

## EFFECT OF THE FATLIQUORING ON LEATHER COMFORT. Part I: Softness and Compressibility of leather.

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### ABSTRACT

The comfort of leather is a relevant aspect that makes the end user to select this material instead of other alternative materials. This comfort depends largely on the physical, mechanical and organoleptic characteristics of the finished leather from which the final articles will be manufactured. Among the post-tanning operations, fatliquoring and retanning plays a great influence on the properties of leather, especially those related to handle.

In this work, the influence of different types of fatliquoring agents on different properties affecting the comfort of leather manufactured goods is studied. The experimental work was performed at the pilot plant of Trumpler Española SA, using wet-blue leathers from Ireland as starting material, which were shaved to a thickness of 1.2-1.4 mm. After washing, rechroming and neutralization, leathers were retanned and dyed following a conventional process and then, they were fatliquored with nine different fatliquoring agents provided by the company. A 7 % of active matter (on shaved weight) was applied. Where required, a final fixation with chromium was carried out. 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. Finally, compressibility and softness were evaluated on both finished and unfinished samples.

To estimate differences between sides, the central parts of them were fatliquored with the same combination used as references consisting of sulphited triglycerides of colza oil and fatty polymer (TCSi/PGR).

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

- Soy lecithin LES
- Sulphited triglycerides of colza oil TCSi
- Acrylic polymer (waterproofing agent) ACR
- Fatty Polymers (sarcosinates) PGR

- Sulphated triglycerides of colza oil TCSa
- Phosphoric Ester ESF
- C14 Paraffin C14
- Sulphonated paraffin PSn
- Sulphited fish oil PSi

Compressibility and softness of both “crust” and finished leathers were evaluated according to the IUP52 and EN ISO 17235 (IUP 36) Standards. Based on the experimental results, treatments with similar effects were grouped, and the characteristic effects of each group on compressibility and softness were identified. Likewise, the effect of the finishing operation on both parameters (compressibility and softness) was studied.

**Keywords:** fatliquoring, compressibility, retanning, polymeric fatliquor.

### INTRODUCTION

The comfort of leather goods is an important aspect that makes the end user prefers this material over others presented as alternatives in footwear and clothing. This comfort depends largely on the physical, mechanical and organoleptic properties of the finished leather from which the final articles are manufactured (1).

Among the post-tanning operations, fatliquoring, together with retanning, is one of the most influencing treatments on leather characteristics, in particular those related to handle of leather (2, 3).

This work is the first in a series in which the influence of various types of fatliquoring agents on different properties affecting the assessment of the comfort of manufactured leather articles will be studied.

Among the characteristics that influence the assessment of leather comfort, the behaviour of leather under compression is one of them. Compressibility allows us to assess features

such as “fullness”, deformability to compression and recovery of its original dimensions when compression is finished (4). Leather softness is another feature closely related to comfort. It depends on the easiness with which it can be deformed, its ductility and the ability to be adapted to new configurations as a result of different applied uniaxial and multiaxial forces. The ability to recover their original dimensions when ceasing the forces applied over it (5, 6) has also to be considered.

Fatliquoring agents act as a lubricant between collagen microfibrils, facilitating their relative movement when subjected to a stress, and recovering the initial dimensions when the stress applied is removed.

The aim of this work is to study the influence of different fatliquoring agents and that of the finishing process on the softness and compressibility of leather measured by the application of the standardized methods.

## 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 provided by Trumpler Española S. A. 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. 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 compressibility and softness 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 related to leather handle.

The fatliquoring process was carried out by applying a 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, the properties of compressibility and softness 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 the rest of each of the treated leathers.

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

- Soy lecithin LES
- Sulphited triglycerides of colza oil TCSi
- Acrylic polymer (waterproofing agent) ACR
- Fatty Polymers (sarcosinates) PGR
- Sulphated triglycerides of colza oil TCSa
- Phosphoric Ester ESF
- C14 Paraffin C14
- Sulphonated paraffin PSn
- Sulphited fish oil PSi

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

## METHODS

**Softness:** The softness of leather (SF) was determined by the Softness Tester ST300 apparatus according to the EN ISO 17235 (IUP 36) standard. The deflection of leather clamped between rings 25 mm in diameter subjected to a load was measured. The higher the deformation, the greater the softness of leather measured as mm of deflection.

**Compressibility:** The behaviour of leather under compression was determined by the MT-LQ dynamometer manufactured by Stable Micro Systems according to the IUP 52 Standard (4). This method is based on the application of a steel cylinder probe  $14 \pm 0.1$  mm in diameter at 6 mm/min from 0.75 to 75 N on the sample. Test plots are similar to that shown in Figure 1, in which the upper curve shows the load applied in compression by the probe from 0.75 to 75 N when is applied at 6

mm/min, and the lower curve, the load when the probe is removed at the same speed

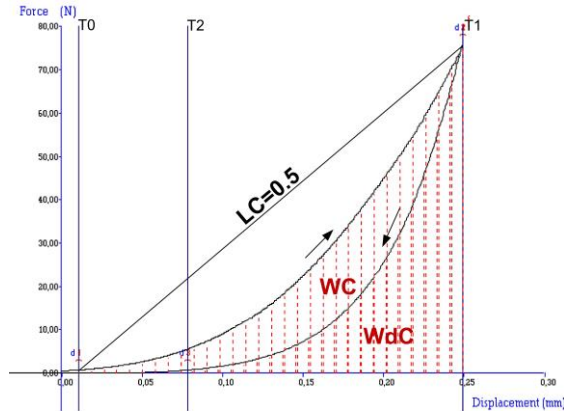


Figure 1: Compression-decompression curve of leather given by the dynamometer MT-LQ when subjected to a compression test according to the IUP 52 standard, for the determination of compressibility, work of compression WC and decompression WdC, and linearity of compression LC, the initial thickness T0 under 0.75 N, the compressed thickness under 75 N T1 and the decompressed thickness T2 under 0.75 N.

**Table 1:** Mean values of softness SF (Softness tester), CO compressibility, linearity LC, recovery RC and elasticity EC of compression, given by the dynamometer MT-LQ, and apparent density AD of the 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 | SF (mm) | CO (%) | LC    | RC    | EC (%) | AD (g/cm <sup>3</sup> ) |
|---------------------------------------|------|---------|--------|-------|-------|--------|-------------------------|
| <b>Side 1:</b>                        |      |         |        |       |       |        |                         |
| Soy lecithin:                         | C    | 3,26    | 21,8   | 0,332 | 0,524 | 69,1   | 0,641                   |
| <b>LES</b>                            | F    | 2,89    | 23,3   | 0,274 | 0,532 | 65,2   | 0,644                   |
| <b>Reference:</b>                     | C    | 3,26    | 24,6   | 0,291 | 0,561 | 72,9   | 0,614                   |
| <b>TCSi/PGR</b>                       | F    | 2,72    | 23,9   | 0,216 | 0,570 | 79,3   | 0,659                   |
| Sulphited triglycerides of colza oil: | C    | 3,25    | 22,7   | 0,308 | 0,542 | 72,9   | 0,640                   |
| <b>TCSi</b>                           | F    | 2,77    | 21,3   | 0,231 | 0,542 | 80,5   | 0,689                   |
| <b>Side 2:</b>                        |      |         |        |       |       |        |                         |
| Acrylic polymer:                      | C    | 3,11    | 23,2   | 0,286 | 0,533 | 70,4   | 0,611                   |
| <b>ACR</b>                            | F    | 2,69    | 18,1   | 0,312 | 0,586 | 69,6   | 0,670                   |
| Acrylic polymer + Cr fixation:        | C    | 3,00    | 22,2   | 0,300 | 0,549 | 69,1   | 0,592                   |
| <b>ACR Cr</b>                         | F    | 2,69    | 17,7   | 0,314 | 0,597 | 72,2   | 0,603                   |
| <b>Reference:</b>                     | C    | 3,10    | 25,0   | 0,237 | 0,508 | 78,4   | 0,629                   |
| <b>TCSi/PGR</b>                       | F    | 2,89    | 21,0   | 0,292 | 0,577 | 69,2   | 0,651                   |
| Fatty polymer:                        | C    | 2,88    | 23,8   | 0,246 | 0,506 | 79,3   | 0,637                   |
| <b>PGR</b>                            | F    | 2,68    | 19,6   | 0,290 | 0,590 | 69,9   | 0,678                   |
| Fatty polymer + Cr fixation:          | C    | 2,66    | 23,6   | 0,270 | 0,541 | 62,4   | 0,654                   |
| <b>PGR Cr</b>                         | F    | 2,44    | 21,5   | 0,265 | 0,587 | 67,4   | 0,657                   |
| <b>Side 3:</b>                        |      |         |        |       |       |        |                         |
| Sulphated triglycerid.                | C    | 2,99    | 19,3   | 0,327 | 0,584 | 71,5   | 0,598                   |
|                                       | F    | 2,87    | 17,6   | 0,312 | 0,592 | 71,1   | 0,669                   |

## RESULTS AND DISCUSSION

Table 1 shows the mean values of the results of compression (CO compressibility, recovery of compression RC, linearity of compression LC and elasticity of compression EC); softness SF and apparent density AD according to the experimental plan, grouped by sides and fatliquoring agents applied to leather. The central area of each side was fatliquored using the same agent, identified by REF, consisting of a mixture of TCSi / PGR. 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.

of colza oil:

**TCSa**

|                   |   |      |      |       |       |      |       |
|-------------------|---|------|------|-------|-------|------|-------|
| Reference         | C | 3,53 | 24,1 | 0,305 | 0,527 | 66,6 | 0,588 |
| <b>TCSi/PGR</b>   | F | 2,94 | 21,6 | 0,286 | 0,556 | 65,1 | 0,670 |
| Phosphoric Ester: | C | 3,09 | 21,0 | 0,315 | 0,529 | 66,7 | 0,632 |
| <b>ESF</b>        | F | 3,09 | 21,0 | 0,270 | 0,543 | 60,0 | 0,653 |

**Side 4:**

|                           |   |      |      |       |       |      |       |
|---------------------------|---|------|------|-------|-------|------|-------|
| C <sub>14</sub> Paraffin: | C | 3,14 | 21,4 | 0,302 | 0,581 | 71,8 | 0,608 |
| <b>C14</b>                | F | 2,92 | 22,7 | 0,271 | 0,599 | 66,2 | 0,597 |
| Reference                 | C | 3,09 | 20,6 | 0,314 | 0,561 | 68,7 | 0,634 |
| <b>TCSi/PGR</b>           | F | 2,91 | 21,7 | 0,285 | 0,559 | 66,4 | 0,666 |
| Sulphonated Paraffin:     | C | 3,02 | 19,4 | 0,319 | 0,554 | 69,4 | 0,605 |
| <b>PSn</b>                | F | 2,79 | 20,0 | 0,274 | 0,581 | 64,6 | 0,613 |

**Side 5:**

|                     |   |      |      |       |       |      |       |
|---------------------|---|------|------|-------|-------|------|-------|
| Sulphited fish oil: | C | 3,78 | 24,6 | 0,294 | 0,496 | 63,0 | 0,656 |
| <b>Psi</b>          | F | 3,13 | 17,1 | 0,316 | 0,595 | 68,5 | 0,699 |
| Reference           | C | 3,28 | 24,2 | 0,291 | 0,529 | 65,0 | 0,588 |
| <b>TCSi/PGR</b>     | F | 2,70 | 20,5 | 0,286 | 0,573 | 66,9 | 0,649 |
| Not fatliquored:    | C | 2,32 | 17,8 | 0,328 | 0,666 | 76,3 | 0,621 |
| <b>NO</b>           | F | 2,08 | 15,6 | 0,313 | 0,697 | 79,2 | 0,650 |

To assess the effect of the different fatliquors on softness, compressibility and apparent density of leather, the percentage of variation induced on these characteristics compared with those given by the non fatliquored sample (lower area of side 5) were calculated.

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 between the characteristics of both substrates ( $X_{ref_i} - X_{ref_j}$ ). 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 ( $X_i - X_{ref_i}$ ) of the same side and, second, the difference between the central part of side 5 to the non-fatliquored (lower) part of this side ( $X_{ref_5} - X_{nf_5}$ ). The variation induced on a property by a

fatliquoring agent in percentage will be calculated as follows:

$$X (\%) = 100 \times [(X_i - X_{ref_i}) + (X_{ref_5} - X_{nf_5})] / X_{nf_5}$$

Being  $X_i$  the value of the characteristic analyzed on the fatliquored sample *i*,  $X_{ref_i}$  the results given by the central part of the same side fatliquored using the reference fatliquor,  $X_{ref_5}$  the value given by the central part of side 5 fatliquored with the reference fatliquor and  $X_{nf_5}$  the results of the property given by the lower part of side 5 (not fatliquored).

Then variations in softness, compressibility and apparent density given by the different fatliquors in percentage vs. the results given by the non fatliquored leather can be calculated. Samples in “crust” (before finishing) has been referred to the results of the non fatliquored “crust” sample, and those of the finished samples, to the results of the finished not fatliquored sample. Table 2 shows the variations (in percentage) induced by the different fatliquors on the characteristics of “crust” leather (C) and after finishing (F).

**Table 2:** Variation (in percentage) induced in softness SF, compressibility CO, linearity and recovery of compression LC and RC, elasticity of compression EC and apparent density AD of leather, caused by different fatliquoring agents measured before (in crust) C and after finishing F. If final fixation with chromium has been needed, Cr is added to the treatment.

| Fatliquoring agent                 | Step | $\Delta$ SF(%) | $\Delta$ CO(%) | $\Delta$ LC(%) | $\Delta$ RC(%) | $\Delta$ EC(%) | $\Delta$ AD(%) |
|------------------------------------|------|----------------|----------------|----------------|----------------|----------------|----------------|
| <b>Side 1:</b>                     |      |                |                |                |                |                |                |
| Soy lecithin:                      | C    | 41,56          | 20,54          | 1,13           | -26,11         | -19,92         | -0,97          |
| <b>LES</b>                         | F    | 38,04          | 27,87          | 9,75           | -23,20         | -33,41         | -2,46          |
| Sulphited triglycer. of colza oil: | C    | 41,13          | 25,65          | -6,10          | -23,41         | -14,86         | -1,13          |
| <b>TCSi</b>                        | F    | 32,40          | 15,25          | -3,93          | -21,76         | -14,09         | 4,46           |
| <b>Side 2:</b>                     |      |                |                |                |                |                |                |
| Acrylic polymer:                   | C    | 41,99          | 25,70          | 3,57           | -16,85         | -25,31         | -8,21          |
| <b>ACR</b>                         | F    | 20,22          | 12,75          | -2,43          | -16,59         | -15,08         | 2,77           |
| Acrylic polymer + Cr fixation:     | C    | 37,25          | 20,15          | 7,74           | -14,54         | -26,99         | -11,27         |
| <b>ACR Cr</b>                      | F    | 20,37          | 10,12          | -1,69          | -15,01         | -11,86         | -7,54          |
| Fatty polymer:                     | C    | 32,07          | 29,12          | -8,54          | -20,95         | -13,64         | -4,03          |
| <b>PGR</b>                         | F    | 19,74          | 22,17          | -9,27          | -15,97         | -14,70         | 4,00           |
| Fatty polymer + Cr fixation:       | C    | 22,57          | 28,00          | -1,31          | -15,70         | -35,73         | -1,29          |
| <b>PGR Cr</b>                      | F    | 8,09           | 34,53          | -17,36         | -16,40         | -17,87         | 0,77           |
| <b>Side 3:</b>                     |      |                |                |                |                |                |                |
| Sulphated triglycer. of colza oil: | C    | 18,39          | 8,92           | -4,39          | -12,05         | -8,43          | -3,70          |
| <b>TCSa</b>                        | F    | 26,34          | 5,45           | -0,32          | -12,63         | -8,15          | -0,31          |
| Phosphoric Ester:                  | C    | 22,83          | 18,57          | -8,14          | -20,31         | -14,71         | 1,77           |
| <b>ESF</b>                         | F    | 37,07          | 27,29          | -13,75         | -19,61         | -22,13         | -2,77          |
| <b>Side 4:</b>                     |      |                |                |                |                |                |                |
| C <sub>14</sub> Paraffin:          | C    | 43,46          | 40,29          | -14,94         | -17,56         | -10,82         | -9,50          |
| <b>C14</b>                         | F    | 30,48          | 38,24          | -13,11         | -12,01         | -15,94         | -10,77         |
| Sulphonated Paraffin:              | C    | 38,28          | 28,96          | -9,76          | -21,61         | -14,01         | -9,98          |
| <b>PSn</b>                         | F    | 24,36          | 20,76          | -12,15         | -14,63         | -17,94         | -8,31          |
| <b>Side 5:</b>                     |      |                |                |                |                |                |                |
| Sulphited fish oil: <b>PSi</b>     | C    | 63,01          | 37,82          | -10,37         | -25,51         | -17,49         | 5,64           |
|                                    | F    | 50,70          | 9,74           | 1,15           | -14,63         | -13,57         | 7,54           |
| Reference:                         | C    | 41,56          | 35,91          | -11,28         | -20,61         | -14,87         | -5,31          |
| <b>TCSi/PGR</b>                    | F    | 29,85          | 31,45          | -8,63          | -17,79         | -15,61         | -0,15          |

**Influence of the treatments on softness, compression and apparent density of leather:**

**Softness:** The analysis of variance shows that leather softness increased significantly (5%) by the fatliquoring process, while softness decreased also

significantly (5%) by the finishing operation.

- Fatliquors with strong influence in SF: **PSi** (+ 56.9%) and **LES** (+ 39.8%)
- Fatliquors with weak influence in SF: **PGRCr** (+ 15.3%) and **TCSa** (+ 22.4%)
- Softness diminished by finishing in a 8.9%



**Compressibility:** The analysis of variance shows that compressibility was significantly (10%) affected by both fatliquoring and finishing.

- Fatliquors with strong influence in **CO**: **CI4** (+ 39.3%) and **REF** (+ 33.7%)
- Fatliquors with weak influence in **CO**: **TCSa** (+ 7.2%) and **ACRCr** (+ 15.1%)
- Compressibility decreased by finishing in a 5.2%.

**Linearity of compression:** The analysis of variance shows that the linearity of compression was slightly affected by fatliquoring with a signification of 10%. This parametes was not affected by finishing.

- Fatliquors slightly increasing **LC**: **LES** (+ 5.44%) and **ACRCr** (+ 3.02%)
- Fatliquors strongly decreasing **LC**: **CI4** (-14.8%) and **PSn**, **ESF** and **REF** (-11.0, -10.9 and -10% respectively).

**Recovery of compression:** The analysis of variance shows that the recovery of compression significantly (5%) decreased by fatliquoring, while this parameter was significantly (5%) enhanced by finishing.

- Factliquors strongly affecting **RC**: **LES** (-24.7%) and **TCSi** (-22.6%)
- Fatliquors weakly affecting **RC**: **TCSa** (-12.3%) and **CI4** and **ACRCr** (-14.8%)
- Recovery of compression was increased by finishing in a 2.9%.

**Elasticity of compression:** The application of the analysis of variance points out that this parameter was not significantly affected by fatliquoring or finishing.

**Apparent density:** The analysis of variance shows that this parameter was significantly (1%) affected by fatliquoring and that finishing also exerted a significant (5%) influence on it.

- Fatliquor strongly increasing **AD**: **PSi** (+ 6.6%)
- Fatliquors strongly decreasing **AD**: **CI4** (-10.1%), **ACRCr** (-9.4%) and **PSn** (-9.2%).

- Apparent density increased by finishing operation in a 2.8%.

### Relationship between the different characteristics of leather

The multiple regression analysis between the different characteristics pointed out the existence of two very significant inverse linear relationships (1%) between compressibility and linearity of compression and between softness and recovery of compression. This means that highly compressive leather shows low linearity of compression and that soft leathers are also leathers with very low recovery of compression. The apparent density seems not to be related with these four characteristics.

The application of the factorial analysis to the experimental results enabled us to identify some hypothetical factors that include the effect of these characteristics. It appear to be two main factors that explain more than 80% of variability observed in the 24 experimental results including the four considered parameters (SF, CO, LC and RC). The two orthogonal factors explaining 80.40% of the variability of the original data using normalized values are explained by the following equations:

$$1^{\text{st}} \text{ Factor} = 0.89 \times \mathbf{SF} - 0.84 \times \mathbf{RC} + 0.41 \times \mathbf{CO} + 0.19 \times \mathbf{LC} \text{ (46.33\% variability)}$$

$$2^{\text{nd}} \text{ Factor} = 0.04 \times \mathbf{SF} + 0.13 \times \mathbf{RC} - 0.81 \times \mathbf{CO} + 0.92 \times \mathbf{LC} \text{ (34.07\% variability)}$$

The “communalities” of the two factors explain the 88% of the variation in **LC**, the 83% of the variation in **CO**, the 79% of the variation in **SF**, and the 72% of the variation in **RC**.

The 1<sup>st</sup> Factor clearly increases with softness **SF** and to a lesser extent with compressibility, and decreases with the recovery of compression **RC**. Leathers corresponding to a high value of this factor are soft, easily deformable and with low recovery of compression. After deformation, they show little capacity to

recover the initial configuration. In this case, it can be assumed that fatliquoring acts as a plasticizer, providing a lubricating effect that makes easy the relative displacement between fibers, fibrils and collagen chains to accommodate the leather to a new more stable configuration.

The 2<sup>nd</sup> Factor grows with the linearity of compression **LC** and decreases with compressibility **CO**. A high value denotes a behavior close, according to the Hooke's law, to that of a "perfect elastic material", which, when deformed, the internal links between collagen fibrils or fibers are subjected to stress that stores energy, which is released after deformation without modifying the internal structure of the leather. "Fullness" seems to be a known characteristic related with this factor.

The results given by the different fatliquors before and after finishing enabled us to distribute the results according to the main two factors: the first related with elasticity-plasticity and the second with emptiness-fullness. The different corners of the distribution will identify groups of fatliquors providing fullness and elasticity (sulfated triglycerides of colza oil), fullness and plasticity (soy lecithin), emptiness and plasticity (sulfited fish oil) and elasticity and emptiness (chromed fatty polymer), and a central group of fatliquors that show more balanced characteristics of fullness and plasticity that includes the fatliquor used as reference, applied to the central part of the five sides, and its components.

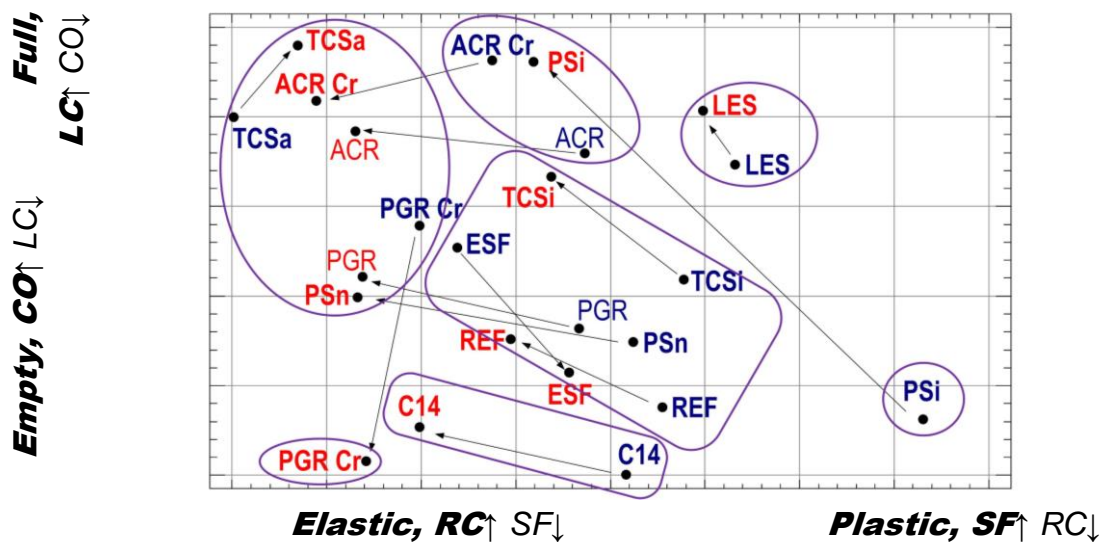


Figure 2: Relative Distribution of experimental results in terms of plasticity (Factor 1) and fullness (Factor 2) of leather, based on softness, compressibility and recovery and linearity of compression before and after finishing. Blue results correspond to samples in "crust" and red results to finished samples.

There are other methods to determine the compressional behavior of leather (8) by the application of a gradient of compression until certain pressure and, when attained, the examination of the relaxation of the stress of compression by time enables us to assess the plasticiser/softening effect of fatliquors,

linkages between fiber bundles and collagen fibrils that remain unbroken after relaxation. This enables the leather to partially recover its original dimensions (9). As regards the results in softness and compression, an analysis of similarities between the results seem to be adequate to attain the objectives of this work.

moisture and other products added to the leather during its industrial processing. The final non-relaxed stress can be related with

**Cluster Analysis:** The application of the Cluster analysis enabled us to group treatments leading to similar variations in

softness and compressibility by considering the Euclidean distance between the results of variation in softness, compressibility and linearity and recovery of compression. It is considered that treatments are similar if the Euclidean distance between results are lower than 3.5. The application of this technique

classifies the treatments on seven different groups that are shown in Table 2. Euclidean distances between groups are presented in Figure 3. The classification of similar treatments has also been plotted in Figure 2.

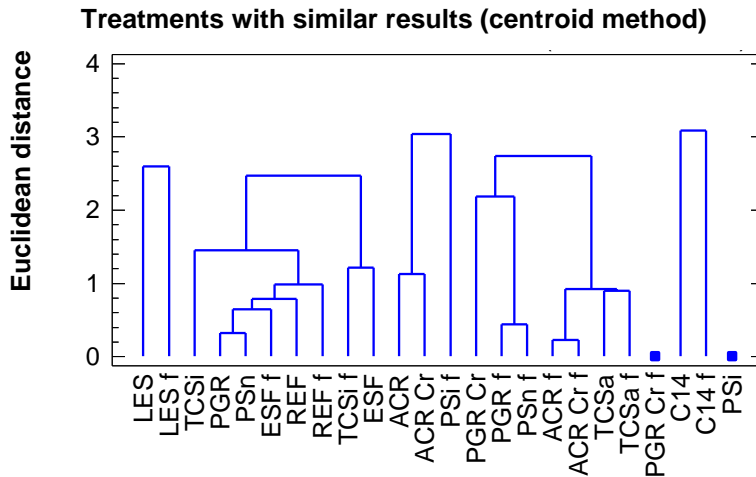


Figure 3: Euclidean distances including variations in softness, compressibility and linearity and recovery of compression of the different treatments, grouping treatments separated lower than 3.5 of Euclidean distance. Added "f" indicates finished leather.

The mean values of variation induced in softness, compressibility, linearity and recovery of compression of each group are shown in Table 3. It can be seen that variations in softness do not follow the same trends to that of compressibility, and

that the negative values in linearity and recovery of compression makes relevant the decrease of these characteristics induced by fatliquoring when compared with the original non fatliquored leather.

Table 3: Mean values of the variation (%) in softness  $\Delta SF$  softness, compressibility  $\Delta CO$ , linearity  $\Delta LC$  and recovery  $\Delta RC$  of compression of the different groups given by Cluster analysis, compared with the non fatliquored leather. Blue treatments are "in crust" before finishing and red corresponds to finished treatments.

| Groups of similar treatments                   | Mean values of each group |                 |                 |                 |
|--|---------------------------|-----------------|-----------------|-----------------|
|  | $\Delta SF$ (%)           | $\Delta CO$ (%) | $\Delta LC$ (%) | $\Delta RC$ (%) |
| <b>PGRCr</b>                                   | 8,09                      | 34,53           | -17,36          | -16,40          |
| <b>PGRCr, TCSa, TCSa, PGR, PSn, ACR, ACRCr</b> | 21,70                     | 15,45           | -4,51           | -14,65          |
| <b>TCSi, TCSi, REF, REF, ESF, ESF PGR, PSn</b> | 34,40                     | 26,53           | -8,77           | -20,76          |
| <b>C14, C14</b>                                | 36,97                     | 39,27           | -14,03          | -14,78          |
| <b>LES, LES</b>                                | 39,80                     | 24,20           | 5,44            | -24,67          |
| <b>ACR, ACRCr, PSi</b>                         | 43,31                     | 18,53           | 4,15            | -15,34          |
| <b>PSi</b>                                     | 63,01                     | 37,82           | -10,37          | -25,51          |

Figure 4 shows a multiparametric diagram of the variations in softness, compressibility and linearity and recovery of compression induced by the different groups compared with the results given by the non fatliquored leather. The analysis of variations enabled us to estimate the effect of the treatments on these characteristics of leather. Schematic representations of

the testing methods are also added to the multiparametric plot.



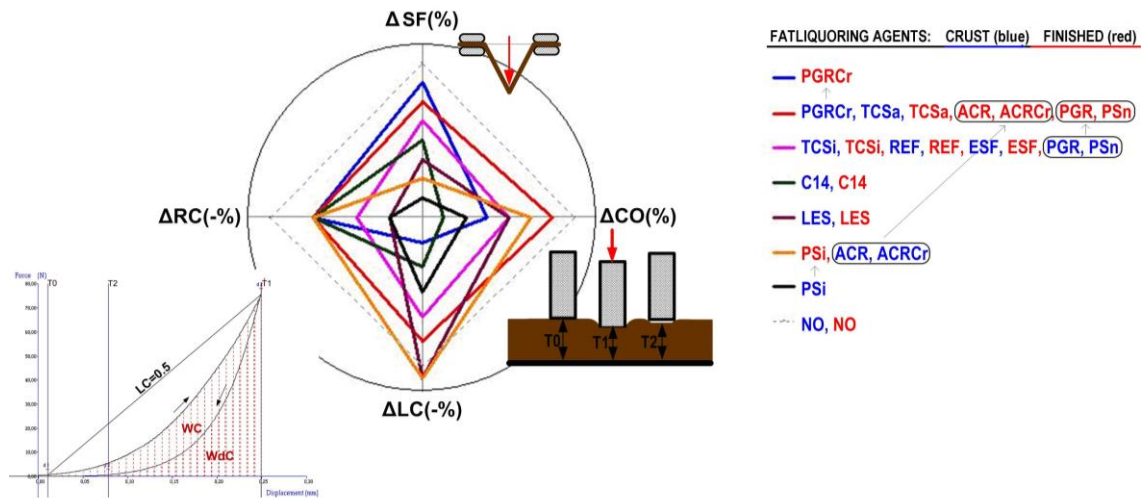


Figure 4: Multiparametric diagram showing the variation in softness  $\Delta SF$ , compressibility  $\Delta CO$ , linearity  $\Delta LC$  and recovery  $\Delta RC$  of compression provided by the different groups of fatliquors in comparison with the non fatliquored leather (dotted line) before (blue) and after (red) finishing.

When the effect of the different treatments is compared with the results given by the non fatliquored leather before and after finishing, it is noted that whatever the fatliquor used even after finishing, samples are softer and more compressible than the non fatliquored one, showing less recovery of compression and less linearity of compression (except when fatliquored with soy lecithin,  $\text{H}_2\text{S}$  sulphited fish oil after finishing and acrylic polymer in "crust").

The **reference** fatliquoring and its components (**sulphited triglyceride of colza oil**, **fatty polymer** before finishing), **phosphoric ester** and the **sulfonated paraffin** before finishing lead to intermediate variations in softness, compressibility and linearity and recovery of compression. It seems that fatliquors act as plasticizers, weaken the internal links of leather and help the migration of collagen chains to reach a new spatial configuration better adapted to the stresses applied to the sample.

Another group with a lower influence on the variation of these characteristics than that of the reference group is that consisting of **sulfated triglycerides of colza oil**, **chromed fatty polymer** before finishing and, after finishing, **fatty polymer**, **sulfonated paraffin** and the unchromed and chromed **acrylic polymer**. The characteristics of the leather produced by this group approaches to those of the non fatliquored one, resulting in a fuller and less soft and compressible leather than that given by the group of the reference fatliquor.

The most relevant fatliquoring agent that greatly modifies the characteristics of leather is **sulphited fish oil** that leads to the highest levels of softness and compressibility. It shows a strong plasticizing effect enabling an easy slippage between collagen chains. When finished, results represented by the black line move to the orange line (being the results similar to those given by the **acrylic polymers** before finishing), with a slow decrease in softness, slightly higher decrease in compressibility and a relevant increase

in the linearity of compression and recovery of compression that attains maximum values. Finishing compacts leather internal structures becoming more elastic (less extensible), full and firm (with good linearity and compression recovery) which can be related with a significant increase on the apparent density of leather.

**Soy lecithin** leads to slightly softer leathers but with the same compressibility of the **reference** fatliquoring, with better linearity and very low recovery of compression, which can be explained by the combination of a plasticizing effect with the improvement of the bonding energy between collagen chain that improves the linearity of compression.

**C<sub>14</sub> paraffin**, results in a less soft but more compressible leathers with a very low linearity and good recovery of compression. In the early stages of compression the fatliquored leather is easily deformed, probably due to the improvement of the compliance of the internal structure of the leather favoured by the fatliquor.

Finally, the finishing of a leather fatliquored by chromed **fatty polymer** would increase the compressibility of leather at the expenses of a decrease on the linearity of compression, a short descend in softness but maintaining the same recovery of compression.

Summarizing it can be stated that finishing decreases the softness and compressibility of the fatliquored leather, the softer leathers are those fatliquored with **sulphited fish oil**, and that the most compressible ones are those fatliquored with **C<sub>14</sub> paraffin**, the effect of which increases after finishing.

## CONCLUSIONS

The influence of the different fatliquoring agents before and after finishing on softness and compressible behaviour of leather enables us to conclude the following:

The results given by the 24 treatments based on the application of 12 fatliquoring agents before and after finishing can be grouped into seven different groups according to the effects induced on softness and compressible behaviour of leather when compared with the non-fatliquored one.

Fatliquored leathers before and after finishing, are softer and more compressible than the non fatliquored ones.

Samples fatliquored with the **reference** fatliquor based on a combination of **sulfited triglyceride (colza oil) rapeseed** and **fat polymer**, its components, **phosphoric ester** and **sulfonated paraffin** before finishing lead to a significant increases in softness, compressibility and linearity and compression recovery.

Samples fatliquored with **sulfated triglyceride rapeseed, chromed fatty polymer** before finishing, and, after finishing, **fatty polymer, sulfonated paraffin** and chromed and non chromed **acrylic polymer** lead to lower increases in softness, compressibility and linearity and recovery of compression so that the behavior approaches that of the non fatliquored leather.

The fatliquoring based on **sulphited fish oil** leads the leather to the highest softness and compressibility. When finished, their behavior approaches to that induced by the acrylic polymer before finishing, where softness and compressibility decreased and both the

linearity and compression recovery increased.

**Soy lecithin** fatliquor leads to somewhat softer and equal compressible leathers as the reference fatliquoring with better linearity and very low recovery of compression.

**C<sub>14</sub> paraffin** fatliquor leads to less softer but more compressible leathers but with a very low linearity and a very good recovery of compression.

Finally, finishing of a leather fatliquored with chromed fatty polymer increases the compressibility of the leather at the expenses of decreasing the linearity of compression, which leads to a slightly less soft leather with the same recovery of compression.

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