycer. of rapeseed oil: ***TCSi***	C	50,18	64,51	44,43	53,75	50,65	210,82
	F	67,51	93,44	26,35	46,39	53,62	164,81
Side 2:							
Acrylic polymer: ***ACR***	C	17,02	23,24	70,98	53,06	43,28	114,79
	F	-20,90	-8,15	-7,04	40,39	6,20	73,23
Acrylic polymer + Cr fixation: ***ACR Cr***	C	37,68	52,58	26,87	35,57	5,33	10,77
	F	18,32	32,24	-25,02	48,63	-9,16	62,24
Fatty polymer: ***PGR***	C	125,06	152,50	-29,08	23,90	-32,90	-37,07
	F	49,27	57,15	55,31	47,08	51,59	142,75
Fatty polymer + Cr fixation: ***PGR Cr***	C	36,46	43,78	90,84	16,05	73,55	115,96
	F	45,75	52,36	44,07	53,66	50,57	153,39
Side 3:							
Sulphated triglycer. of rapeseed oil: ***TCSa***	C	45,76	63,76	25,38	16,96	-21,32	-61,80
	F	27,87	38,53	12,12	29,95	37,64	123,39
Phosphoric Ester: ***ESF***	C	126,21	156,93	78,91	42,27	72,37	193,17
	F	127,61	144,37	138,08	41,96	212,48	458,25
Side 4:							
C_{14} Paraffin: ***C14***	C	17,23	25,75	72,35	31,20	51,07	95,42
	F	15,57	27,93	46,60	36,57	62,26	155,76
Sulphonated Paraffin: ***PSn***	C	61,00	73,70	34,17	19,74	89,92	214,94
	F	53,46	77,48	-29,51	-2,05	61,44	192,67

Table III continued on following page.

Table III continued.

Side 5:							
Sulphited fish oil: ***PSi***	C	94,33	128,95	46,68	50,19	46,49	159,52
	F	88,31	121,89	0,85	22,43	55,78	208,10
Reference: ***TCSi/PGR***	C	42,14	57,42	37,71	32,00	22,54	69,18
	F	28,98	45,15	-4,37	26,78	20,65	95,26

The energy consumed in pulling fibers from the corium is expended against friction in pulling the length of the fibers through the feltwork until it becomes completely liberated. Fibers connecting the two sides of the growing tear crack make the tear tip blunting by increasing the diameter of the crack tip and, consequently, the tearing energy. The relative weakness of the grain layer is attributed to the relatively low amount of fiber pull out that occurs during tear propagation. It is reasonable to assume that pulling fibers from the entangled mass of fibers in the corium layer consumes much more energy than in the grain layer, mainly contributing to improve the tear behavior and the bursting characteristics of leather. This situation is similar to that of the fiber composites where the degree of pull out from the matrix is regarded as an important factor controlling the strength of the composite. The pulling out of the fiber from the matrix[13] involves the expenditure of usually larger pull out energy than in debonding. It is expected that fatliquors act as a plasticizer, providing a lubricating effect that makes easy the relative displacement between fibers, fibrils and collagen chains making easy the pull out phenomenon that promotes better tear, grain and bursting characteristics of leather.

The comparative distribution of the experimental results according to the two factors given by the factorial analysis enables to place the groups according to the grain quality and bursting behavior explaining the multidimensional ability of deformation of the grain and corium layers and the tear behavior mainly dependent on the pull out effect of the corium layer (see Figure 4).

Cluster Analysis: The application of the Cluster analysis enables to group the treatments that cause similar variations in surface free energy ***ΔTE***, grain load ***ΔGL*** and bursting load ***ΔBL*** by considering the Euclidean distance between the experimental results. It is considered that treatments are similar if the Euclidean distance between the results of the treatments is lower than 1.5. Euclidean distances between groups are presented in Figure 5. The application of this technique classifies the treatments in nine different groups of treatments with similar results within each group.

The characteristic results (mean values) of the different groups given by the Cluster Analysis are shown in Table IV. Mean values of the variation in grain distension, work of bursting and tear strength are also included.

When compared with the non-fatliquored leather, all treatments increased the surface free energy of tearing, although groups 1, 2 and 3 led to a decrease in the grain crack load. Treatments in groups 4, 5 and 6 led to a relevant increase in both grain crack load and bursting load, and treatments in groups 7, 8 and 9 led to the strongest increase in both grain crack and bursting loads combined with an important ascend in the surface free energy of tearing. A graphical representation of the characteristic values of the groups using a bubble chart is shown in Figure 6. Group bubbles are placed in a diagram representing variations in grain crack load vs. those in surface free energy and the diameter of the bubbles are related with variations in bursting load.

As explained, treatments belonging to the same group gave rise to similar results on the variation of grain and corium mechanical properties measured through lastometer and tearing tests. When the effect of the different treatments was compared with that of the non-fatliquored leather, before and after finishing, it has to be noted that whatever the fatliquors used, an increase in the surface free energy of tearing was observed, even after finishing and the bursting load also increased except when fatliquoring was carried out with the fatty polymer on the crust sample. Six groups of treatments improve the grain crack load and the other three decrease it.

The effect of finishing on the variation of grain and corium mechanical behavior of finished leather samples when subjected to ball burst and tearing tests was clearly depended on fatliquor composition. The effect of some fatliquoring agents was not influenced by finishing remaining in the same group due to the irrelevant effect of finishing on the variations induced by the fatliquor. The fatliquor used as **reference** (***TCSi/PGR***, sulphited trigliceride of rapeseed oil and fatty polymer mixture), and the **sulphated triglyceride of rapeseed oil (*TCSa*)**, slightly improves the grain crack and bursting loads and also fairly improved the surface free energy of tearing. The **sulphited fish oil** (***PSi***) slightly increased the grain crack load, fairly the bursting load and strongly the surface free energy of tearing. The **chrome fixed fatty polymers** (***PGRCr***) and the **C_{14} paraffin** (***C14***) induced a relevant increase in grain and bursting load and just a slight increase in the surface energy of tearing. All these treatments belong to the central groups 4, 5 and 6 (cfr. Table IV). The application of these fatliquoring agents provided relevant increases in grain crack load, bursting load and surface free energy of tearing being not influenced by finishing. In these central groups, the treatments that led to the softer (sulphited fish oil) and the most compressible (C_{14} paraffin) leathers (3) are included.

The effect of some fatliquors was positively affected by finishing: **fatty polymer** (***PGR***), **soy lecithin** (***LES***) or **phosphoric ester** (***ESF***). Those finished leather samples fatliquored with these three compounds underwent a relevant

TABLE IV

Mean values of the variation (%) in grain load ***ΔGL***, bursting load ***ΔBL*** and surface free energy ***ΔTE***, of the different groups given by Cluster analysis, compared with the non-fatliquored leather. Parameters were measured in "crust" state (fatliquors in blue) or in finished state (fatliquors in red). Mean values of variation in grain distension ΔGD, work of bursting ΔBW and tear strength ΔTS are also included.

Groups of similar treatments in **crust** and **finished**	Mean values of each group					
	ΔGL(%)	**ΔBL(%)**	**ΔTE(%)**	ΔGD(%)	ΔBW(%)	ΔTS(%)
1: ACR, ACRCr	**-16,03**	**-1,48**	**12,05**	44,51	67,74	-1,29
2: PGR	**-29,08**	**-32,90**	**152,50**	23,90	-37,07	125,06
3: PSn	**-29,51**	**61,44**	**77,48**	-2,05	192,67	53,46
4: ACRCr, TCSa, TCSa,, REF, REF,	**19,54**	**19,97**	**51,49**	28,25	47,36	36,49
5: LES, PSi, PSn, TCSi, PSi	**29,75**	**54,82**	**112,06**	38,50	181,47	83,25
6: TCSi, PGRCr, PGRCr, PGR, C14, C14, ACR	**60,65**	**54,71**	**42,10**	41,62	141,27	33,07
7: ESF	**78,91**	**72,37**	**156,93**	42,27	193,17	126,21
8: LES	**63,84**	**148,04**	**109,06**	68,87	536,30	79,22
9: ESF	**138,08**	**212,48**	**144,37**	41,96	458,25	127,61

TABLE V

Classification of fatliquors according to the improvement induced in grain crack load, bursting load and surface free energy of tearing of finished samples with respect to the non-fatliquored leather.

Fatliquor	***ΔGL***	***ΔBL***	***ΔTE***
Phosphoric ester ***ESF***	●●●●	●●●●	●●●●
Soy lecithin ***LES***	●●	●●●	●●●
Sulphited triglicerides of rapeseed oil ***TCSi***, Sulphited fish oil ***PSi***	●	●●	●●●
Chrome fixed ***PGR Cr*** and unfixed fatty polymers ***PGR***, C_{14} Paraffin	●●	●	●
Sulphated triglicerides of rapeseed oil ***TCSa***, Reference (***TCSi/PGR***)	●	●	●●

increase in grain crack and bursting loads. As regards the **fatty polymer** (***PGR***), this increase was associated with a strong decrease in surface free energy of tearing whereas for **soy lecithin** (***LES***) and **phosphoric ester** (***ESF***) this characteristic was unaffected by finishing.

Finishing can also negatively influence the effect of some fatliquors on these properties. The most negatively affected were the **acrylic polymers** (***ACR***) and the **chrome fixed acrylic polymers** (***ACRCr***) for which the three characteristics (grain crack, bursting load and surface free energy of tearing) decreased due to finishing. For the **sulphonated paraffin** (***PSn***), finishing negatively influenced the grain crack load and the surface free energy of tearing but the bursting load remained similar. As regards the **sulphited triglycerides of rapeseed oil** (***TCSi***), a decrease in the grain crack load was observed due to finishing while the surface free energy of tearing underwent a strong increase and the bursting load remained similar.

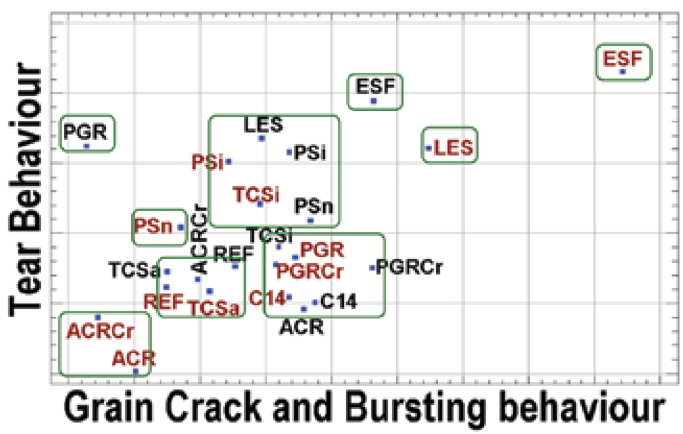

Figure 4. Relative distribution of the experimental results given by the Lastometer (Factor 1) which reflects the grain and corium quality of leather, and Tearing (Factor 2) which reflects the corium quality of leather in crust (black) and in finished (red) state.

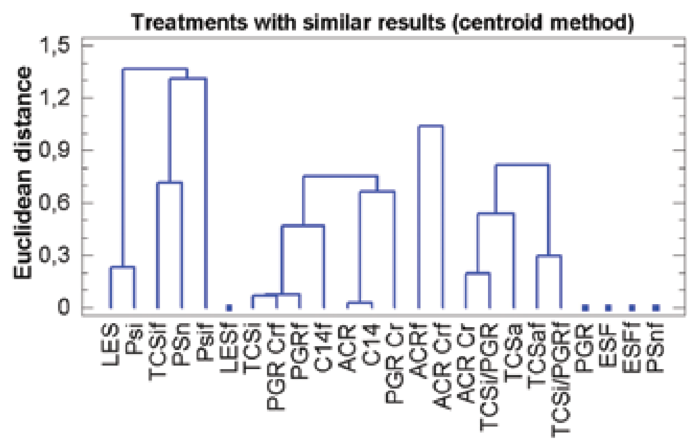

Figure 5. Euclidean distances including variations in surface free energy of tearing ***ΔTE***, grain load ***ΔGL*** and bursting load ***ΔBL*** of the different fatliquored samples, grouping results separated lower than 1.5 of Euclidean distance. Added "f" indicates finished leather.

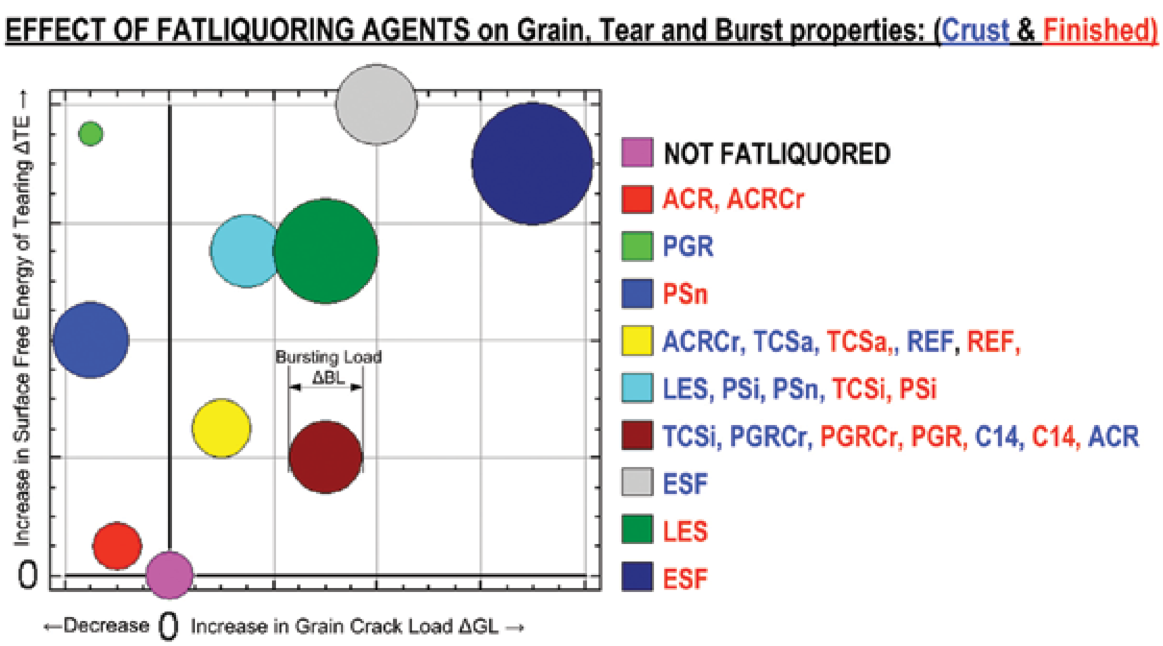

Figure 6. Bubble diagram of variations in bursting load ΔBL placed in a graph of variations in grain crack load ΔGL vs. surface free energy of tearing ΔTE provided by the different groups of fatliquors applied on crust (blue) or finished (red) leather. The results of the non-fatliquored leather correspond to the magenta bubble plot in (0, 0) place.

Finishing tends to compact the different levels of the internal structure of leather by increasing their apparent density. However, some fatliquors can counteract this effect in a different extent. The fiber pull out that prevents crack propagation caused by the lastometer and tearing varies according to fatliquor and finishing. Table V classifies the fatliquors that improve the grain crack load, the bursting load and the surface free energy of tearing of finished samples according to the intensity of their effects.

The most soft and compressible leather after finishing were those fatliquored with sulphited fish oil and C_{14} paraffin that correspond to a moderate/medium increase in the quality of the grain and corium layers. The highest qualities in grain and corium layers were obtained by soy lecithin and phosphoric ester that resulted in a medium range of softness and compressibility.[3]

The influence of different fatliquoring agents on the quality of the grain and corium layers of "crust" and finished leather measured by the ball burst and tearing tests enables concluding the following:

The results given by the application of 12 fatliquoring agents can be grouped into nine different groups according to the effects induced on grain crack load, bursting load and surface free energy of tearing of leather when compared with the non-fatliquored one.

Whatever the fatliquor used, an increase in the surface free energy of tearing was observed, even after finishing and the bursting load also increased except when fatliquoring was carried out with the fatty polymer on the crust sample. Six groups of treatments improve the grain crack load and the other three decrease it.

Fatliquors can be classified in accordance with the influence exerted by finishing on their effects:

- Fatliquors non influenced by finishing:
  - For the **reference** fatliquor (sulphited trigliceride of rapeseed oil and fatty polymer mixture) and the **sulphated triglyceride of rapeseed oil**, finishing slightly improved the grain crack and bursting loads and fairly improved the surface free energy of tearing.
  - For the **sulphited fish oil,** finishing slightly increased the grain crack load, fairly improved the bursting load and strongly increased the surface free energy of tearing.
  - For the **chrome fixed fatty polymers** and the **C_{14} paraffin,** finishing induced a relevant increase in grain and bursting load and just a slight increase in the surface energy of tearing.
- Fatliquors positively affected by finishing:
  - For **the fatty polymer**, **soy lecithin** or **phosphoric ester,** finishing led to a relevant increase in grain crack and bursting loads.
  - As regards the **fatty polymer**, this increase was associated with a strong decrease in surface free energy of tearing.
  - In the case of **soy lecithin** and **phosphoric ester**, the surface free energy of tearing was unaffected by finishing.
- Fatliquors negatively affected by finishing:
  - Finishing exerted the most negative influence on fatliquors based on **acrylic polymers** and the **chrome fixed acrylic polymers** since the three characteristics studied (grain crack, bursting loads and the surface free energy of tearing) decreased when compared with the "crust" leather samples.
  - For the **sulphonated paraffin,** finishing led to decrease in the grain crack load and in the surface free energy of tearing whereas the bursting load was unaffected
  - As regards the **sulphited triglycerides of rapeseed oil,** finishing exerted a different influence on the studied characteristics. Finishing gave rise to a decrease in the grain crack load and a strong increase in the surface free energy while the bursting load was unaffected by finishing.

CONCLUSIONS

The classification of the fatliquors according to their effect on grain crack, bursting load and surface free energy of tearing of finished leather samples when compared with their effect on softness and compressibility of leathers enables the following conclusions:

- The softer and more compressible leathers were those fatliquored with sulphited fish oil and C_{14} paraffin that correspond to a moderate/medium improvement in the quality of the grain and corium layers with respect to the non-fatliquored samples.
- The highest qualities in grain and corium layers were obtained by soy lecithin and phosphoric ester that result in a medium range of softness and compressibility.

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