SHEEPSKIN AND CATTLE HIDE DEGREASING

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Ramón Palop
PhD in Chemistry
Introduction

Natural fat extraction from skins and leathers is mandatory to prevent the appearance of undesirable effects in finished items. Non-extracted natural fat is responsible for hard feel, decreased physical resistance and dye stains, and is also partly responsible for the appearance of the dreaded repousse—a white veil on the skin surface due to the efflorescence of certain free fatty acids and/or triglycerides of the skin.

Natural fat content in sheepskin is highly variable and depends on the animal's origin, diet, surrounding climate, etc. These contents range from 30% in Australian or American lamb to 7% in Spanish lamb.

Fat content is much lower in cattle hide. It is estimated at 2-3% and its distribution in the leather is different from that in sheepskin. However, its removal before tanning is also mandatory to avoid problems like those found in sheepskin.

The advantages of degreasing before tanning are obvious; indeed, metal soap formation is prevented and natural fat is removed from the interfibrillar spaces, thus allowing better and larger penetration of tanning liquids, fatliquoring agents, dyestuffs, etc. In the past few years, great progress has been made in the field of degreasing in an aqueous medium, both regarding the use of less polluting surfactants and the application technology of these products.

This book offers our best solutions to achieve:

1- Improved degreasing efficacy.
2- Decreased pollution.

This book consists of two parts:

Part I, where Theoretical and Experimental Parts I and II stem from PhD thesis “Decreasing the pollutant load in sheepskin degreasing by means of enzymes”, defended by Ramón Palop at the Autonomous University of
Barcelona in 1999. This same section also includes Experimental Part III “A comparative study of the surfactants most frequently used at C.U.” an extension and update of the first two parts carried out in February 2016 under the guidance of Ramón Palop and Olga Ballús and the assistance of Meritxell Guix and Carles Chiva.

Part II, where cattle hide degreasing is addressed by Mariana Lorenzo in the scope of collaboration between Units Sudamericana and CEPROCOR in Argentina. This study was presented at the IULTCS Congress, held in Brazil in 2015, under the title “Degreasing optimization in cattle hide”.

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1. THEORETICAL PART

1.1. FAT CONTENT IN SKIN

The natural fat content in raw skins varies greatly depending on the animal's origin. The mean fat values found in the most commonly used skins are shown in Table 1.

Table 1. Fat content in skins of different origin

<table>
<thead>
<tr>
<th>Origin</th>
<th>Spanish Entrefino</th>
<th>Spanish Merino</th>
<th>French</th>
<th>English</th>
<th>Australia</th>
<th>USA</th>
<th>New Zealand</th>
<th>South America</th>
<th>Russia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8%</td>
<td>12%</td>
<td>20%</td>
<td>25%</td>
<td>30%</td>
<td>38%</td>
<td>35%</td>
<td>16%</td>
<td>20%</td>
</tr>
</tbody>
</table>

Figure 1. Fat cell distribution in a cross section of sheepskin (V.L. Addy)
In live animals, natural fat\(^{(9,30,31)}\) is found at three main locations of the skin (Figure 1):

a) The sebaceous glands near the pillous follicles (10% of total)

b) The grain-corium junction (40% of total)

c) The subcutaneous adipose tissue adhering at the flesh side (50% of total)

In addition to the differential distribution of fat along the whole thickness of the skin, there is also a topographic distribution of the different parts of sheepskin. Most fat is found in the neck, the butt and the backbone, and a lesser amount is found in the belly (see Figure 2).

Figure 2. *Topographic distribution of natural fat in two types of skin: a) very fat, b) moderately fat (Pankhurst)*
In the skin, fat is located inside cells (Figure 3) whose walls are formed by a protoplasmic envelope surrounded by reticular tissue\textsuperscript{(141)}.

![Figure 3. Fat cells (in orange) and protoplasmic envelope (in blue) in an adipose tissue cross section. (x 530) (Addy)](image)

Any satisfactory degreasing process must be preceded by the rupture of the protoplasmic envelope.

In sun-dried skins fat oozes from the interfibrillary channels and can be easily extracted. Conversely, in salted skins the cell walls are not as completely ruptured and therefore surfactants and solvents are not as effective at degreasing.

Jordan-Lloyd, Humphrays and Pankhurst\textsuperscript{(142)} studied the amount of extractable fat in sun-dried sheepskin as compared to salted skins and obtained higher fat removal in sun-dried skins.

MacLaughlin and This\textsuperscript{(175)} showed that 1% sulfuric acid pickling in a 10% sodium chloride bath followed by storage for approximately 6 weeks leads to fat cell rupture in sheepskin, with total rupture achieved after storage for 8 months (Figure 4).
Therefore, non-sun-dried skins require special treatment to ensure ruptured fat cell walls.

Balfe, Bowes, Innes and Please\textsuperscript{(146)} showed that 1% sulfuric acid pickling in a 10% sodium chloride bath followed by storage for approximately 6 weeks leads to fat cell rupture in sheepskin, with total rupture achieved after storage for 8 months (Figure 4).

![Fat cell distribution in a cross section of sheepskin](image)

**Figure 4.** Fat cell rupture according to pickling time

This storage period is frequently used in sheepskin, mainly in those originating from Australia and New Zealand, because they are marketed in this state.

The chemical composition of this fat varies from one breed to another, and to a lesser degree between individuals of the same species. A standard chemical composition is depicted below\textsuperscript{(39)}. 
1.2. SURFACTANTS IN THE DEGREASING PROCESS

1.2.1. SURFACTANT TYPES

Generically, surfactants are substances that lower the surface tension of water. Their chemical structure is ambivalent in nature and includes a polar, hydrophilic (water-soluble) part and a non-polar, lipophilic (oil-soluble) part. This ambivalence allows surfactants to disperse, emulsify and solubilize non-polar substances in water and vice versa.

The ability to emulsify non-polar substances depends on the surfactant's chemical structure, that is, on the constitution of each (polar and non-polar) part of the molecule, as well as on their relationship, known as hydrophilic-lipophilic balance (HLB).

Figure 5. Chemical composition of sheepskin fat
Table 2. Application scale of the HLB values of different surfactants

<table>
<thead>
<tr>
<th>HLB</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-3</td>
<td>DEFOAMER</td>
</tr>
<tr>
<td>3-6</td>
<td>W/O (water/oil) EMULSIFIER</td>
</tr>
<tr>
<td>7-9</td>
<td>WETTER</td>
</tr>
<tr>
<td>8-16</td>
<td>O/W (oil/water) EMULSIFIER</td>
</tr>
<tr>
<td>13-15</td>
<td>DETERGENTS</td>
</tr>
<tr>
<td>15-18</td>
<td>SOLUBILIZERS / EMULSIFIERS</td>
</tr>
</tbody>
</table>

Depending on the ionic character of their polar part, surfactants are classified as anionic, cationic and amphoteric.

**Anionic** surfactants have a negative charge in the group:

- R-COO⁻ Na⁺ .................................................. Soap
- R-CH₂SO₃⁻ Na ............................................. Alkyl sulfate
- R-CH₂SO₃⁻ Na ............................................. Alkane sulfonate
- R-CH₂OPO₃⁻ Na₂ ............................................ Alkyl phosphate

R = Hydrophobic remainder formed by a simple or modified long hydrocarbon chain.

Table 3. *Cromogenia* surfactants

<table>
<thead>
<tr>
<th>NON-IONIC</th>
<th>NAME</th>
<th>Active matter (approx.)</th>
<th>Nature</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CELESAL DL</td>
<td>85 %</td>
<td>ALM-EOM (Low)</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>CELESAL K-6</td>
<td>50 %</td>
<td>ALM-EOM (Low) + ad 1</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>CELESAL K-3</td>
<td>43 %</td>
<td>ALM-EOM (Md-high)</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>CELESAL K-7</td>
<td>65 %</td>
<td>ALM-EOM (Md-high) + ad 2</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>CELESAL K-7 CONC</td>
<td>80 %</td>
<td>ALM-EOM (Md-high) + ad 3</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>CELESAL INP</td>
<td>32 %</td>
<td>ALM-EOM (Md-high) + ad 4</td>
<td>12.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANIONIC</th>
<th>NAME</th>
<th>Active matter (approx.)</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HUMECTOL AS-21</td>
<td>50 %</td>
<td>Dialkyl Sulfosuccinate + ad 5</td>
</tr>
<tr>
<td></td>
<td>CELESAL BE-50</td>
<td>40 %</td>
<td>Benzene derivative + ad 6</td>
</tr>
<tr>
<td></td>
<td>DETERPIEL PF-14</td>
<td>27 %</td>
<td>Lauryl ether + ad 7</td>
</tr>
</tbody>
</table>
**Non ionic** surfactants have a differentiated electrical charge in their hydrophilic group. They are generally obtained by reaction of ethylene oxide and/or propylene oxide with organic compounds that have an active hydrogen atom, such as fatty alcohols, fatty amines, alkyl phenols, fatty acid amides, etc.

\[
\text{R-CH}_2\text{OH} + \text{X CH}_2\text{-O-CH}_2 \rightarrow \text{R-CH}_2\text{(OCH}_2\text{)}_x\text{OH (Ethoxylated fatty alcohol)}
\]

**Cationic** surfactants have a positive charge in their polar group and are generally composed of quaternary ammonium salts ionized in solution to yield an organic cation.

\[
\begin{align*}
\text{CH}_3 \\
\text{C}_{16}\text{H}_{33} & \text{----- N}^+ \text{----- CH}_3 \text{ Cl}^- \\
\text{CH}_3
\end{align*}
\]

**Amphoteric** surfactants contain or may contain, under certain pH conditions, both (anionic and cationic) ionic groups in the same molecule. For instance, betaines, sulfobetaines, etc.

\[
\text{R-CH}_2\text{-NH-CH}_2\text{SO}_3\text{-Na}^+
\]

### 1.2.2. PHYSICAL-CHEMICAL MECHANISM OF DEGREASING WITH SURFACTANTS

A surfactant is able to emulsify, disperse and solubilize non-polar substances such as **fat in water (O/W system)**.

For effective degreasing, a surfactant must be able to:

1. Penetrate the interfibrillar channels of the skin and reach the fat deposits.
2. Come into close contact with the fat of the skin and emulsify it.
3. Lead the emulsified fat out of the skin.
4. Maintain the stability of the created emulsion during the process.
5. Not cause any irreversible alteration in the skin structure likely to cause defects in the final leather.
These considerations allow elucidating the surfactants that can be applied in sheepskin degreasing.

Anionic surfactants, for instance, are strongly absorbed by collagen fibers and therefore are not available to emulsify skin fat.

McLaren (185) compared many surfactants for aqueous degreasing of pickled sheepskin and concluded that cationic and non-ionic surfactants were very poorly absorbed by the skin under acidic conditions. The laboratory results obtained with three (anionic, non-ionic and cationic) surfactant types in pickled sheepskin degreasing are shown in Figure 6.

In addition to the surfactant type, other factors have an influence on aqueous degreasing with surfactants. These factors are:

1º- **pH**: Optimal pHs (maximum emulsifying efficacy of the surfactant) usually range from 5 to 6, and therefore skins must be depickled before or during degreasing.

2º- **Sodium chloride content**: The use of baths with high salt contents causes salted-into, i.e. a fastest penetration of the surfactant into the skin on account of decreased solubility in water, thus reaching fat more efficiently. The disadvantage is that emulsions are more unstable. However, both factors can be used if good process control is ensured.

**Figure 6.** *Extracted fat according to concentration and surfactant type on pickled skin*
3° - **Surfactant concentration (g/l):** Because the amount of extracted fat is increased by increasing the surfactant concentration, an approximate water content of 60-80% at the beginning of degreasing is recommended.

4° - **Degreasing duration:** Reaching steady state requires a minimum amount of time that will depend on the conditions used (speed, concentration, temperature, drum type, etc.).

5° - **Temperature:** The amount of fat extracted with surfactants is increased by increasing temperature. On account of its chemical composition, the melting point of skin fat ranges from 38 to 42°C, and liquefied fat is required for effective degreasing.

### 1.2.3. DEGREASING EFFICACY WITH ETHOXYLATED FATTY ALCOHOLS

Degreasing efficiency was studied by comparing a medium-chain fatty alcohol (ALM) and a long-chain fatty alcohol (ALL) at different oxyethylenation degrees. As shown in Figure 7, the highest ALM efficacy is reached at 12 Ethylene Oxide Moles (EOM).

![Figure 7. Degreasing efficacy according to the degree of oxyethylenation of the fatty alcohol](image)

**Figure 7.** Degreasing efficacy according to the degree of oxyethylenation of the fatty alcohol
The strong dependence of degreasing efficacy on EOM content can be interpreted in terms of the hydrophilic-lipophilic balance (HLB) of surfactants. The HLB of a surfactant expresses the balance between the size and the strength of the surfactant groups. Thus, low-EOM surfactants are predominantly lipophilic in nature.

P.J. Waters\textsuperscript{(145)} extended his study on optimal HLB to unit surfactant mixtures.

\textbf{Figure 8. Degreasing efficacy according to the HLB of ethoxylated fatty alcohols}

It is concluded that surfactants with HLB similar to the material to be emulsified do emulsify very well. This efficacy, however, is reduced in case of significant HLB differences between the material and the surfactant.

The efficacy of a system formed by mixtures of two surfactants at 45\degree C for six hours is shown in Figure 8.

Mixtures were obtained at the following ratios: 100\%-80\%-60\%-40\%-20\%-0\%. As shown in Figure 8, the pure unit surfactant (ALM) has an efficacy similar to that of the mixture at a ratio of 60A+60B (point nr. 1).
The ALL unit component is somewhat less effective than the corresponding mixture at the same HLB (14.8) (point nr. 2).

As shown in both Figures 7 and 8, maximum degreasing efficacy is obtained with the medium-chain fatty alcohol (ALM), with 12 EOM and HLB of 14.8.

This phenomenon was extensively studied by J. Poré (162) (163) who named "RHLB" the HLB required to emulsify a specific fatty matter. In his paper, each fatty compound and each type of natural fat has a different "RHLB", for which reason, **one should not use same type of emulsifier to degrease sheepskin, Cattle hide, pigskins or hides from other animals.**

Professor Heideman (141) reported degreasing efficacy values of 40% with medium-chain alcohol with 12 EOM in depickled New Zealand skins.

### 1.3. ENZYMES IN THE DEGREASING PROCESS

Enzymatic degreasing can be performed by using the lipase/emulsifier, protease/lipase, phospholipase/emulsifier or phospholipase/lipase systems.

In the lipase/emulsifier system, the application of a specific lipase for sheepskin and cattle hide degreasing was studied (188). This type of lipase can be used at pH and temperature ranges of 3-13 and 25-30ºC, respectively.

Lipases and phospholipases are enzymes of the esterase class. However, while lipases react with triglycerides, phospholipases attack phospholipids.

Reaction products are composed of glycerides, monoglycerides, diglycerides, fatty acids and soaps that are easily emulsified by surfactants.

The reaction between triglycerides and lipases is outlined in Figure 9.
Some lipases preferably hydrolyze the C_{12}-C_{10}, short chains, while other lipases hydrolyze unsaturated long chains such as those of oleic and linoleic acid. There are also other types of lipases that attack triglycerides at the C_1 position, and others do so at the C_3 position.

Because lipases tend to react in the water/oil interface, their activity can be influenced by the presence of surfactants, by mechanical action (stirring) and, in general, by anything that changes the emulsion particle size.
Figure 10. Free fatty acids can be visualized by saponification with lead ions. Fatty acid distribution can be observed in the lipase-treated sample (15) and the untreated Reference (16)

To break apart phospholipids such as lecithin, a Phospholipase is required. This phospholipase is known as Phospholipase A1, A2, C or D depending on the site where the reaction takes place (Figure 11).

Figure 11. Reaction point between Phospholipase and Lecithin
Phospholipases A$_2$ are used for degreasing. They react with the phospholipids that form the cell membranes that contain the fat and yield isophospholipids, fatty acids and fatty acid soaps as reaction products.

Figure 12. Reaction of phospholipids with Phospholipase A$_2$
Figure 13. Fat cell packs before (A) and after (B) treatment with Phospholipase A2 using Sudan IV as differential dye (x40)

Figure 13 depicts a pack of intact fat cells in their natural state. On the right, the result of the attack of Phospholipase A2, which breaks apart much of the protoplasmic envelope and thus allows fat to come out.

Table 4. *Cromogenia* lipases

<table>
<thead>
<tr>
<th>ENZYME</th>
<th>TYPE AND USE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEFAT 50</td>
<td>LIPASE for neutral/alkaline medium</td>
</tr>
<tr>
<td>DEFAT 70 AL</td>
<td>LIPASE for acidic medium</td>
</tr>
<tr>
<td>DEFAT 80 PA</td>
<td>PROTEASE for acidic medium</td>
</tr>
</tbody>
</table>
2. EXPERIMENTAL PART I.
Variable optimization

2.1. SUBSTRATE USED

One of the first questions we asked ourselves when we started this book was: ¿What substrate that is uniform enough can we use as starting substrate?

The bibliographic search conducted on this subject always refers to taking samples "from the most representative parts of the skin(136,138)". However, how can we ensure a specific degreasing efficacy if analyzing the same piece of skin before and after degreasing is impossible?

Pr. Heideman(141) provides a statistical response: "The high dispersion of fat in the skin hugely increases the number of skins required to obtain reliable mean values. With such dispersion, it is estimated that 40 skins are required for each variable, that is, 20 skins to ascertain the initial fat content and another 20 skins to ascertain the final fat content." Thus, the large number of variables involved makes this system practically inapplicable to our work.

The papers by Mc Laren V.T.(169) and P.J.Waters(145) led us to prepare the following standard substrate:

Twelve English domestic sheepskin in the pickled state at pH=2.5 and weight 16 Kg (22ºC and 60% RH) were used.

These skins were die cut into pieces using a 30 x 3 cm stencil with 1 x 2 cm subdivisions by means of the "ATOM" press available at the laboratory. All these small pieces were further homogenized in a DUPLEX-2 drum for 48 hours.
We thus obtained 16 Kg of substrate composed of 1-cm² pieces from which 6 samples were obtained. Fat analysis according to the Official Method (IUC-4) was performed.

2.2. METHOD USED

SIMPLEX-4 drum batteries were used for the process defined in Figure 17. In order to omit the lack of mechanical action in the drums of such small skin pieces, rubber stoppers were placed in each drum to enable hitting and mechanical action.

Figure 14. *Pieces that compose the substrate*

Figure 15. *A SIMPLEX-4 drum battery*

Figure 16. *DET-GRAS (Fat extractor)*
Values of 11% of fat with a maximum deviation of +/- 0.5% were obtained, thus ensuring assay reproducibility.

Importantly, however, this "standard substrate" is valid only in comparative studies and is not valid to assess whole skins; indeed, die cutting breaks the cell membranes that contain the fat cells.

While the amount of extracted fat is appreciably lower than the amount of natural fat in whole skins, die cutting the skin exerts pressure on it and the fat on the surface is thus lost during skin handling (weighing, etc.) before placement in the treatment drums.

2.3. SURFACTANT USED

A balanced, maximum efficacy combination of ethoxylated medium-chain fatty acids (ALM) at a medium/high degree of ethoxylation, called **CELESAL K-3**, was used.

2.4. INFLUENCE OF pH ON DEGREASING EFFICACY

The influence of bath and skin pH has been widely studied\(^{137, 141, 142}\).

All the authors consulted agree that the best degreasing efficacy is obtained in depickled skins. However, most of these authors report a wide pH range (between 4 and 6).

The following method was used:

Reference weight = pickle + 50%

100% Water at 37°C and 6°Be

5.0% CELESAL K-3(m.a.)

Run 60 min

Adjust pH with sodium formate and sodium bicarbonate for each variable

Run 3 hours

Figure 17. *Standard method used*
The values in our assays ranged from 3 to 7 using 5% CELESAL K-3 (m.a.).

**Figure 18.** Influence of pH on degreasing efficacy

As shown in Figure 18, the amounts of fat extracted at pH 3 and 4 are very low (11 and 14%, respectively). At pH 5, however, the amount increases up to 25%. From then on (pH 6 or 7) efficacy is significantly increased up to 55% and 58%, respectively.

**2.5. INFLUENCE OF CELESAL K-3 CONCENTRATIONS ON DEGREASING EFFICACY**

The process depicted in Figure 17 was applied, with CELESAL K-3 concentrations ranging between 0 and 7%(m.a.).

**Figure 19.** Influence of Celesal K-3 concentrations on degreasing efficacy
As shown in Figure 19, the greater the concentration, the greater the degreasing efficacy. This increase, however, is relatively small at values between 5 and 7.

Importantly, in the assay without Celesal K-3, an efficacy of 12% (an efficacy even greater than that obtained at pH = 3 with 5% Celesal K-3) was obtained merely by depickling at pH = 7 and washing with water at 37°C.

2.6. INFLUENCE OF TIME ON DEGREASING EFFICACY

The optimal conditions for application (pH = 7, Celesal K-3 concentration = 5%(m.a)) were selected from the above assays, with times between 4 and 24 hours based on the process described in Figure 17.

As shown in Figure 20, degreasing efficacy shows little variation as of 4 hours and the variation is even smaller between 8 and 24 hours.

Figure 20. Influence of time on degreasing efficacy
2.7. INFLUENCE OF NEUTRAL LIPASES (DEFAT-50) ON DEGREASING EFFICACY

Assays were performed with (active at neutral pH) lipases on skins previously neutralized at pH = 7. The degreasing process was run with 5% Celesal K-3(m.a.) for 4 hours.

![](chart.png)

**Figure 21.** Influence of neutral lipases on degreasing efficacy

As shown in Figure 21, degreasing efficacy is increased with increasing concentrations of lipase and reaches steady state at values of 3%. As compared to the efficacies obtained in previous treatments, these efficacies have increased considerably.
3. EXPERIMENTAL PART II.
Process optimization

3.1. SUBSTRATE AND PROCEDURES

Seven English domestic sheepskin in pelt weight were used. Upon the completion of the Soaking-Dehairing-Liming-Bating-Washing phases, the left halves underwent pickling with the Reference (Figure 22).

Pelt weight reference

100% Water at 30ºC and 10ºBe

1.0% Sulfuric acid

Run 3 hours

Adjust to pH = 2.5

Figure 22. REFERENCE pickling

In turn, the right halves underwent the following processes:

Skin nr. 1 = Reference pickling + Phospholipase A2 → Standard degreasing
Skin nr. 2 = Reference pickling + DEFAT 80 PA → Standard degreasing
Skin nr. 3 = Reference pickling + DEFAT 70 AL → Standard degreasing
Skin nr. 4 = Reference pickling → Standard degreasing
Skin nr. 5 = Reference pickling + Phospholipase A$_2$ + DEFAT 80PA + DEFAT 70 AL → Standard degreasing + DEFAT 50
Skin nr. 6 = Reference pickling + Phospholipase A2 + DEFAT 80 PA → Standard degreasing
Skin nr. 7 = Reference pickling → Degreasing (kerosene + nonylphenol 8 EOM)

Figure 23. Design of the variables applied
Upon completion of the relevant process, skins halves were dried, die cut, reduced to powder, and homogenized. Four fat determinations were performed in each half skin according to analytical method IUC-4.

Samples of (non-decanted) residual baths were taken at the end of the process for COD evaluation.

**LAY DOWN ON BEAM FOR ONE WEEK**

*Standard degreasing:*

100% Water at 37°C and 6ºBe

5.0%(m.a.) CELESAL K-3

Run 60 min

2.0% Sodium formate

Run 15 min

2.0% Sodium bicarbonate

Run 30 min

1.2% Sodium carbonate

Run 2 hours. pH = 7.0

Drain bath. Take samples for COD

*Figure 24. Standard degreasing process*
Maximum efficacies (78 and 88%) were obtained in skins 3 and 5, which included lipase treatment. The third best efficacy was obtained with standard degreasing with kerosene and nonylphenol in skin 7 (72%).

The process of skin 5, however, is practically unfeasible because Phospholipase A-2 costs 1,500 €/liter. Also, this process involves adding acid proteases (DEFAT 80 PA) and neutral lipases (DEFAT 50). In comparison, process 3 is much simpler, cheaper, and offers very good efficacy (78%).

The addition of acid protease and/or phospholipase A_2, either in isolation or jointly (skins 1, 2 and 6), does not substantially increase the efficacy of degreasing (skin 4: reference).

It can be deduced that the action of acid pickling as fat cell rupturing agent is not improved by the action of phospholipases or by acid proteases. However, both acid (3) and neutral lipases are highly effective in rupturing triglycerides and therefore add to degreasing efficacy (skin 3).

Regarding COD, the baths at the end of the main degreasing were analyzed without product decanting to avoid supernatant emulsion losses (para evitar pérdidas de la emulsión que sobrenada).
Maximum pollution is obtained with the kerosene + nonylphenol (nr. 7) process (63,000 p.p.m.), followed by processes 3 and 5.

As shown in Figure 26, the greater the degreasing efficacy, the greater the COD. However, the process performed with kerosene —with an efficacy somewhat lower than that of process 3 and considerably lower than that of process 5— yields considerably higher COD values (63,000 ppm).

Thin layer chromatography (TLC) of fat extracts shows very strong staining of natural fat (R) in the triglyceride region.
As shown in Figure 27, (lipase containing) processes 3 and 5 produce weak staining in the triglyceride region and process 5 shows very weak staining in the rest of its column. Also, processes 1, 2 and 4 produce medium staining in the triglyceride region and quite weaker staining in the rest of components.

3.2. SUBPRODUCTS OF THE DEGREASING PROCESS

The pollution originated at degreasing with surfactants is caused by two factors: the residual surfactant that remains in the bath (A) and the fat-surfactant emulsion (B).

A) Residual surfactant
The evaluation of the environmental pollution\(^{(137)}\) caused by surfactants is based on two parameters: the product's own toxicity and its concentration in the environment, including its biodegradability and the rate and the mecha-
nisms by which the products degraded in the environment and all intermediate components can actually be degraded in the process.

The toxicity of the different surfactants in water is primarily measured with two parameters:

On the one hand, the BSBT% parameter, which consists of the sum of parameters\(^{(138)}\) to measure the total degradation of all organic components, such as biochemical oxygen demand (BOD), dissolved organic carbon (DOC), total organic carbon (TOC), carbon dioxide (CO\(_2\)), and chemical oxygen demand (COD).

### Table 5. Non-ionic surfactant biodegradability

<table>
<thead>
<tr>
<th>SURFACTANT</th>
<th>BSBT %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonylphenol 9 EOM</td>
<td>6-7</td>
</tr>
<tr>
<td>Fatty alcohol 5 EOM</td>
<td>1-3</td>
</tr>
<tr>
<td>Fatty alcohol 10 EOM</td>
<td>2-3</td>
</tr>
<tr>
<td>Fatty alcohol 14 EOM</td>
<td>3-4</td>
</tr>
</tbody>
</table>

On the other hand, the LCo parameter, which is equivalent to the maximum concentration at which a school of fish can live without any individual dying off. The lowest values indicate that fish start dying at that concentration (poisonous values), while the highest values indicate much lower toxicity.

### Table 6. Non-ionic surfactant toxicity

<table>
<thead>
<tr>
<th>SURFACTANT</th>
<th>LCo (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonylphenol 9 EOM</td>
<td>9</td>
</tr>
<tr>
<td>Fatty alcohol 5 EOM</td>
<td>60-70</td>
</tr>
<tr>
<td>Fatty alcohol 10 EOM</td>
<td>65-75</td>
</tr>
<tr>
<td>Fatty alcohol 14 EOM</td>
<td>65-75</td>
</tr>
</tbody>
</table>

Importantly, achieving good and fast biodegradability (low BSBT%) is better than achieving low toxicity because poor biodegradability leads to lethal conditions faster than a simple increase of the surfactant concentration.
**B) Fat-surfactant emulsion**

In the degreasing process double walled drums are key to achieve maximum skin washing efficacy and maximum bath exhaustion and, if possible, lead the bath to decantation.

Washing in short, high-mechanical action baths is more effective because lower flows are treated. Importantly, the grain must not suffer during this process and accordingly a balance between mechanical action and bath duration should be sought. Slip agents can also be used to avoid friction in the grain layer.

### 3.3. INFLUENCE OF THE PROCESS ON THE PHYSICAL-CHEMICAL PROPERTIES OF SKIN

The assays performed have allowed defining a process with 70% efficacy and 50,000 p.p.m. COD, thus being more effective than kerosene + nonyl-phenol. However, for this process to be industrially applicable, all the physical-chemical properties of skin must be checked to be at least equal to the properties known so far. To do so, a number of comparative assays involving degreasing with kerosene + nonylphenol (nr. 7) and degreasing with enzymes (nr. 3) were performed.

Six pickled English domestic skins were split in half along the backbone for maximum symmetry. The left halves were degreased with kerosene + nonyl-phenol and the right halves underwent process nr. 3 (pickling + DEFAT 70 AL).

After degreasing the skins were tanned with 33ºSch chrome salt, neutralized and fatliquored separately but with the same process. Skins were then dried and led to the crust state (llevadas al estado de crust).

Two of these skins (4 halves) were used to evaluate:

- Chrome oxide \((\text{Cr}_2\text{O}_3)\) in the tanned skin
- Degree of white
- Light fastness
- Temperature fastness
The four remaining skins (8 halves) were neutralized, dyed and fatliquored. After drying and conditioning, the following was evaluated:

- Tensile strength (IUP-6)
- Color (E*)
- Color levelness (ΔE)
- Degree of softness (IUP-36)

The values obtained are summarized in Table 7 below:

**Table 7. Physical-chemical properties**

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>% Cr₂O₃</th>
<th>Whiteness degree</th>
<th>ΔW Light fastness</th>
<th>ΔW Heat resistance</th>
<th>N/cm² Tensile strength</th>
<th>E* Color levelness</th>
<th>ΔE Unifor. color</th>
<th>IUP-36 Softness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene + Nonylphenol</td>
<td>3,8</td>
<td>38</td>
<td>6</td>
<td>9</td>
<td>220</td>
<td>37</td>
<td>± 1,1</td>
<td>7 ± 0,6</td>
</tr>
<tr>
<td>Enzymatic</td>
<td>4</td>
<td>40</td>
<td>5,8</td>
<td>6</td>
<td>222</td>
<td>37,7</td>
<td>± 0,7</td>
<td>7,6 ± 0,4</td>
</tr>
</tbody>
</table>

- The quantity of fixed \( \text{Cr}_2\text{O}_3 \) is somewhat higher in the enzymatic process.
- The degree of white is also somewhat higher in the enzymatic process.
- Good light fastness values are obtained in both processes (Section 4.2.5), somewhat better in the enzymatic process.
- Good temperature fastness values are also obtained in both processes, significantly better in the enzymatic process.
- Tensile strength values are also somewhat better in the enzymatic process.
- The E* values that define color are also very similar. Color levelness, however, shows substantially different values in favor of the enzymatic process.
Color levelness is defined as the color variation ($\Delta E^*$) measured at different parts of the skin surface; the lower the difference, the better the levelness.

Twenty $E^*$ readings were performed in each comparative half skin in both degreasing processes. Maximum deviations were $\pm 1.1$ and $\pm 0.7$ for kerosene + nonylphenol degreasing and enzymatic degreasing, respectively.

As far as feel is concerned, measuring with the Softness Tester allows numerical quantification of this value (admitted IUP-36 standard).

Twenty readings were performed in each comparative half skin: a degree of softness of 7 with maximum deviation of 0.6 Å was obtained in kerosene + nonylphenol degreasing, and a degree of softness of 7.6 with maximum deviation of 0.4 Å was obtained in enzymatic degreasing.

As seen, most values are generally somewhat better in the enzymatic process. Most significant, however, is the improved skin LEVELNESS provided by enzymes, as evidenced by the lower deviations obtained after 20 readings. This may be related to the higher uniformity obtained with enzymatic degreasing.

### 3.4. DEGREASING WITH PRETANNING

Many studies listed in the References include pre-degreasing treatments with polyphosphates$^{(2,3)}$, potassium aluminum silicates$^{(3)}$ or aluminum salts$^{(14)}$.

Applications with aldehydes have been most widely studied. However, only a few authors$^{(2,11)}$ mention fiber separation as a mechanism to improve degreasing efficacy. Most authors$^{(1,5,11,14)}$ point out the advantages of increasing degreasing temperature up to 40-45ºC to approach the melting point of natural fats, thus making the process of emulsion with surfactant much more effective.

We have worked with skins pretanned with RETANAL TAL fixed at pH = 4.5 with sodium formate and sodium bicarbonate; a shrinkage temperature (St) of 72ºC was reached after 2 hours.

Another assay was performed on skins pretanned with RETANAL DFS NEW. Treatment was started on pickled skin at bath pH = 2, which was then raised to 6.5 with formate, sodium bicarbonate and sodium carbonate; a shrinkage temperature (Ts) of 60ºC was reached after 2 hours (at pH 6.5).
Upon the completion of both pretanning processes, skins were degreased with 5% CELESAL K-3 according to the following formulas:

**Pickled skin pH 2.7**

**Dose on pickle weight + 50%**

200% Water at 35°C and 6°Be

6.0% RETANAL TAL

Run 45 min

2.0% Sodium formate

Run 15 min

X% Sodium bicarbonate

Run 45 min. Adjust pH = 4.5

Run 2 hours. St = 70°C

Drain bath

100% Water at 40°C *(maintained)*

5.0%(m.a.) CELESAL K-3

Run 60 min

3.0% Sodium bicarbonate

Run 3 hours. pH = 6.5

Drain bath

300% Water at 40°C

Run 20 min

Drain bath

**Figure 28. Process with RETANAL TAL pretanning**
Pickled skin pH 2.7

**Dose on pickle weight + 50%**

200% Water at 35°C and 6°Be

2.0% RETANAL DFS NEW
  Run 45 min

2.0% Sodium formate
  Run 15 min

4.0% Sodium bicarbonate
  Run 45 min. pH = 6.5
  Run 2 hours. St = 60 °C
  Drain bath

100% Water at 40°C *(maintained)*

5.0%(m.a.) CELESAL K-3
  Run 4 hours. Drain bath

300% Water at 40°C
  Run 20 min
  Drain bath

---

**Figure 29. Influence of pretanning on degreasing efficacy**

As shown in Figure 29, the efficacies of all three degreasing systems are very similar, but COD values (Figure 26) are decreased by 20%.
3.5. COMPARATIVE RESULTS OF THE STUDIED PROCESSES

An overview of all (enzymatic and with pretanning) degreasing systems is shown in Figure 30.

1. Ref. pickling → Standard degreasing
2. Ref. pickling + DEFAT 80 PA → Standard degreasing
3. Ref. pickling + DEFAT 70 AL → Standard degreasing
4. Ref. pickling + DEFAT 80 PA + DEFAT 70 AL → Standard degreasing
5. Ref. pickling → Degreasing with Pretanning agent RETANAL DFS New
6. Ref. pickling → Degreasing with Pretanning agent RETANAL TAL
7. Ref. pickling → Kerosene + Nonylphenol
8. Ref. pickling + DEFAT 80 PA + DEFAT 70 AL → Standard degreasing + DEFAT 50

Figure 30. Degreasing processes used

Figure 31. Comparison of all degreasing processes used
Because industrial practice involves pickling and marketing skins with a simple standard formula, the technician’s task will focus on the processes of degreasing with pretanning. Among these, the recommended process is number 5: pretanning with RETANAL DFS New (70% Efficacy).

Should the technician get to conduct the whole process (including pickling) with very fatty/greasy skins (pieles muy grasas), process number 8 is recommended (88% Efficacy).
4. EXPERIMENTAL PART III.
       Comparative study of the surfactants most commonly used at C.U.

4.1. METHOD USED

The degreasing obtained with process number 5 (pretanning with RETANAL DFS New) is the simplest, easiest to apply one. We shall thus define it as the "Maximum-efficacy sheepskin degreasing process" (see Figure 32).

**Pickled skin pH 2.7**

**Dose on pickle weight + 50%**

200% Water at 35°C and 6°Be

2.0% RETANAL DFS NEW

   Run 45 min

2.0% Sodium formate

   Run 15 min

4.0% Sodium bicarbonate

   Run 3 hours pH = 6.5. Uniform cut (Corte Uniforme). St =60°C

   Drain bath

100% Water at 40°C (maintained)

5.0% SURFACTANT(m.a.)

   Run 4 hours

   Drain bath

300% Water at 40°C

   Run 20 min. Drain bath

**Figure 32. Process used in the study of different surfactants**
### 4.2. PRODUCTS USED

A comparative study of the (non-ionic and anionic) surfactants most commonly used at Cromogenia, as well as a surfactant-free reference assay, were performed.

**Table 8. Surfactants used**

<table>
<thead>
<tr>
<th>NAME</th>
<th>Active Matter</th>
<th>NATURE</th>
<th>EFFICACY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NON-IONIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CELESAL DL</td>
<td>85%</td>
<td>ALM-EOM (Low)</td>
<td>57</td>
</tr>
<tr>
<td>CELESAL K-6</td>
<td>50%</td>
<td>ALM-EOM (Low) + ad1</td>
<td>62</td>
</tr>
<tr>
<td>CELESAL K-3</td>
<td>43%</td>
<td>ALM-EOM (Md-high)</td>
<td>70</td>
</tr>
<tr>
<td>CELESAL K-7</td>
<td>65%</td>
<td>ALM-EOM (Md-high) + ad2</td>
<td>75</td>
</tr>
<tr>
<td>CELESAL K-7 Conc</td>
<td>80%</td>
<td>ALM-EOM (Md-high) + ad3</td>
<td>80</td>
</tr>
<tr>
<td>CELESAL INP</td>
<td>32%</td>
<td>ALM-EOM (Md-high) + ad4</td>
<td>59</td>
</tr>
<tr>
<td>ANIONIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HUMECTOL AS-21</td>
<td>50%</td>
<td>Dialkyl sulfosuccinate + ad5</td>
<td>55</td>
</tr>
<tr>
<td>CELESAL BE-50</td>
<td>40%</td>
<td>Benzene derivative + ad6</td>
<td>40</td>
</tr>
<tr>
<td>DETERPIEL PF-14</td>
<td>27%</td>
<td>Lauryl ether + ad7</td>
<td>77</td>
</tr>
<tr>
<td>REFERENCE</td>
<td></td>
<td></td>
<td>12</td>
</tr>
</tbody>
</table>

ALM = Medium-chain fatty alcohol  
EOM (Low) = 4.5-5.5  
EOM (Md-high) =11-12  
ad1-ad2-ad3-ad4-ad5-ad6-ad7 = Additives  
The relevant additives are considered to be part of the active matter.
4.3. RESULTS AND DISCUSSION

4.3.1. DEGREASING EFFICACY

1º- CELESAL DL and CELESAL K-6 differ only in the addition of an additive (ad1) to CELESAL K-6. This addition increases efficacy from 57% to 62%.

2º- CELESAL K-3 has the same chain as CELESAL DL (ALM) but a higher number of ethylene oxide moles, thus increasing efficacy from 57% to 70%.

3º- CELESAL K-3, CELESAL K-7, CELESAL K-7 conc. and CELESAL INP have the same chain (ALM) and the same number of ethylene oxide moles (Md-high). Adding the additive (ad2 and ad3) to CELESAL K-7 and CELESAL K-7 conc. increases efficacy from 67% to 75% and 80%, respectively, with ad3 being somewhat more effective. However, adding ad4 to CELESAL INP reduces efficacy to 59%, probably because ad4 is less effective than the base.

4º- HUMECTOL AS-21 AND CELESAL BE-50 have low efficacy (55% and 40%, respectively), while Deterpiel PF-14 has high efficacy (77%). Importantly, the latter produces foam and therefore should be used together with defoamers.

5º- The surfactant-free reference has an efficacy of 12% on account of the action of washings with water at 38- 40°C. This value is consistent with that obtained in the study performed 15 years ago (see Section 2.5 of this book).
5. CONCLUSIONS

1 - The higher the pH, the higher the degreasing efficacy.

2 - The higher the concentration of CELESAL K-3, the higher the efficacy, with steady state being reached as of 4-5% of active matter.

3 - Degreasing efficacy increases with time, with steady state being reached within 6 to 8 hours.

4 - Degreasing efficacy increases with enzymatic pickling with acid lipases, more so when neutral lipases are added when degreasing at neutral pH.

5 - Pretanning with RETANAL TAL and with RETANAL DFS NEW improve efficacy because degreasing can be performed at 40-42°C.

6 - Because pretanning with RETANAL TAL changes the characteristics of the skin to a greater extent (more cationic), pretanning with RETANAL DFS NEW is recommended.

7 - The maximum efficacy of the surfactants currently manufactured by Cromogenia Units is that provided by CELESAL K-7 conc.
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1. THEORETICAL PART

1.1. FATTY MATTER PRESENT IN THE SKIN

In cattle hide, fatty matter is basically distributed in two well-differentiated areas:\(^1\)\(^6\)

a) In the fleshings or tallows, adhered to the external part on the flesh side.

b) In the sebaceous glands and dermal tissue (in red in Figure 33).

Figure 33. Fat distribution in cattle hide
While the total amount of fat in intradermal tissue and sebaceous glands depends on the animal's origin, size, diet, etc., most authors establish a percentage of 2-4% of the total components of the leather.\(^{(3)}\)\(^{(4)}\)

These same authors define the chemical composition as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRIGLYCERIDES</td>
<td>80%</td>
</tr>
<tr>
<td>DIGLYCERIDES</td>
<td>7.0%</td>
</tr>
<tr>
<td>MONOGLYCERIDES</td>
<td>6.0%</td>
</tr>
<tr>
<td>FREE FATTY ACIDS</td>
<td>5.1%</td>
</tr>
<tr>
<td>PHOSPHOLIPIDS</td>
<td>1.0%</td>
</tr>
<tr>
<td>ESTERS</td>
<td>0.9%</td>
</tr>
</tbody>
</table>

Table 9. Chemical composition of fat in cattle hide

Importantly, while fat distribution is different at the different areas of the skin, the adipose tissue is mostly composed of triglycerides and diglycerides. Waxes predominate in the grain side —that is, the sebaceous glands— while the intermediate corium area (zona intermedia corium) abounds in phospholipids and esters\(^{(2)}\).

On account of the larger triglyceride ratio in cattle hide (80%) as compared to sheepskin (56%), the different stratigraphic distribution and the different processes undergone (there is no preservation pickling (pique de conservación) in cattle hide), the degreasing method varies according to skin type.

The fact that the amount of intradermal and sebaceous gland fat is quantitatively small (2-3%) cannot be underestimated. Indeed, sebaceous gland fat may lead to poor dehairing, and intradermal fat may cause lime and/or chrome soap stains.

1.2. PHYSICAL-CHEMICAL MECHANISMS THAT AFFECT FAT DURING THE BEAMHOUSE PROCESS

The fleshings and tallow that remain in the skin during the soaking, dehairing and liming processes hinder the penetration of water and alkaline products, thus making emulsification indispensable to allow deep, uniform soaking and effective fleshing.
Fat in fleshings is a true barrier to soaking and consequently to good mechanical fleshing.

**Figure 34.** Fleshings hinder water penetration during the soaking process

Among all skin fats, those in the sebaceous glands must be removed during the dehairing process to facilitate hair removal, while dermal tissue fat components must be removed before the tanning process to prevent chrome soap formation.

In the liming process\(^{(2)}\) free fatty acids are converted into insoluble calcium soaps; in the deliming and bating process, soap calcium is solubilized and extracted in the form of calcium and ammonium salts. *This part of the process offers the best conditions for fat component removal: pH = 8 and temperature = 35-37\(^{\circ}\)C.*

**Figure 35.** Beamhouse processes and fat component variation

While the use of lime alone has shown to neutralize fatty acids at the epidermis and the corium\(^{(3)(4)}\), triglycerides are not saponified in lime baths. However, using sodium sulfide in the unhairing bath together with lime increases the saponifying effect on triglycerides. Saponification is intensified with increasing concentrations of sodium sulfide, and the addition of appropriate surfactants helps remove fat during the liming process.
2. EXPERIMENTAL PART\(^{(9)}\)

2.1. PURPOSE OF THE STUDY

The purpose of this study was to compare the fat component composition in tallows and intradermal tissue to define which surfactant is most appropriate for fat removal, and to assess the influence of lipase enzymes (DEFAT-50) on degreasing efficacy.

2.2. MATERIALS AND METHOD

2.2.1. SAMPLE PREPARATION

Because both (tallow and intradermal tissue) raw materials contained a certain amount of water, they were frozen until use. During application fats underwent different conditions, and therefore extractions were performed with samples prepared as follows:

1. Tallow: extraction was performed as is, with fat being removed according to the method described below (Tallow extract)

2. Intradermal fat extraction was performed in two different ways:

   a) Intradermal fat as is (IF extract)

   b) Intradermal fat after liming at pH: 11-12 (ILF extract 2)

2.2.2. FAT EXTRACTION

The Bligh and Dyer method (Bligh, G. E., et al. 1959), an adaptation of the Folch method (Folch, J.et al.1957), was used.

The method consists in wet homogenization of intradermal fat with methanol and chloroform at ratios suitable to form a single water-miscible phase. Upon the addition of chloroform and water, the two phases are separated with lipid materials in the chloroform layer.
Samples obtained:

- Tallow (T)
- Intradermal fat (IF)
- Intradermal limed fat (ILF)

2.2.3. FAT TREATMENT WITH LIPASES

A sample of 30 grams of fat was heated at 40°C until liquefied and 10 ml of ethanol were added for emulsification. Then, 35 ml of "miliRo" water were added slowly with stirring (also at 40°C) and the pH was adjusted between 10 and 12 (with NaOH).

(1:10 diluted) lipase was then added at 0.3 ml and allowed to react for 2 hours at 40°C with stirring. Upon time completion, it was extracted with hexane in a separating funnel and taken to the rotavap for solvent extraction.

Samples obtained:

- Tallows with enzyme (TE)
- Intradermal fat with enzyme (IFE)
- Intradermal limed fat with enzyme (ILFE)

2.2.4. FATTY ACID DETERMINATION

The procedure of reference was performed according to (AOAC) 969.33 (1990).

Analysis: 14-B FID Detector, Shimadzu GC, DB-Wax 30 m x 0.32 mm ID x 25um column. Quantification was performed with a standard 37 fama MIX Supelco fatty acid solution.
2.2.5. FATTY ACID MELTING POINT

<table>
<thead>
<tr>
<th>FATTY ACID</th>
<th>MP (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MYRISTIC 14:00</td>
<td>54.4</td>
</tr>
<tr>
<td>PALMITIC 16:00</td>
<td>62.6</td>
</tr>
<tr>
<td>STEARIC 18:00</td>
<td>69</td>
</tr>
<tr>
<td>MYRISTOLEIC 14:01</td>
<td>-4</td>
</tr>
<tr>
<td>PALMITOLEIC 16:01</td>
<td>1</td>
</tr>
<tr>
<td>OLEIC 18:01</td>
<td>13</td>
</tr>
<tr>
<td>LINOLEIC 18:02</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 10. Melting point of different fatty acids

2.2.6. FATTY ACID PROFILE

<table>
<thead>
<tr>
<th>FATTY ACIDS</th>
<th>TALLOW</th>
<th>TALLOW + ENZYME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOTAL</td>
<td>PROFILE</td>
</tr>
<tr>
<td></td>
<td>(g/100 g)</td>
<td>(%)</td>
</tr>
<tr>
<td>Myristic 14:00</td>
<td>3.17</td>
<td>5.01</td>
</tr>
<tr>
<td>Myristoleic 14:01</td>
<td>0.81</td>
<td>1.13</td>
</tr>
<tr>
<td>Pentadecylic 15:00</td>
<td>0.43</td>
<td>0.63</td>
</tr>
<tr>
<td>Pentadecanoic 15:01</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>Palmitic 16:00</td>
<td>21.3</td>
<td>26.69</td>
</tr>
<tr>
<td>Palmitoleic 16:01</td>
<td>2.65</td>
<td>3.34</td>
</tr>
<tr>
<td>Margaric 17:00</td>
<td>1.46</td>
<td>1.18</td>
</tr>
<tr>
<td>Heptadecanoic 17:01</td>
<td>0.78</td>
<td>0.79</td>
</tr>
<tr>
<td>Stearic 18:00</td>
<td>16.97</td>
<td>17.07</td>
</tr>
<tr>
<td>Oleic 18:01</td>
<td>31.05</td>
<td>42.79</td>
</tr>
<tr>
<td>Linoleic 18:02</td>
<td>0.74</td>
<td>1.18</td>
</tr>
<tr>
<td>TOTAL</td>
<td>79.52</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 11. Fatty acid composition in tallow and tallow + enzyme
The composition of total fatty acids is slightly increased with enzymatic treatment (DEFAT -50) (1.8%).

In tallow and tallow + enzyme, myristic, palmitic, stearic and oleic acid are most commonly found.

Bearing in mind the melting points of each acid and their ratio in each substrate, tallows melt at 36.4°C and tallows + enzyme melt at 38.0°C (see Table 9). This variation is due to the slightly increased ratio of fatty acids with high melting point (myristic, palmitic and stearic) and a slightly decreased ratio of oleic acid (low melting point).

<table>
<thead>
<tr>
<th>FATTY ACIDS</th>
<th>INTRADERMAL TISSUE</th>
<th>INTRADERMAL TISSUE + ENZYME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOTAL</td>
<td>PROFILE</td>
</tr>
<tr>
<td></td>
<td>(g/100 g)</td>
<td>(%)</td>
</tr>
<tr>
<td>Myristic 14:00</td>
<td>2.44</td>
<td>3.96</td>
</tr>
<tr>
<td>Myristoleic 14:01</td>
<td>0.78</td>
<td>1.23</td>
</tr>
<tr>
<td>Pentadecylic 15:00</td>
<td>0.31</td>
<td>0.49</td>
</tr>
<tr>
<td>Pentadecanoic 15:01</td>
<td>0.07</td>
<td>0.1</td>
</tr>
<tr>
<td>Palmitic 16:00</td>
<td>20.71</td>
<td>26.6</td>
</tr>
<tr>
<td>Palmitoleic 16:01</td>
<td>2.82</td>
<td>4.1</td>
</tr>
<tr>
<td>Margaric 17:00</td>
<td>1.32</td>
<td>1.1</td>
</tr>
<tr>
<td>Heptadecanoic 17:01</td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>Stearic 18:00</td>
<td>14.04</td>
<td>13.8</td>
</tr>
<tr>
<td>Oleic 18:01</td>
<td>30.05</td>
<td>46.5</td>
</tr>
<tr>
<td>Linoleic 18:02</td>
<td>0.46</td>
<td>0.85</td>
</tr>
<tr>
<td>TOTAL 73.9</td>
<td>100</td>
<td>34.4</td>
</tr>
<tr>
<td>FATTY ACIDS</td>
<td>INTRADERMAL TISSUE LIMING</td>
<td>INTRADERMAL TISSUE LIMING + ENZYME</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td></td>
<td>TOTAL (g/100 g)</td>
<td>PROFILE (%)</td>
</tr>
<tr>
<td>Myristic</td>
<td>14:00</td>
<td>2.89</td>
</tr>
<tr>
<td>Myristoleic</td>
<td>14:01</td>
<td>1.07</td>
</tr>
<tr>
<td>Pentadecylic</td>
<td>15:00</td>
<td>0.4</td>
</tr>
<tr>
<td>Pentadecanoic</td>
<td>15:01</td>
<td>0.11</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:00</td>
<td>21.01</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>16:01</td>
<td>4.18</td>
</tr>
<tr>
<td>Margaric</td>
<td>17:00</td>
<td>1.3</td>
</tr>
<tr>
<td>Heptadecanoic</td>
<td>17:01</td>
<td>1.15</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:00</td>
<td>12.05</td>
</tr>
<tr>
<td>Oleic</td>
<td>18:01</td>
<td>35.6</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:02</td>
<td>0.51</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>80.31</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Table 12. *Fatty acid composition in intradermal tissue with different treatments*

The total fatty acid ratio is increased from 73.9% to 82.8% by enzymatic treatment (DEFAT-50), with a 12% increase. This increase is only 7% (80.31%) with liming treatment. When enzymatic treatment is preceded by liming, the total amount of fatty acids is increased up to 92.95%, i.e. 25.7% total increase of total fatty acids.

The different fatty acid rates in tallow and tissue are shown in Tables 11 and 12. Acids with the highest melting point (myristic and stearic) are more predominant in tallows. Palmitic acid remains as is, whereas the acid with the lowest melting point (oleic) is predominant in tissue. Consequently, the melting point in tissue is **2ºC** lower than that in tallow.
Tissue treatment with enzymes (DEFAT -50) also increases the rate of fatty acids with high melting point, which is increased by 1.2°C and thus follows the same tendency as in tallows.

Tissue treatment with lime decreases (high melting point) palmitic and stearic acids and also (low melting point) oleic acid. This results in limed tissue melting point being decreased by 1.8°C. Enzymatic treatment of limed tissue has no influence on the final melting point.

These small variations in fatty acid compositions—and hence in the melting points of the different substrates—are of paramount importance in application processes. Indeed, soaking, unhairing and liming are performed at temperatures ranging between 25-29°C and bating is performed at 38°C. Therefore, the lower the melting point, the higher the efficacy of the degreasing surfactant (limed tissue + enzymes = 32.7°C).

2.2.7. EXTRACT COMPOSITION

Thin-layer chromatography was performed to ascertain the qualitative composition of each extract.

![Thin-layer chromatography of extracts](image)

**Figure 36.** Thin-layer chromatography of extracts

- **TG** = Glycerides (standard reference)
- **FFA** = Free fatty acids (standard reference)
1 = Tallow
2 = Tallow + Enzyme
3 = Tissue
4 = Tissue + Enzyme
5 = Limed tissue
6 = Limed tissue + Enzyme

Extract composition matches that of glycerides, and the ratio of free fatty acids is close to nil. Small differences between extracts at the low part of glycerides are found, probably due to the small variation in fatty acid types as shown in Tables 8 and 9.
3. SURFACTANTS STUDIED

In the references\(^{(7)}\), many studies focus on sheepskin degreasing —12% fatty matter in Spanish lambs and up to 30% in Australian and New Zealand lambs.

Regarding cattle hide, however, references are more scarce\(^{(8)}\). The differences from sheepskin lie in the content of natural fat and its distribution in the skin. Also, as far as application is concerned, cattle hide degreasing is performed in the soaking-liming and bating processes, that is, at alkaline or neutral pH.

A medium-chain fatty alcohol with four degrees of oxyethylenation was selected (Table 13).

<table>
<thead>
<tr>
<th>Sample nr.</th>
<th>TYPE (Chain length)</th>
<th>Ethylene Oxide Moles EOM</th>
<th>HLB</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Medium-chain fatty alcohol</td>
<td>Very low (2.5-3)(MB)</td>
<td>6,9</td>
<td>Experim.</td>
</tr>
<tr>
<td>2</td>
<td>Medium-chain fatty alcohol</td>
<td>Low (5,5-6) (B)</td>
<td>10,4</td>
<td>CELESAL DL</td>
</tr>
<tr>
<td>3</td>
<td>Medium-chain fatty alcohol</td>
<td>Medium (8,5-9,5) (M)</td>
<td>12,8</td>
<td>Experim.</td>
</tr>
<tr>
<td>4</td>
<td>Medium-chain fatty alcohol</td>
<td>Medium/High (12-13)(M-A)</td>
<td>14,6</td>
<td>CELESAL K-3</td>
</tr>
<tr>
<td>5</td>
<td>Additivated medium-chain alcohol</td>
<td>Medium/High (11-12) + ad3</td>
<td>11,4</td>
<td>CELESAL K-7 CONC</td>
</tr>
</tbody>
</table>

The method consisted in assessing the stability (values of 0-5) over time (24 hours) of emulsions resulting from adding 20 ml of a 5% surfactant solution (active matter) at a temperature of 22°C to 1 g of each substrate.
The results suggest the absence of influence of the degree of oxyethylenation on tallow (seb) and tissue (tej).

In the rest of substrates —tallow with enzymes (seb+enz), tissue with enzymes (tej+enz), limed tissue (tej enca) and limed tissue with enzymes (tej enca+enz)— the maximum stability is obtained with medium-chain fatty alcohols with low EOM.

This study justifies the use of CELESAL DL (corresponding to the fatty alcohol with low degree of oxyethylenation (B) of Figure 37) as degreasing agent in beamhouse processes.

While CELESAL K-7 has a medium/high degree of oxyethylenation, the additive makes its HLB higher than that expected from its degree of oxyethylenation. That is why it is also very effective against cattle hide fat.

CELESAL DL was used as comparative, additive-free agent vs. experimental agents. However, CELESAL K-6 —more effective on account of the addition of additive ad1— can also be used.

The same assay was performed with HUMECTOL AS-21 to ascertain its stability with the different substrates.

**Figure 37.** Influence of the degree of oxyethylenation of a medium-chain fatty alcohol on stability with extracts of the different substrates
As shown in Figure 38, its stability is very high with all substrates. These values indicate its suitability as a tallow emulsifier to facilitate wetting, but also as a degreasing agent of limed leather treated with DEFAT-50.
4. COMPARATIVE RESULTS BETWEEN SHEEPSKIN AND CATTLE HIDE

In addition to ascertaining the different parts were fat is found and the chemical composition thereof, the present study also showed that ideal degreasing surfactants are different in sheepskin (optimal HLB = 14.6), while in cattle hide this value is 10.5 for the same type of fatty alcohol.

SHEEPSKIN:

Maximum efficacy is obtained with CELESAL K-7 conc. (Medium/high degree ethoxylated fatty alcohol + ad3)

CATTLE HIDE:

The best fat stabilities are obtained with CELESAL DL/ CELESAL K-6 (Low degree ethoxylated fatty alcohol + ad1) and CELESAL K-7 CONC.

Just as a reminder:

J. Poré studied this phenomenon thoroughly and named “RHLB” the HLB required to emulsify a specific fatty matter. Each natural fat type has a different “RHLB”, and therefore one should not use the same type of emulsifier.
5. CONCLUSIONS

1. Treatment with DEFAT-50 at the different phases of the process increases degreasing efficacy.

2. The melting point of fats indicates that the highest degreasing efficacy is obtained at the BATING phase.

3. CELESAL DL/CELESAL K-7 CONC. is the most stable degreasing agent in cattle hide.

4. HUMECTOL AS-21 has maximum stability with the extracts of the different substrates.
6. REFERENCES


**PRODUCTS USED**

**SURFACTANTS**

*Non-ionic*

CELESAL K-3 = Ethoxylated fatty alcohol (Medium/high degree)

CELESAL K-7 = Ethoxylated fatty alcohol (Medium/high degree) + ad2

CELESAL K-7 Conc = Ethoxylated fatty alcohol (Medium/high degree) + ad3

CELESAL DL= Ethoxylated fatty alcohol (Low degree)

CELESAL K-6 = Ethoxylated fatty alcohol (Low degree) + ad1

*Anionic*

HUMECTOL AS-21 = Dialkyl sulfosuccinate + ad5

CELESAL BE-50 = Benzenesulfonylic derivative + ad6

DETERPIEL PF-14 = Lauryl ether sulfate derivative + ad7

**ENZYMES**

DEFAT -50 = Active lipase in neutral medium

DEFAT 70 AL = Active lipase in acidic medium

DEFAT 80 PA = Active protease in acidic medium

TRIPSOL DOBLE = Active protease in alkaline medium

**PRETANNING AGENTS**

RETANAL DFS NEW = Modified aldehyde

RETANAL TAL = Aluminum triformate