CATTLE HIDE IN THE BEAMHOUSE

BARCELONA 2017

Enrique Comes
B.S. in Chemistry
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In the tanning process, the beamhouse has always been the most discussed, controversial and, at times, unknown stage of the complex leather and hide tanning process.

In the past, as is often the case with man’s knowledge, tanning was totally empirical and was based on trade practice. In the 20th Century, scientists trained in different European universities strove to give chemical explanations to the phenomena that took place during this process. So far, so good. Yet, predicting what will happen and thus improving the process by applying theoretical principles is quite a different matter. The skin is far too complex a substance, even more so when dealing with its behavior in different chemical reactions.

In the last few decades, however, we seem to have forgotten theory, and this may be due to the low level of scientific literacy shown by the professionals of the sector. We have returned to absolute pragmatism and therefore little innovation has been provided to this process. The major advances are made in the presence of a strong chemical-technical background and in-depth knowledge of the trade.

I have been working with my friend and workmate Enrique Comes for forty years, and I am certain that he has the skills to provide knowledge, experience and innovation, as well as the ability to combine theoretical studies with a strict compilation of practical experiences.

His scientific training (B.S. in Chemistry), his observation skills, his preciseness in data collection tasks, his methodical spirit, his dedication to tanneries for many years to compile industrial experiences and, mainly, his professionalism and commitment, have borne fruit in the form of this thorough treatise on the BEAMHOUSE.

This work by Enrique Comes would not have been possible without the complicity of CROMOGENIA UNITS, S.A. Ever since its foundation, this chemical company has devoted itself to the world of tanning and has always pursued a policy of reliability and respect for the tanner’s trade, a policy that has become one of the company’s hallmarks. The work conducted by its technicians has oriented and guided the tasks of development and innovation laboratories. This has allowed Enrique Comes to dedicate his time and effort to the BEAMHOUSE issue and to provide major theoretical contributions along with strict data collection. This combination broadens our knowledge and improves our systems to ensure the best results.

Vicente Benedito
Intended as an eminently practical work, this book gathers personal experiences accumulated over the years and discussions on technical innovations provided by new products as they come onto the market. The purpose is to help better understand the chemical reactions that take place, and why each operation is performed.

We all know the complexity of the soaking-unhairsing processes due to the many factors involved in chemical operations.

To begin with, the first irregularity factor is introduced by leathers themselves on account of their varying structure, natural fat content, size, state of preservation (fresh, salted, dried), thickness, flaying type, season of sacrifice, etc.
THE OPTIMAL CONDITIONS FOR LEATHER PRESERVATION ARE:

- 15% sodium chloride. For this 15% to remain in the leather, the quantity of salt to be added must range between 40% - 50% of leather weight.
- 45% humidity.
- Storage temperatures below 18º C.

The leather loses 30% of its weight 3 or 4 weeks after being salted.

Correct leather salting and further piling is shown in the pictures below:
MOST FREQUENT DEFECTS:

Raw Hide: Knife Cuts/Holes

Raw Hide: Poor Preservation
Due to Bacteria

Raw Hide: Poor Preservation
Due to Dry Out
OTHER FACTORS INVOLVED IN THIS COMPLEXITY ARE THE WORK SYSTEMS USED AT TANNERIES, INCLUDING:

- 24-hour or 48-hour soaking-unhairing processes.
- Recirculation or non-recirculation of residual baths of previous operations or consignments.
- Processes with destructive unhairing or hair-save unhairing.
- Processes carried out in traditional drums, cangilones drums or paddle vats.
- Drum size and batches in each drum.
- Full substance or split pelt, etc...

The chemical characteristics of water also modify the stability of the products involved in the processes, thus altering their penetration.

The most frequent problem results from using very hard water (above 150°HF). This impairs the stability of chemicals and therefore their penetration.
It is well known that heavier leathers always tend to be more wrinkled at the heads, cheeks and bellies than lighter ones.

It would seem logical that these wrinkles result from leather contraction, with leather shrinking leading to area loss.

Also, there are leather batches of the same origin and weight which, despite using the same formulation and mechanical system, result in either more open batches or more shrunken batches.

In all leather processes, from soaking to finishing, the final area is addressed depending on whether the products are more or less astringent.

In order to better understand how open leathers without wrinkles or shrunken effect are obtained in wet-blue conditions, and also to improve yield on the leather surface, the structure of the hide is briefly outlined below.

### CATTLE HIDE COMPOSITION

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>64%</td>
</tr>
<tr>
<td>Protein</td>
<td>33%</td>
</tr>
<tr>
<td>Fats</td>
<td>2%</td>
</tr>
<tr>
<td>Mineral Salts</td>
<td>0.5%</td>
</tr>
<tr>
<td>Other Substances</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

#### Structural Proteins
- Insoluble in water
- Soluble in acids and strong bases

#### Non-Structural Proteins
- Soluble in water

<table>
<thead>
<tr>
<th>Protein</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastin</td>
<td>0.3%</td>
</tr>
<tr>
<td>Collagen</td>
<td>29%</td>
</tr>
<tr>
<td>Keratin</td>
<td>2%</td>
</tr>
<tr>
<td>Albumins</td>
<td>1%</td>
</tr>
<tr>
<td>Mucins, Mucoids...</td>
<td>0.7%</td>
</tr>
</tbody>
</table>
**Water** is the most abundant component of the hide (64%).

The most important component of the hide is the **Protein** (33%).

Most of these proteins are structural proteins (insoluble in water, but soluble in acids and strong bases): collagen (29%), keratin (2%) and elastin (0.3%).

Much smaller quantities of non-structural (water soluble) proteins are found, namely: albumins and globulins (1%), mucins, mucoids, etc. (0.7%).

**Fats** account for 2% of the total, and the rest is composed of **Mineral Salts** (0.5%) and other substances (0.5%) (pigments, etc.)

These are approximate percentages that can vary slightly according to animal age, breed, feeding, etc.

**Non-structural** proteins are removed in raw leather **soaking**.

**Keratin** (hair and epidermis) is removed in **unharing**.

**Elastin** is removed in **bating**.

The separation of collagen fibers and the subsequent creation of reagent groups are performed in **unharing-liming**.

---

**COLLAGEN IN THE HIDE PROTEIN**

- After removing the rest of proteins, collagen accounts for the remaining 29%.
- Collagen is a simple fibrous protein composed exclusively of alpha amino acids.
- The Pauling model on proteins is characterized by atom arrangement in an alpha helix structure, as shown in the figure below:

To be highlighted are the hydrogen bonds, which maintain turn spacing.

Hydrogen binding requires that N-H bonds and C=O groups be arranged in such a way that stable hydrogen bonds are obtained.

The type of protein will be determined by the amino acids in each radical (“R” groups).
CROSS SECTION OF A FRESH COW HIDE

- Intertwined strands of a fibrous protein

Hydrogen bonds

3.6 units of amino acid 5.4 Å

@ Helix diagram

Large helix structure

Small α helices

Large helix turn

Alpha helix has a weak curvature so that 3-7 strands of intertwined rope can be formed
One of the main causes of **loose grain** is fiber degradation by dissolution (hydrolysis) or rupture (due to sudden and excessive swelling) at the junction of the papillary and reticular layers, where fibers are thinner and shorter.

In the above cross section of fresh cow hide, three areas are clearly differentiated:

- **Grain.**
- **Grain/Corium junction.**
- **Corium.**

The difference between the three lies in the way fibers agglutinate. During the animal's lifetime, skin collagen undergoes **degradation** (which continues during leather storage), and this results in other compounds derived from the protein, and different therefrom, being linked to the protein by hydrogen bonds. These compounds are acidic and neutral Polysaccharides (glycosaminoglycans or glycogen).

Glycogen, also called **DERMATAN SULFATE**, is the carbohydrate reserve of the animals, and is found both in free state and in association with the protein.

These acidic polysaccharides resulting from protein degradation are amorphous, hard, brittle, water-insoluble solids.

By hydrolysis, each polysaccharide molecule leads to the formation of “dextrin”, then maltose, then finally a large number of glucose molecules, all soluble in water.

Glycogen, or animal starch, has a structure similar to that of starch, with a large number of glucose molecules linked by means of alpha-glycosidic bonds. The main chain is formed by 12 to 18 glucose units, and another large number of similar side chains are linked to the main chain. Glycogen is a branched polysaccharide with a molecular weight ranging between 4,000,000 and 14,000,000 (25,000 to 90,000 glucose units).

For all the above, **their complete removal in the beamhouse is of utmost importance.**
DERMATAN SULFATE

1 Composition.
2 When and how it is removed.
3 Why it must be removed. Consequences of residues left on the hide.
4 Consequences if the attack (to remove it) is excessive.
5 Leathers at higher risk of undissolved residues.
6 New technology for hydrolysis.

1 Composition

- Dermatan Sulfate is composed of the substances resulting from the degradation of collagen proteins, also called interfibrillar or cementing proteins.
- It is composed of highly charged acidic polysaccharides (glycogen) whose side chains bind to the protein by means of alpha-glycosidic bonds and wrap the collagen fibers.
- Dermatan Sulfate is insoluble in water under environmental conditions.
- Dermatan Sulfate keeps the collagen fibers compacted to prevent the creation of reactive groups.
- Dermatan Sulfate is a hard, brittle solid.

2 When and how it is removed

The studies performed at the British Leather Confederation Laboratories showed that:

- The opening of the fibrillary structure in unhairing-liming is associated with the removal of Dermatan Sulfate or Proteoglycan.
- **18 hours under high alkalinity conditions** (unhairing-liming) are required to separate the Dermatan Sulfate-protein bond, where the protein is attacked by OH- ions and hydrolyzed on the ionic bonds of hyaluronic acid.

This allows removing and creating a larger number of reactive (amino acid) groups where chromium atoms will bind to amine groups in tanning and result in a greater reactivity of the leather, in a greater exhaustion of chromium in tanning, and in further reactivity with anionic products in retanning.

3 Why it must be removed

If Dermatan Sulfate residues reach the finished hide, the consequences are:

- Wrinkles in neck and bellies.
- Less surface of leather.
- Different feel between heads and the rest of the leather.
- Irregularities between different batches.
- Lower chromium fixation in tanning.
- Lower anionic product fixation in retanning.
- Hardening of the leather when pressed (pressure and temperature) in finishing.

The larger the quantity of Dermatan Sulfate in the leather, the bigger the problem.
Consequences of excessive attack to remove dermatan sulfate in unhairing

In an attempt to completely remove Dermatan Sulfate, the liming conditions can be forced by any of the following actions:

- Increasing liming time.
- Increasing lime %
- Performing further reliming.
- Decreasing lime liquor volume.
- Increasing lime liquor temperature.
- Decreasing sulfide (Na ions) percentage.

The dissolution of the collagen protein leads to:

- More attacked, thinner and shorter fibers.
- Decreased physical resistances (tensile strength, tear load and grain burst).
- Emptier, loose grain leathers.
5 LEATHERS AT HIGHER RISK OF RETAINING UNDISSOLVED DERMATAN SULFATE RESIDUES

- **Thick and heavy leathers.** (Leathers where alkaline hydrolysis in the middle stripe in liming was insufficient. Hydrolyzation time is always shorter in thicker heads).
- Leathers with **short liming.** (24-hour soaking-unhairing processes).
- Leathers with a **tighter structure** where lime penetration is slower.

6 New process for the hydrolysis of dermatan sulfate

**Cromogenia Units** has developed a product that acts by selectively hydrolyzing Dermatan Sulfate **without affecting the collagen protein.**

This product, called DECALIM PLUS, has an optimum pH application range between 7.5 and 8.5. Comparative tests are performed in successive batches with the following variables:

- Leather origin (Spain, Germany, Mexico, USA...).
- Leather weight (heavy, medium, light).
- Duration of unhairing liming process (24 or 48 hours).
- Full substance or pelt split leathers.

Tests performed in a minimum of 30 batches per variable, as shown in the Table (page 16):

- The heavier the leather, the higher the area increase. Heavy leathers > medium leathers > light leathers (no area increase in cows).
- Full substance leathers area increase higher than in split leathers.
- Short unhairings (24 h) area increase higher than in long processes.
- All result in improved selection.
The results obtained by using DECALIM PLUS are:

- Increased leather area.
- Very uniform dyeing.
- Grain defects (scratches, ticks, etc.) dyed to match tone.
- Better selection because defects are not marked.
- Uniform feel between head and butt of the same leather.
- Uniform feel between different batches.
- Better physical resistance of finished leather (tensile strength, tear load and grain burst).
- Better grain tightness.
- Less wrinkles on account of reducing unhairing-liming (lime % and time).
- Does not attack collagen fibers.

The Table below is in order of leather size, from higher to lower weight, and reflects the surface and selection increase of the different batches.

The greatest increase in surface occurs in heavier weights, and lessens with lighter weights to reach “zero” increase in light (21.74 Kg/leather) cow leathers with very open structures.

A significantly increased surface is also observed in goat and calf leathers, which have a very tight structure.
COMPARATIVE RESULTS OF STANDARD FORMULATIONS AT DIFFERENT TANNERIES, ADDING **DECALIM PLUS 0.6%** IN DELIMING  
(SUMMARY OF A MEAN HIGHER THAN 30 BATCHES PER LEATHER TYPE)

<table>
<thead>
<tr>
<th>SOA-UNH PROCES</th>
<th>ORIGIN</th>
<th>LEATHER TYPE</th>
<th>WEIGHT (KG) BATCHES</th>
<th>N° LEATHERS Batches</th>
<th>WEIGHT (KG) PELT</th>
<th>SURFACE INCREASE</th>
<th>SELECTION IMPROVEMENT</th>
<th>REASON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salting 48 h</td>
<td>Full substance</td>
<td>Spain</td>
<td>Steer</td>
<td>8,000</td>
<td>180</td>
<td>44.44</td>
<td>5.33%</td>
<td>4.3% of 1&lt;sup&gt;st&lt;/sup&gt; 7.2% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 48 h</td>
<td>Split pelt</td>
<td>Spain</td>
<td>Steer</td>
<td>7,030</td>
<td>185</td>
<td>37.84</td>
<td>3.56%</td>
<td>3.2% of 1&lt;sup&gt;st&lt;/sup&gt; 8.1% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 24 h</td>
<td>Full substance</td>
<td>Germany</td>
<td>Steer</td>
<td>10,000</td>
<td>285</td>
<td>35.08</td>
<td>4.81%</td>
<td>3.5% of 1&lt;sup&gt;st&lt;/sup&gt; 5.8% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 48 h</td>
<td>Split pelt</td>
<td>Mexico</td>
<td>Steer</td>
<td>4,800</td>
<td>145</td>
<td>33.1</td>
<td>3.12%</td>
<td>4.1% of 1&lt;sup&gt;st&lt;/sup&gt; 4.5% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 24 h</td>
<td>Full substance</td>
<td>Mexico</td>
<td>Steer</td>
<td>3,000</td>
<td>95</td>
<td>31.58</td>
<td>3.75%</td>
<td>3.7% of 1&lt;sup&gt;st&lt;/sup&gt; 5.6% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 48 h</td>
<td>Split pelt</td>
<td>Ireland</td>
<td>Steer</td>
<td>6,000</td>
<td>195</td>
<td>30.77</td>
<td>3.23%</td>
<td>2.5% of 1&lt;sup&gt;st&lt;/sup&gt; 5.2% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 24 h</td>
<td>Full substance</td>
<td>USA</td>
<td>Steer</td>
<td>5,300</td>
<td>200</td>
<td>26.5</td>
<td>2.25%</td>
<td>2.2% of 1&lt;sup&gt;st&lt;/sup&gt; 5.3% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 24 h</td>
<td>Full substance</td>
<td>Spain</td>
<td>Steer</td>
<td>9,000</td>
<td>370</td>
<td>24.32</td>
<td>1.63%</td>
<td>1.2% of 1&lt;sup&gt;st&lt;/sup&gt; 2.4% of 2&lt;sup&gt;nd&lt;/sup&gt;</td>
</tr>
<tr>
<td>Salting 24 h</td>
<td>Full substance</td>
<td>France</td>
<td>Cow</td>
<td>5,000</td>
<td>230</td>
<td>21.74</td>
<td>0%</td>
<td>0</td>
</tr>
<tr>
<td>Salting 24 h</td>
<td>Full substance</td>
<td>Spain</td>
<td>Cow</td>
<td>3,200</td>
<td>180</td>
<td>17.7</td>
<td>0.10%</td>
<td>0</td>
</tr>
</tbody>
</table>

THE PHYSICAL RESISTANCES OF FINISHED LEATHER ARE IMPROVED:

- **TENSILE STRENGTH**
- **TEAR LOAD**
- **GRAIN BURST**
- **GRAIN TIGHTNESS**

WRINKLING IS DECREASED AND THIS HELPS DECREASE LIMING (LIME % AND TIME)

THE COLLAGEN FIBER IS NOT ATTACKED BY THIS PRODUCT
We shall define a work system providing the highest possible uniformity in the final article and, from there on, we shall approach the different modifications to adjust to the above mentioned variables.

In all processes, from soaking to tanning, the main purpose is to reach equilibrium between the bath pH and the inner leather pH in each and every operation performed.

The evolution of product penetration inside the leather is ascertained by means of different indicators, which depend on the pH range:

- Universal Indicator in *soaking*
- Phenolphthalein in *deliming*
- Bromocresol green in *pickling*

The color of the leather will indicate the exact stage of product penetration in *unhairing* and *tanning*.

Water penetration inside the hide must be controlled in soaking to ensure complete moistening.

To do this we rely on the fact that water acts as a mere carrier of the alkalinity of the bath. Because the bath pH is higher than the hide pH, the inner hide pH will also increase as water penetrates.

Therefore, controlling this pH allows controlling soaking penetration and water penetration inside the leather.

This is performed with the **UNIVERSAL INDICATOR**, as follows:

- 6,5 → Intense red
- 7 → Yellow
- 7,5 → Greenish yellow
- 8,5 → Green
- 9 → Bluish green
- 9,5 / 10 → Blue
Fresh leather has a pH of 7.5. In piled salted leather, fat breaks down into fatty alcohols and fatty acids that decrease the leather’s pH. The longer the time elapsed, the lower the leather’s pH.

**Salted leather:** previous desalting in desalting drum is advised to remove salt and reduce waste water conductivity.

**Fresh leather:** previous fleshing is advised.

Soaking can be divided into two clearly differentiated parts: pre-soaking and main soaking.

### PRE-SOAKING

Before this process, and depending on how dirty the leathers are, initial washing with cold water can be performed.

- **The purpose of pre-soaking is two-fold:**
  - Removal of dirty and water soluble proteins.
  - Leather tempering before starting actual soaking.

- **Pre-soaking characteristics:**
  - Short duration (15 min – 60 min) and little movement.
  - Water levels equal to or higher than 200%.
  - Water temperature between 25º and 29º, depending on the origin of the leathers (warm or extremely cold climates).

- **Use of a bactericidal agent and a small quantity of moistening agent.**
MAIN SOAKING

The purpose of soaking is to return the leather to its natural swelling state and to remove dirt, soluble protein substances, and preserving agents.

The duration of soaking depends on whether the soaking-unhairing process lasts 24 or 48 hours. In either case, however, complete moistening must be reached. Therefore, short soakings require that the remaining factors involved in achieving a good soaking (auxiliary product offer, mechanical work, temperature, etc.) be increased to make up for the shorter duration of soaking.

The rotational speed of the drum also depends on the duration of soaking. Thus, rotational speeds of 2 rpm can be used in 48-hour processes, but mechanical work must be increased in 24-hour processes and go up to 4 rpm.

The ideal pH for good moistening is around 9.5. We must always pay attention to the pH-related collagen swelling curve. In this curve, the leather starts swelling significantly in an alkaline area of pH around 10.5, with maximum swelling at pH around 12.5.

Once stabilized, the temperature of the soaking bath should range between 24-26°C in long soakings—even a bit less in hot climates—and between 26-28°C in short soakings.

This small increase in temperature increases the moistening speed.

If the leather has a tendency to blind grain due to a significant presence of bacteria, the soaking temperature must never exceed 25°C.
Histologic evaluations have shown bacteria to **degrade the papillary and reticular junction**.

Bacteria are first responsible for blind grain and finally cause loose grain.

**If bating is omitted, the damage caused by bacteria is barely visible.**

Two soaking formulations are proposed:
**OPTION A** is a simple option where one single product is used to obtain complete soaking. This product is called HUMECTOL RAPID and combines surfactant, moistening and pH- correction properties.

Only a bactericidal agent needs to be added in poorly preserved leathers or in leathers with a tendency to blind grain due to bacterial action.

**OPTION B**, where the products are provided separately.

In the scope of Surfactants, the action of CELESAL CN is emphasized. This energetic wetting agent (a fatty acid with a very high number of moles of ethylene oxide) outstands for its great stability in hard water (170ºHf or greater), that is, the wetting effect of Celesal CN remains intense in extremely hard water.

While the use of degreasing agents like CELESAL DL, CELESAL INP, etc. (oxiethylenated fatty alcohols with a low number of moles of ethylene oxide) favors good moistening, overusing these agents poses a latent danger: if the natural fat of the leather is moved at that time, the spaces filled by fat become empty and the fibers are less protected against the attack of sulfide —and mainly lime— in unhairing; also, a larger amount of collagen protein is dissolved.

The consequence of this increased attack is seen at the end of the process in what is known as “loose grain”.

In very fatty hides it can be used at a larger percentage because it will act more as an emulsifier of the bath’s fat than as a degreasing agent.

The right time to degrease leather is after deliming or in bating, but not in soaking.

Both CELESAL DL and CELESAL INP are highly appropriate for this subsequent degreasing process.

HUMECTOL ULTRA is proposed as a concentrated enzymatic agent that increases the speed of soaking.

The use of enzymatic products at either soaking or unhairing must be considered when the enzymatic offer is formulated during the bating process. The higher the enzymatic offer in soaking and unhairing, the lower the enzymatic offer in bating.

The commonest alkaline products are sodium carbonate, sodium hydroxide and sodium tetrasulfide (HUMECTOL TS).

The pH of the soaking bath must never exceed 10.5. If this pH were reached, the leather surface would start to swell, lead to hair root choking (producing hair root in unhairing), and also negatively affect the grain burst values in the finished hide.
In order to ensure pH stability in the soaking bath, Cromogenia offers a buffering agent called HUMECTOL TPH; this product is most suitable in very fatty leathers (U.S.A. or Australia types). Indeed, when common alkalis are used in these very fatty leathers, alkalinity saponifies fat and the pH of the soaking bath decreases with running time. pH values down to 7 may be reached and the desired moistening is not attained.

Conversely, if Humectol TPH is used, the bath pH is kept constant at 9.5 throughout soaking, and better moistening is attained.

ASEPTANTE DMC (dimethyldithiocarbamate) is proposed as bactericidal agent.

Because the use of bactericidal agents has become more and more restricted across the world for ecological reasons, a small quantity (0.2 – 0.4) of sodium sulfide or sodium hydrosulfide can be used in soaking.

Its use is well accepted by some technicians because, in addition to alkalinizing the bath, it starts loosening the hair root and also allows slowing down bacterial development on account of its bacteriostatic action.

Once the soaking process is complete, the following FINAL SOAKING CONTROLS must be performed:

- **Bath control:**
  - pH = 9.5
  - T = 26º C

The density of the final soaking bath of salted leather should range between 3-4º Bé.

Values exceeding 4 suggest that the initial soaking baths have been insufficient. Ten-minute washing in closed door and bath draining must be performed. In subsequent batches, the number of initial baths must be increased to improve soaking.

- **Leather control:**

  The section in the thicker and tighter areas (neck and butt, respectively), must be white and show no blood.

Penetration control in soaking with a Universal Indicator, as follows:

- 7.5 → Greenish yellow
- 8.5 → GREEN
- 9 → Bluish green
- 10 → Blue
The section must be as uniformly bluish green as possible.

Lateral pressure exerted on a section must result in a “concertina effect” rather than in one single fold.

A more objective method is to weigh a piece of hide and dry it totally to obtain its water content. A proper soaking is that where the amount of water in the leather is 65 - 68%.

**Hide areas not properly rehydrated may remain without unhairing.**
With the same unhairing, we may obtain:

- **Insufficient soaking**, which provides harder leather with poorer grain tightness and prevents unhairing products from properly penetrating the leather, resulting in irregularities and more marked wrinkles at the head and the belly.

- **Excessive soaking**, which provides a more open leather with less wrinkles, but emptier and with a clear tendency to loose grain.
In view of all the above, the following Soaking formulations can be implemented:

All referring to salted hide sweeping weight.
SOAKING OPTION A
Process for salted leather in soaking - Unhairing for 48 hours in drum.

<table>
<thead>
<tr>
<th>Cold Water</th>
<th>200%</th>
<th>Run 10 min. (slow running)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water 26° C</td>
<td>200%</td>
<td>Run 10 min. (slow running)</td>
</tr>
<tr>
<td>Celesal DL</td>
<td>0.05%</td>
<td>Run 10 min. (slow running). Stop 30 min. Run 20 min. Drain bath 20 min.</td>
</tr>
<tr>
<td>Aseptante DMC</td>
<td>0.04% (poorly preserved leather only)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water 26° - 28° C</td>
<td>120% (according to outdoor temperature)</td>
<td></td>
</tr>
<tr>
<td>Aseptante DMC</td>
<td>0.04% (poorly preserved leather only)</td>
<td></td>
</tr>
<tr>
<td>Humectol Rapid</td>
<td>0.9%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>0 - 0.3% (according to bath pH)</td>
<td></td>
</tr>
<tr>
<td>Sodium Sulfide</td>
<td>0 - 0.3%</td>
<td></td>
</tr>
<tr>
<td>Run 180 min. Automatic, running 10 min / hour</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Following day:</strong> Run 30 - 120 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bath control:</strong> pH = 9.5; T = 26° C, d &lt; 4° Bé</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Leather control:</strong> The section at the thicker areas of the hide must be white, without blood, and crossed greenish blue on the Universal Indicator. Drain bath 15 min. to start unhairing.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SOAKING OPTION A
Process for salted leather in soaking - Unhairing for 24 hours in drum.

<table>
<thead>
<tr>
<th>Cold Water</th>
<th>200%</th>
<th>Run 10 min. (slow running). Drain bath 15 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water 26° C</td>
<td>200%</td>
<td>Run 10 min. (slow running). Stop 30 min. Run 20 min. Drain bath 20 min.</td>
</tr>
<tr>
<td>Celesal DL</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>Aseptante DMC</td>
<td>0.04% (poorly preserved leather only)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water 26° - 28° C</td>
<td>120% (according to outdoor temperature)</td>
<td></td>
</tr>
<tr>
<td>Aseptante DMC</td>
<td>0.04% (poorly preserved leather only)</td>
<td></td>
</tr>
<tr>
<td>Humectol Rapid</td>
<td>1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>0 - 0.3% (according to bath pH)</td>
<td></td>
</tr>
<tr>
<td>Sodium Sulfide</td>
<td>0 - 0.3%</td>
<td></td>
</tr>
<tr>
<td>Humectol Ultra</td>
<td>0 - 0.05% (according to leather dryness)</td>
<td></td>
</tr>
<tr>
<td>Run 6 hours.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bath control:</strong> pH = 9.5; T = 26° C, d &lt; 4° Bé</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Leather control:</strong> The section at the thicker areas of the hide must be white, without blood, and crossed greenish blue on the Universal Indicator. Drain bath 15 min. to start unhairing.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### SOAKING OPTION B

**Process for salted leather in soaking - Unhairing for 48 hours in drum.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER 20º C</td>
<td>200%</td>
<td>Run 10 min. (slow running). Drain bath 15 min.</td>
</tr>
<tr>
<td>WATER 26º C</td>
<td>200%</td>
<td></td>
</tr>
<tr>
<td>CELESAL DL</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>ASEPTANTE DMC</td>
<td>0.04%</td>
<td>(poorly preserved leather only)</td>
</tr>
<tr>
<td>Run 10 min. (slow running). Stop 30 min. Run 20 min. Drain bath 20 min.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WATER 26º - 28º C</td>
<td>120% (according to outdoor temperature</td>
<td>(poorly preserved leather only)</td>
</tr>
<tr>
<td>ASEPTANTE DMC</td>
<td>0.04%</td>
<td></td>
</tr>
<tr>
<td>CELESAL CN</td>
<td>0.3 - 0.5%</td>
<td>(according to leather thickness or water hardness)</td>
</tr>
<tr>
<td>SODIUM CARBONATE</td>
<td>0.2 - 0.3%</td>
<td>(according to water pH)</td>
</tr>
<tr>
<td>HUMECTOL TPH</td>
<td>0.2 - 0.3%</td>
<td>(according to water pH)</td>
</tr>
<tr>
<td>CELESAL DL</td>
<td>0.02 - 0.2%</td>
<td>(according to leather fat)</td>
</tr>
<tr>
<td>Run 180 min. (normal run). pH = 9.5; T = 26º C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RIBERSAL LA</td>
<td>0 - 0.2%</td>
<td>(in heavy or dirty leather)</td>
</tr>
<tr>
<td>VERDITAN CV</td>
<td>0 - 0.6%</td>
<td>(in leather with blood veins)</td>
</tr>
<tr>
<td>SODIUM SULFIDE</td>
<td>0.2 - 0.3%</td>
<td></td>
</tr>
<tr>
<td>Run 180 min. Automatic, running 10 min / hour. Total 16 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Following day:</strong> HUMECTOL ULTRA 0-0.03% (according to soaking state) Run 30 - 120 min.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bath control: pH = 9.5; T = 26º C; d &lt; 4º Bé</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leather control: The section at the thicker areas of the hide must be white, without blood, and crossed greenish blue on the Universal Indicator. Drain bath 15 min. to start unhairing.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### SOAKING OPTION B

**Process for salted leather in soaking - Unhairing for 24 hours in drum.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER 20º C</td>
<td>200%</td>
<td>Run 10 min. (slow running). Drain bath 15 min.</td>
</tr>
<tr>
<td>WATER 26º C</td>
<td>200%</td>
<td></td>
</tr>
<tr>
<td>CELESAL DL</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>ASEPTANTE DMC</td>
<td>0.04%</td>
<td>(poorly preserved leather only)</td>
</tr>
<tr>
<td>Run 10 min. (slow running). Stop 30 min. Run 20 min. Drain bath 20 min.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WATER 26º - 28º C</td>
<td>120% (according to outdoor temperature</td>
<td>(poorly preserved leather only)</td>
</tr>
<tr>
<td>ASEPTANTE DMC</td>
<td>0.04%</td>
<td></td>
</tr>
<tr>
<td>CELESAL CN</td>
<td>0.3 - 0.5%</td>
<td>(according to leather thickness or water hardness)</td>
</tr>
<tr>
<td>SODIUM CARBONATE</td>
<td>0.2 - 0.3%</td>
<td>(according to water pH)</td>
</tr>
<tr>
<td>HUMECTOL TPH</td>
<td>0.2 - 0.3%</td>
<td>(according to water pH)</td>
</tr>
<tr>
<td>CELESAL DL</td>
<td>0.02 - 0.2%</td>
<td>(according to leather fat)</td>
</tr>
<tr>
<td>Run 60 min. (normal run). pH = 9.5; T = 26º C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RIBERSAL LA</td>
<td>0 - 0.2%</td>
<td>(in heavy or dirty leather)</td>
</tr>
<tr>
<td>VERDITAN CV</td>
<td>0 - 0.6%</td>
<td>(in leather with blood veins)</td>
</tr>
<tr>
<td>SODIUM SULFIDE</td>
<td>0.2 - 0.3%</td>
<td></td>
</tr>
<tr>
<td>HUMECTOL ULTRA</td>
<td>0 - 0.06%</td>
<td>(according to leather dryness)</td>
</tr>
<tr>
<td>Run 6 hours.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bath control:</strong> pH = 9.5; T = 26º C; d &lt; 4º Bé</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leather control: The section at the thicker areas of the hide must be white, without blood, and crossed greenish blue on the Universal Indicator. Drain bath 15 min. to start unhairing.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CANGILONES DRUM

This is basically a standard wooden drum where classical stakes have been replaced with four internal spades (buckets) arranged transversely and parallel to their horizontal axis.

Up to 20 tons of gross weight can be processed.

The soaking-unhairing chemical processes are similar to those performed in a conventional drum, although a higher product concentration is used — work being done with reduced bath percentages (no room available for more bath). The active principle that yields the mechanical effect changes from centrifugal force to friction and gravity.

Because both operations are exothermic, the temperatures of the unhairing and pickling processes must be controlled.

In these two processes, temperature increases at a rate of 1 °C / hour of running.

There are peripheral elements (coolers) that control temperature increase in unhairing and pickling, and peripheral elements (heaters) that heat the tanning bath.

If coolers are not available, ice bars are added directly to the bath.

In deliming-tanning processes, new cangilones drums have been marketed which have three blades instead of four and that increase the penetration rate of the products in a way similar to traditional stake drums.
SOAKING IN CANGILONES DRUM  OPTION B

Process for salted leather in Soaking- Unhairing for 48 hours.

<table>
<thead>
<tr>
<th>Water Temp</th>
<th>Quantity</th>
<th>Components</th>
<th>Concentration</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER 20º C</td>
<td>150%</td>
<td></td>
<td></td>
<td>Washing with water entering one side and exiting the opposite side  5 min.</td>
</tr>
<tr>
<td>WATER 25º C</td>
<td>100%</td>
<td>DETERPIEL PF-14</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>SODIUM SULFIDE</td>
<td>0.15%</td>
<td>ASEPTANTE DMC</td>
<td>0.04% (in poorly preserved leather only)</td>
<td>Run 60 min. (slow running). Drain bath 20 min.</td>
</tr>
<tr>
<td>WATER 26º - 28º C</td>
<td>100%</td>
<td>ASEPTANTE DMC</td>
<td>0 - 0.04% (poorly preserved leather only)</td>
<td></td>
</tr>
<tr>
<td>CELESAL CN</td>
<td>0.3 - 0.5% (according to leather thickness or water hardness)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CELESAL DL</td>
<td>0.02 - 0.2% (according to leather fat)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SODIUM SULFIDE</td>
<td>0.2%</td>
<td>Run 30 min. pH = 8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% Na (OH)</td>
<td>0.1% (according to water pH)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rodar 120 min. pH = 9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% Na (OH)</td>
<td>0.1% (according to water pH)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 120 min. pH = 9.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RIBERSAL LA</td>
<td>0 - 0.2% (in heavy or dirty leather)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VERDITAN CV</td>
<td>0 - 0.2% (in leather with blood veins)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 8 hours in slow running. Total soaking 16 hours.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Following day:</strong> Run 15 min.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bath control:</strong> pH = 9.5; T = 26º C; d &lt; 4º Bé</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Leather control:</strong> The section at the thicker areas of the hide must be white, without blood, and crossed greenish blue on the Universal Indicator.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drain bath 15 min. to start unhairing.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## SOAKING IN 16.000-L PADDLE VAT

**Hide type:** Salted cattle hide

**Size:** 30 / 35 Kg

**Weight:** 4.500 Kg

**Soaking-Unhairing - Process:** 48 hours

<table>
<thead>
<tr>
<th>Water Temperature</th>
<th>AT Axis</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>22º C</td>
<td>0.04%</td>
<td><strong>ASEPTANTE DMC</strong> Run 30 min. Stop 30 min. Drain bath</td>
</tr>
<tr>
<td>22º C</td>
<td>0.2%</td>
<td><strong>CELESAL DL</strong> Run 60 min. Control: density &lt; 2 Bé. Drain bath</td>
</tr>
</tbody>
</table>
| 28º C             |         | **SODIUM CARBONATE** 0.2 - 0.3%
|                   |         | **CELESAL CN** 0.6 – 0.8%
|                   |         | **CELESAL DL** 0.05 – 0.2%
|                   |         | Run 180 min. Control: density, pH, temperature |
|                   |         | **SODIUM SULFIDE** 0.3%
|                   |         | Run 60 min. Control: pH = 9.5 |
|                   |         | **SODIUM CARBONATE** 0 / 0.2 (according to pH)
|                   |         | Run 4 hours. pH = 9.5. Run 4 hours
|                   |         | Automatic run 10 min / hour

**Following day:** density, pH and temperature control

The section at the thicker areas of the hide must be white, without blood.

Uniform greenish color on the Universal Indicator.

Drain.

Wash 5 min. Drain.
EVOLUTION OF SOAKING PENETRATION IN SALTED LEATHER

1.- Cross section of raw hide without indicator

2.- Cross section of leather at 3 hours of soaking

3.- Cross section of leather at 4 hours of soaking
3’.- Difficult penetration due to the presence of flesh

3’’.- Difficult penetration due to the presence of fat

3”.- Homogeneous, correct penetration at 5 hours of soaking
4.- Cross section at 5 hours of soaking

5.- Cross section at 6 hours of soaking

6.- Cross section at 7 hours of soaking
Evolution of the different pHs depending on soaking penetration (alkalinity)

Different penetrations in butt and neck of the same leather at 4 hours

Soaking penetration at 3 hours

Soaking penetration is more difficult in dried out areas
**pH = 7.5**

**pH = 9.5**

*Much more defined penetration line*

---

**Bath pH = 9.5**

**Leather pH = 8.5**

*Penetrated soaking, at low pH*

---

**Bath pH = 9.5**

**Leather pH = 9**

*Correctly penetrated final soaking*

---

*Soaking without auxiliary products (alkalis only)*
PART II  UNHAIRING

Purpose of unhairing:

1  Total removal of hair and epidermis.
2  Loosening of collagen fibers to give a relaxed effect more commonly known as “liming effect” or “fibrous structure loosening effect”.
3  Partial fat saponification

In order to devise a correct unhairing system whose formulation can be modified as required, the **physical aspects of leather undergoing the soaking and unhairing chemical processes** are now addressed.

Important concepts to be remembered are:

With the same soaking, unhairings with strong structural loosening will yield softer and more pliable finished leathers with less marked wrinkles, but at risk of loose grain, emptier leathers, worse bellies, and greater water absorption.

Conversely, unhairings with insufficient loosening will yield finished leathers with tighter and finer grain, better and fuller bellies, but also with a tendency to form wrinkles at the neck.

Experience has shown that the lower the swelling, the higher the loosening; conversely, the tighter the fibrous structure of the hide, the lower the loosening.
This can be explained by the fact that, if swelling and tightness are scarce, chemicals can diffuse better and more deeply into the fibrous structure, and also by the fact that a tight collagen fiber is less attacked than a loose tissue.

Swelling (thickness variation) and hardening (turgidity) depend on two factors:

- **The pH value**

According to the pH-related swelling of the leather, the higher the pH, the higher the swelling up to pH=13.

The final pH of unhairing should never be lower than 12. Minimum swelling—that is, minimum fiber separation and fibrous structure loosening—must be obtained.

Once minimum swelling is obtained, the more progress is made from swelling to turgidity (or maximum swelling), the lower the loosening effect.

This is achieved by adding more water during the liming process.

This fiber separation allows creating reactive groups (amine groups and acid groups) which, before fiber separation, made up for each other.

At the same time, this fiber separation leads to a higher penetration rate of deliming, pickle acids, and chromium.

Also, a better fixation of chromium in tanning is obtained.

- **The type of cation**

At the same pH, sodium ions always cause greater swelling and greater turgidity than calcium ions.

In unhairings where the quantity of lime is kept constant (5.93 kilos/cubic meter, i.e. three times the value of saturation), where increasing amounts of sodium hydroxide or sodium sulfide are added, and where pH is slightly increased, the ratio of sodium ions is also increased. This, however, occurs not only proportionally to the added quantities, but also on account of the strongly decreased dissociation of lime—whose solubility is lower. This results in significant calcium ion removal from the unhairing bath that favors a greater presence of strongly swelling sodium ions.

The addition of sodium hydroxide at the end of unhairing causes swelling and slows down, or stops, the loosening effect.

Therefore, the higher the pH and the presence of sodium ions, the higher the swelling and the turgidity.

The higher the swelling, the lower the structural loosening effect.

The lower the offer of sodium sulfide, the higher the structural loosening effect.

In short:

- The lower the loosening, the better the bellies but the stiffer and the harder the leather, with wrinkles at the neck.

- The higher the loosening, the softer and more pliable the leather; however, loose grain, empty bellies and worse physical resistance are apparent in the finished leather.
Empirically, the **FACTORS THAT INFLUENCE SWELLING**, and therefore the loosening effect, are:

1 **Temperature variation**

   The higher the temperature, the lower the swelling and the turgidity, and therefore the higher the structural loosening effect. A temperature of 25° C must not be exceeded in the unhairing bath to avoid excessive loosening.

2 **Calcium hydroxide and sodium sulfide ratio**

   The higher the quantity of lime and the lower the quantity of sodium sulfide, the higher the structural loosening effect.

3 **Partial replacement of sodium sulfide with sodium hydrosulfide**

   It is well known that replacing sodium sulfide with sodium hydrosulfide maintains the dehairing effect, decreases swelling and turgidity, and increases the structural loosening effect.

   Using calcium sulfhydrate instead of sodium hydrosulfide increases the structural loosening effect even more. This product is used in leather glove and upholstery making.

4 **Salt addition**

   Adding small quantities of calcium chloride in unhairing always leads to decreased swelling and turgidity, therefore increasing the structural loosening effect.

   However, if high amounts (greater than 1.5%) are used, the ensuing hydrotropic action should be considered. While calcium chloride does not cause swelling by itself, it does intensify the action of swelling agents by breaking hydrogen bonds between polypeptide chains.

5 **Influence of the amount of bath**

   The use of a system called “drum painting” is becoming widespread. This consists in using a small quantity of bath, which is brought to customary volume (200%) only after unhairing product penetration.

   The advantage of this system lies in very limited swelling being obtained in the first phase of unhairing, on account of the lack of water. However incipient, hair is totally destroyed by the strong concentration of chemicals, which penetrate very deeply on account of the lack of swelling.
At a later phase, the quantity of bath is increased and the necessary swelling and turgidity take place. This system is as follows:

- Start with a short float (30 – 40%, depending on soaking draining) and add the auxiliary products. These will act as bridges, remove wrinkles and emulsify fats present in the bath (amines or polysaccharides and surfactants or lipases).
- Add reducing agents (sulfide, sulfhydrate, and a little lime (1%) to reach pH=12.4) and allow for sufficient time to remove all keratin residues (3-4 hours).
- Add the rest of lime for liming and allow for sufficient time to obtain the desired fiber structure loosening for each treated leather (1-4 hours).
- Add water to swell the leather across the whole section at the same time without causing different tensions between layers on account of the penetrations of the above products. This will also slow down liming.

In contrast, unhairing processes starting with abundant water lead to swelling from the very beginning and from the surface down, and cause pH-related tensions between layers that lead to more marked wrinkles at the neck. This drawback should be overcome by gradually adding chemicals.

6 Duration of unhairing

There is a direct relationship between the structural loosening effect and the duration of the process: the longer the duration, the stronger the loosening effect.

In short, we may conclude that the structural loosening effect will be stronger in unhairing with:

- A higher temperature (always within the established range of 22 - 28º C).
- A higher quantity of lime.
- A lower quantity of sulfide.
- A higher quantity of sulfide being replaced with sulfhydrate.
- The addition of 1% calcium chloride.
- A short float (30 – 40%).
- A longer time.
Therefore, the different events during the unhairing process can be outlined as follows:

1. **Reaction of anti-wrinkle agents** (amines, thioglycolates, mercaptanes, etc.) with collagen, yielding secondary products that will act as reaction buffers to slow down the penetration rate of unhairing products and obtain a much slower swelling of the leather — and less wrinkles.

2. **Addition of lime** for hair immunization. The greater the % of lime and the longer the reaction time, the greater the immunization.

   Importantly, the immunization process keeps acting by lime diffusion even after the drum has been stopped.

3. **Unhairing:** Unharing is obtained by adding sodium sulfide and/or sodium hydrosulfide at a pH > 11.5. This is when keratin hydrolysis occurs.

   The initial concentration (first addition) of $\text{SNa}_2$ or $\text{SHNa}$ should be high enough to attack the hair root. A bath rich in Ca** ions allows more sulfide to be added to the initial take without fear of excessively fast swelling; indeed, Na+ ions are displaced by Ca** ions and swelling is reduced.

   Good unhairing and a keratin-free surface are required before liming is initiated. If hair or keratin residues are found, duration should be increased and/or sulfide should be added.

4. **Liming:** Addition of remaining lime. Because the bath again contains a greater number of Ca** ions, these again displace Na+ ions and the abovementioned structural loosening effect of collagen begins.

   Collagen hydrolysis occurs in this phase, the leather relaxes and its surface is extended, and neck and shanks wrinkles disappear.

   Collagen fibers get finer and shorter, which allows obtaining emptier leathers with a tendency to looser grain.

   As already mentioned, the duration of liming will depend on the leather structure, weight and size and on the article to be manufactured.

5. **Final swelling:** The leather may absorb water up to 55% of its weight. This maximum absorption occurs with the final addition of water and allows obtaining the swelling desired to cause the appearance of the reactive groups (amine groups and acid groups).
Water addition must always be performed once the leather has been fully penetrated by reducing agents (the section is brown) so as not to cause different swellings in the different areas of the leather, which leads to wrinkles.

Once a general Soaking – Unhairing formulation has been established, the possible modifications thereof should be considered, depending on several factors.

For instance, an already established and authorized formulation for 25 Kg/leather fresh cattle hide will be modified according to the following:

1. **Leather preservation conditions**: if SALTING conditions are used, increase batch weight to make up for weight loss at salting.

   Increase by 10% if moisture is still well maintained.

   Increase by 15% if the tips of cheeks and shanks begin to dry.

   Increase by 20% if the entire leather begins to dry.

2. **Leather weight** (for both fresh leathers and salted leathers):

   - Leathers < 25 Kg/leather: increase sulfide-hydrosulfide % and decrease lime % and/or time.
   - Leathers > 25 Kg/leather: decrease sulfide-hydrosulfide % and increase lime % and/or time.

3. **Leather thickness** (for both fresh leathers and salted leathers):

   - In fine or thin leathers (as in cow leather): increase sulfide-hydrosulfide % and decrease lime % and/or time.
   - In heavy and thick cattle hide, decrease sulfide-hydrosulfide % and increase lime % and time.
Special mention must also be made of cangilones drum processes, which always involve very low bath volumes and a very strict control of bath temperatures.

Once the washings after unhairing-liming have been performed, it is important for the leather to effortlessly pass through the fleshing machine so that fleshing is performed without excessively tightening the machine. This would result in fiber burst and further loose grain, or, in extreme cases, in grain burst and crack, mainly in the middle area of the butt in case of bulge due to excessive turgidity in unhairing. That is why the leather surface must be devoid of fat.

In general, the most frequently used products in all systems are:

**SODIUM SULFIDE** Destroys hair with little loosening of hide

**SODIUM SULFHYDRATE** Less alkaline than sulfide (less swelling).
To be preferably used at the beginning of unhairing for a more moderate swelling of the hide. A smoother, firmer grain is obtained.

**CALCIUM HYDROXIDE** Strong loosening of hide.
The lower the temperature, the higher the solubility.

While standard unhairings can already be obtained with these products, other auxiliary products are used to improve the quality of the final article:

**MOLASSES** It increases the solubility of lime. Hence, at 20º C:

- The solubility of lime without molasses addition is: 1.56 gr / l
- With 1%: 2.05 gr / l
- With 2%: 2.73 gr / l

**CALCIUM CHLORIDE** It decreases swelling of unhairing added with the first lime.

**AMINES** They loosen the hair root and favor the penetration of other chemicals, thus resulting in improved regularity of penetration and in less wrinkled hides.

**MERCAPTANES** Have these same properties, but their use has fallen appreciably.

The **AUXILIARY PRODUCTS FOR UNHAIRING** offered by Cromogenia are:

**RIBERSAL PLE** A combination of several amines for best homogeneity of penetration of the rest of chemicals, resulting in wrinkle-free leathers.
Lately, the use of amines is being called into question in several countries for ecological reasons.

As an alternative to amines, Cromogenia offers RIBERSAL LA (an amine-free polysaccharide). In addition to its antiwrinkling effect, this product increases the penetration rate of lime in liming and helps decrease the penetration time of lime, yielding more relaxed, less wrinkled leathers. It is strongly advised for heavy leathers. It levels the in-depth relaxation effect.

Comparative tests of Ribersal PLE (amine) versus Ribersal LA (polysaccharide) used at the same stage (at the beginning of unhairing) with an offer of 1% PLE and 0.7% LA have shown Ribersal LA to provide:

- Higher deharing rates (particularly observed in hair-save unhairing).
- Higher lime penetration rates
- Cleaner leathers.
- Less swelled, more relaxed leathers.
- Fuller wet-blue.

As compared to PLE, with similar wrinkles at the neck.

Experiments have shown that the addition of 0.2 – 0.3% Ribersal LA in the last lime take favors the disappearance of wrinkles at the neck. This is ideal in heavy leathers (40 kg or more).

RIBERSAL PLE-40 —a modification of RIBERSAL PLE designed for faster dissolution of dark stains produced by epidermis residues— is a very effective product in leathers tending to have keratin residues left on their surface. It is used at the same stage and doses as RIBERSAL PLE.

RIEBRSAL TD Reduced wrinkles. Blend of reducing substances. Amine-free product.

RIBERZYM MPX An enzymatic product composed of proteases that helps selectively solubilize the keratin of the hair —yielding cleaner leathers— and decrease the offer of sodium sulfide.

Both the epidermis and the hair are removed and separated from the dermis during unhairing by means of reducing chemicals.

Occasional areas with adhered epidermis can be found, which eventually appear as dark areas on the surface. The use of Riberzym MPX is highly appropriate in leathers with epidermis residues at the end of unhairing, despite good soaking.
RIBERZYM AT  An enzymatic product, similar to Riberzym MPX, with protease and elastase to help remove blood veins.

DEFAT 50 An enzymatic product composed of lipases that dissolve the fat of the adipose follicle of the hair root. Because the hair is not retained on account of fat dissolution, it goes off much more easily. This product is ideal in case of hair root problems.

Lipase breaks down natural fat (triglyceride) into diglycerides and monoglycerides, and finally into fatty acids and fatty alcohols.

Defat 50 favors lime penetration and is a very effective product in short unhairings of heavy leathers.

The offer should not exceed 0.1% —excessive action results in empty hide.

Some technologies use lipases in soaking. My personal experience is that, while more soaked and more open leathers are obtained, lipases always increase loose grain in the final article (see above).

Because enzymes (both proteases and lipases) lose activity in the presence of anionic surfactants, they must never be added together in the same bath.

CELESAL CN This product has already been discussed in the Soaking section as a moistening agent.

It is recommended in unhairings of heavy leathers (more than 35 kilos per leather) and in fatty leathers to favor the penetration of the rest of chemicals.

CELESAL INP, CELESAL DL Degreasing products. Oxyethylated fatty alcohols with a small number of moles of ethylene oxide.

It is appropriately used at the beginning of unhairing, together with the amine, in fatty leathers and in leathers undergoing short soaking. Its use with the last lime take yields cleaner leathers and helps emulsify the fat present in the liming bath (excessive fat can remain stuck to the drum walls).

CELESAL BE - 50 An exceptional emulsifier of fat originated in unhairing. While it does not degrease the leather, it keeps all the fat emulsified. It is highly advisable for empty leather unhairing, where the entire natural fat of the leather must be preserved to avoid loose grain.

Also important is unhairing with hair-save unhairing, where the hair is immunized with lime before adding sulfide. Once the hair has gone off, it is filtered and further separated.

Lime penetration must be just as required to reach the hair root for correct dehairing and complete hair extraction.

The degree of penetration is controlled with phenolphthalein.
Several factors are involved in this system:

1. The percentage of lime offered. A quantity between 1.2 and 2% is sufficient. The higher the amount of lime, the higher the degree of immunization.

2. The time of reaction of lime with the leather before adding sulfide or sulphydrate. A time between 45 minutes and 1 hour is sufficient.

3. The presence of fat in the leather and hair surfaces hinders lime penetration. The longer the time, the higher the immunization. Most importantly, lime penetration continues even in a static drum.

Now that the processes that take place in unhairing have been discussed, let's see a practical case.

Different views exist on whether unhairing should or should not be started in the bath used for soaking. I personally believe that the soaking bath must at least be drained and that the bath density should range between 1 and 2 °Bé in water at the beginning of unhairing.

In case of higher densities, draining and using new water is preferred.

Unhairing in the same bath can only be performed with raw fresh leather already pre-fleshed and with a density between 0.6 and 1 °Bé at the end of the main soaking bath.

In view of the above, five different phases can be distinguished when unhairing in short bath (between 30 and 50%, depending on soaking drum draining):

**PHASE 1** CONDITIONING of the leather coming from soaking at pH = 9 / 9.5, running time between 45 and 60 minutes, using the following products:

- **Anti-wrinkle** RIBERSAL PLE or RIBERSAL LA or RIBERSAL TD (between 0.7 and 1%). These products condition the pH and allow for a much greater regularity at reducing product penetration, without creating tension.

- **Fat emulsifier** CELESAL BE - 50 (between 0.1 and 0.2%), which emulsifies fat likely to be deposited on the hair and leather surfaces, and likely to slow down the action of sulfide and leave keratin on the surface.

- **Lipase** DEFAT 50 (between 0.02 and 0.03%), which dissolves the small quantity of fat in the pilous follicle for easy removal of the hair and the hair root.

**PHASE 2** HAIR IMMUNIZATION. Use **Ca(OH)₂** (offer between 1 and 1.6%).
**PHASE 3** UNHAIRING, with a duration between 2 and 4 hours running intermittently until no keratin is left and at least three quarters of the section are crossed. The most frequently used products are:

- **Sodium sulfide** (between 1.2 and 2%)
- **Sodium hydrosulfide** (between 0.5 and 1%)

In case of keratin residues left for any reason (poor soaking, fatty hair at the end of soaking, fatty surface, etc...), the following must be added:

- **Sodium sulfide** (between 0.3 and 1%) and/or **RIBERZYM MPX** or **RIBERZYM AT** (0.1 - 0.2%).

Then run intermittently in automatic until total removal.

**PHASE 4** STRUCTURAL LOOSENING, with a duration between 30 minutes and 7 hours (footwear or upholstery and according to leather size) to obtain relaxed, totally crossed final leathers.

The appearance or non-appearance of wrinkles will greatly depend on total crossing and on the time that lime acts at the center of the leather. The product used is:

- **Lime** (between 2 and 2.5%)

**PHASE 5** SWELLING and fiber separation with water (between 70 and 100%)

A formulation of **UNHAIRING** with **HAIR IMMUNIZATION** without filtering in standard footwear drum for leathers weighing between 25 and 30 Kg is shown below:

### PHASE 1: CONDITIONING

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER at 22° C</td>
<td>40%</td>
</tr>
<tr>
<td>RIBERSAL PLE or LA or RIBERSAL TD</td>
<td>0.8%</td>
</tr>
<tr>
<td>CELESAL BE-50 (or Defat 50)</td>
<td>0.10%</td>
</tr>
<tr>
<td>VERDITAN CV</td>
<td>0.2% (only in leather with blood veins) Run 50’, pH=9.5</td>
</tr>
</tbody>
</table>

### PHASE 2: HAIR IMMUNIZATION

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime</td>
<td>1.2 %</td>
</tr>
</tbody>
</table>

Run 15 min.
PHASE 3: UNHAIRING

| SODIUM SULFIDE | 0.8%       |
| SODIUM SULFHYDRATE | 0.8%       |


Penetration and keratin control. In case of stuck keratin, add

| SODIUM SULFIDE | 0 – 0.6% |
| RIBERZYM AT     | 0 – 0.1% |

Run from 0 to 30’

Keratin control. Increase time if necessary (up to 2 hours).

PHASE 4: LOOSENING

| Lime               | 1.8 – 2.3%       |
| RIBERSAL PLE or LA or RIBERSAL TD | 0 - 0.2% (only in leathers heavier than 35 Kg) |
| CELESAL BE - 50    | 0 – 0.2% (in fatty leathers that slip in fleshing machine) |

Run 30’

Penetration control: brown color.

(In case of upholstery leathers, heavy leathers or wrinkled leathers, gradually increase the duration of the loosening phase (up to 2 hours in footwear and up to 7 hours in upholstery) running 1’ every 10’ and with lime offer (up to 4% in total).

PHASE 5: SWELLING

| Water | 60%       |

Run 30’. Automatic 5’/ h. Total 16 h from start.

PHASES 3 and 4 are shown in the pictures below:
Phase 3: Correct

Stuck keratin stain

NOT OK

Phase 3: Not correct

Loose keratin stains

OK
Adding water at this stage causes alkaline swelling only in the area with pH = 12.5. The surface of this area is increased and the central part remains unswelled. This causes internal tensions and the appearance of wrinkles.

Because the pH is homogeneous throughout the section, water can be added to swell the hide. This swelling will thus **evenly affect the whole thickness** of the leather without creating internal tensions leading to fiber rupture (loose grain) and wrinkles.

**Phase 4:**
Correct
## UNHAIRING IN PADDLE VAT

**WATER at 28º C**

**AT AXIS (Bath temp.: 25º C)**

**RIBERSAL PLE**

1%

**CELESAL BE - 50**

0 – 0.3% (depending on leather fat)

Run 45 min.

**SODIUM SULFHYDRATE**

2%

**LIME**

1.5%

**CELESAL BE - 50**

0.2%

**RIBERSAL LA**

0.3 % (in leathers heavier than 35 Kg)

Run 30 min. Stop 30 min. Rodar 20 min. Run 30 min.

**SODIUM SULFIDE**

0.8%

**LIME**

2%

**CELESAL BE - 50**

0.2%

Run 20 min. Stop 60 min.

**LIME**

1%

Run 20 min. Automatic running 10 min. / hour.

**Following day:** Wash with water at 22-24º C.

### NOTE:

- In leathers of **larger sizes** (i.e. thicker and with a smaller surface of hair per kilo of raw hide), soaking should be reinforced and the sulfide or sulfhydrate content in unhairing should be decreased.

- In leathers of **smaller sizes** (i.e. less thick and with a larger surface of hair per kilo of raw hide), the offer of soaking products should be decreased and the sulfide or sulfhydrate content in unhairing should be increased.
HAIR-SAVE UNHAIRING

- The hair is immunized before undergoing sulfide attack.
- Immunization is performed with Ca(OH)$_2$, just up to the hair root.
- This penetration is controlled with phenolphthalein.

**INSUFFICIENT**

**CORRECT**

**EXCESSIVE**
### HAIR-SAVE UNHAIRING PROCESS

At the origin, a well-soaked hide, with a **WHITE** section, and **greenish crossed** as per Universal Indicator. Process used with **footwear**.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>WATER at 26° C</td>
<td>40% (Bath temp.: 25° C)</td>
<td></td>
</tr>
<tr>
<td>CELESAL BE - 50</td>
<td>0 - 0.2% (according to leather fat)</td>
<td></td>
</tr>
<tr>
<td>RIBERSAL PLE (LA) or RIBERSAL TD</td>
<td>1 - 1.2% (according to leather thickness)</td>
<td></td>
</tr>
<tr>
<td>SODIUM SULFHYDRATE</td>
<td>0.1%</td>
<td></td>
</tr>
<tr>
<td>DEFAT 50</td>
<td>0 – 0.02% (according to leather fat)</td>
<td></td>
</tr>
<tr>
<td>RIBERSAL LA</td>
<td>0 - 0.3% (according to leather thickness)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Run 50 min. (3rpm). pH = 9.5.</td>
<td></td>
</tr>
<tr>
<td>LIME</td>
<td>1.2%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Run 20 min (1.5 rpm). Stop 15’. Run 15’. Stop 10’. pH = 12.2.</td>
<td>Phenolphthalein penetration control (up to hair root only).</td>
</tr>
<tr>
<td>SODIUM SULFHYDRATE</td>
<td>0.6 - 0.8%</td>
<td></td>
</tr>
<tr>
<td>SODIUM SULFIDE</td>
<td>0.6 - 0.8%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Run 20 min. Stop 20 min. Run filtering for 20 min.</td>
<td>Stop 30 min. Run 3 min. Stop 30 min. Run 3 min. Stop 30 min. FILTER 60–90 min. (1.5 rpm). Keratin removal control.</td>
</tr>
<tr>
<td>SODIUM SULFIDE</td>
<td>0 - 0.6% (according to cleaning)</td>
<td></td>
</tr>
<tr>
<td>RIBERZYM AT</td>
<td>0 - 0.1% (according to cleaning)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Run 30’. Keratin removal control. Increase time if necessary (up to 2 hours).</td>
<td></td>
</tr>
<tr>
<td>LIME</td>
<td>1.8 - 2.3% (according to size and thickness)</td>
<td>Run 15 min. Stop 30 min. Increase this period for a better loosening effect in larger leathers (up to 7 hours in the case of upholstery leathers). Unhairing penetration control. No water must be added until the inner color of the hide is entirely BROWN.</td>
</tr>
<tr>
<td>CELESAL BE – 50</td>
<td>0 - 0.2% (according to size and thickness)</td>
<td>Run 15 min. Stop 30 min. Increase this period for a better loosening effect in larger leathers (up to 7 hours in the case of upholstery leathers). Unhairing penetration control. No water must be added until the inner color of the hide is entirely BROWN.</td>
</tr>
<tr>
<td>RIBERSAL LA</td>
<td>0 - 0.2% (according to leather size)</td>
<td>Run 15 min. Stop 30 min. Increase this period for a better loosening effect in larger leathers (up to 7 hours in the case of upholstery leathers). Unhairing penetration control. No water must be added until the inner color of the hide is entirely BROWN.</td>
</tr>
<tr>
<td>WATER at 26 °C</td>
<td>60%</td>
<td>Run 30 min. Stop 30 min. Automatic running 5 min. every hour up to 16 hours.</td>
</tr>
</tbody>
</table>
## HAIR-SAVE UNHAIRING PROCESS AND UNHAIRING BATH RECIRCULATION FROM PREVIOUS BATCHES

At the origin, a well-soaked hide, with a **WHITE** section, and **greenish crossed** as per Universal Indicator. Process used with **footwear**.

### WATER at 26º C
- **CELESAL BE - 50**
- **RIBERSAL PLE (LA) or RIBERSAL TD**
- **SODIUM SULFHYDRATE**
- **DEFAT 50**
- **RIBERSAL LA**

40% (Bath temp.: 25º C)

0 - 0.2% (according to leather fat)

1 - 1.2% (according to leather thickness)

0.1%

0 – 0.02% (according to leather fat)

0 - 0.3% (according to leather fat)

Run 50 min. (3 rpm). pH = 9.5.

### LIME
- 1.2%


Phenolphthalein penetration control (up to hair root only).

### SODIUM SULFHYDRATE
- 0.6 - 0.8%

### SODIUM SULFIDE
- 0.6 - 0.8%

Run 20 min. Stop 20 min. Run filtering for 20 min.

Stop 30 min. Run 3 min. Stop 30 min. Run 3 min. Stop 30 min.

FILTER 60 – 90 min. (1.5 rpm). Keratin removal control.

### SODIUM SULFIDE
- 0 - 0.6% (according to cleaning)

0 - 0.1% (according to cleaning)

Run 30’. Keratin removal control. Increase time if necessary (up to 2 hours).

### LIME
- 1.6 - 2.1% (according to size and thickness)

0 - 0.2% (according to leather fat)

0 - 0.2% ( according to leather size)

Run 15 min. Stop 30 min. Increase this period for a better loosening effect in larger leathers (up to 7 hours in the case of upholstery leathers).

Unhairing penetration control.

No bath must be added until the inner color of the hide is entirely BROWN.

### BATH RECOVERED AT 26 º C
- 60%

Run 30 min. Stop 30 min. Automatic running 5 min. every hour up to 16 hours.
# Cangilones Drum Unhairing with Hair Immunization

At the origin, a well-soaked hide, with a **WHITE** section, and **greenish crossed** as per Universal Indicator. Process for **footwear**.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WATER at 20º C</strong></td>
<td>40-50% (Bath temp.: 23º C). Density control &lt; 1.2Bé</td>
</tr>
<tr>
<td><strong>CELESAL BE - 50</strong></td>
<td>0 - 0.2% (according to leather fat)</td>
</tr>
<tr>
<td><strong>RIBERSAL PLE (LA) or RIBERSAL TD</strong></td>
<td>1 - 1.2% (according to leather thickness)</td>
</tr>
<tr>
<td><strong>SODIUM SULPHYDRATE</strong></td>
<td>0.1%</td>
</tr>
<tr>
<td><strong>DEFAT 50</strong></td>
<td>0 – 0.02% (according to leather fat)</td>
</tr>
<tr>
<td><strong>RIBERSAL LA</strong></td>
<td>0 - 0.3% (according to leather thickness)</td>
</tr>
<tr>
<td></td>
<td>Run 50 min. (3 rpm). pH = 9.5.</td>
</tr>
<tr>
<td><strong>LIME</strong></td>
<td>1.5 – 1.8%</td>
</tr>
<tr>
<td><strong>Polyphosphate</strong></td>
<td>0 - 0.05%</td>
</tr>
<tr>
<td></td>
<td>Run 20 min (0.6 rpm). Stop 15’. Run 15’. Stop 10’. pH = 12.5. Phenolphthalein penetration control (up to hair root only).</td>
</tr>
<tr>
<td><strong>SODIUM SULPHYDRATE</strong></td>
<td>0.8%</td>
</tr>
<tr>
<td><strong>SODIUM SULFIDE</strong></td>
<td>0.6%</td>
</tr>
<tr>
<td></td>
<td>Run 20 min. Stop 20 min. Run filtering for 20 min. Stop 30 min. Run 3 min. Stop 30 min. Run 3 min. Stop 30 min. FILTER 60 –90 min. (1.5 rpm). Keratin removal control</td>
</tr>
<tr>
<td><strong>SODIUM SULFIDE</strong></td>
<td>0 - 0.6% (according to cleaning)</td>
</tr>
<tr>
<td><strong>RIBERZYM AT</strong></td>
<td>0 - 0.1% (according to cleaning)</td>
</tr>
<tr>
<td></td>
<td>Run 30’. Keratin removal control. Increase time if necessary (up to 2 hours).</td>
</tr>
<tr>
<td><strong>LIME</strong></td>
<td>1.5 – 1.6% (according to size and thickness)</td>
</tr>
<tr>
<td><strong>CELESAL BE – 50</strong></td>
<td>0 - 0.2% (according to leather fat)</td>
</tr>
<tr>
<td><strong>RIBERSAL LA</strong></td>
<td>0 - 0.2% ( according to leather size)</td>
</tr>
<tr>
<td></td>
<td>Run 15 min. Stop 30 min. Increase this period for a better loosening effect in larger leathers (up to 7 hours in the case of upholstery leathers). Unhairing penetration control. No water must be added until the inner color of the hide is entirely BROWN and at least 2 hours have elapsed.</td>
</tr>
<tr>
<td><strong>WATER at 23 ºC</strong></td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>Run 30 min. Stop 30 min. Automatic running 5 minutes every hour. Total 16 hours.</td>
</tr>
</tbody>
</table>
ECO UNHAIRING

One of the biggest challenges facing tanneries worldwide is the odor they generate and further spread to neighboring areas.

One of the main sources of smell is the SULFIDE used in leather unhairing processes in all tanneries.

- Its “rotten egg” smell is widely spread and neighbors complain
- Spending in the purification plant is increased when sulfide is oxidized to sulfate
- The smell reaches even the finished leather. Leathers for car upholstery do not pass the smell test.

Accordingly, the technique to remove smell has been developed in two ways:

1º. - Using a lower amount of sulfide in unhairing processes: ECO UNHAIRING

2º. - Using a product that destroys the sulfide used and not consumed during the unhairing-liming process: DECALIM S/S.

1º. - In this ECO Unhairing, almost the full amount of sulfide is replaced with a selection of enzymes and unhairing is performed by mixed (reducing agent-enzyme) hydrolysis of Keratin, which results in a sulfide offer reduced down to 0.6%.

This amount of sulfide, together with 1 – 1.2% of lime used in immunization, allows reaching a sufficiently high pH (11.7 – 12.6, depending on the leather having more or less natural fat) to obtain an adequate activity of the enzyme (RIBERZYM ECO C) used at 0.6 – 0.7%.

An ideal temperature of 28°C±1 should be maintained throughout the dehairing process. Temperatures lower than 3°C slow down the process.

In natural-fat-rich leathers, fat reduces the activity of Riberzym ECO C, and a higher amount of Celesal BE-50 should be added to emulsify this fat.
Verditan CV is used as anti-swelling and anti-bloodvein agent.

Riberzym ECO C is composed of a selection of enzymes.

This ECO Unhairing is similar in time and process to conventional unhairing with sulfide and lime. The COD values of the residual bath are reduced to less than half.

HUMECTOL ECO A or RAPID should be used in the soaking process with this system.

2º. - Use of DECALIM S/S

- This product is a combination of oxidizing agents and special additives.

- It is an off-white powder with a 10% pH of 11.

- It reduces and/or eliminates sulfide in the waste water of unhairing baths.

- It reduces and/or eliminates residual sulfide in the leather (and therefore reduces and/or eliminates smell in the finished leather).

- DECALIM S/S is added to the final unhairing-liming bath 30 minutes (approximately depending on the the leathers and the tannery) before washing is started.

- After running for 30 minutes, the bath is washed as usual.

- The % of DECALIM S/S offer will depend on the amount of sulfide used: for an offer of 1.5% sulfide, the DECALIM S/S offer should range between 0.5% and 0.8%.

- In addition to these characteristics, using Decalim S/S has a side effect on the performance of the waste water treatment plant: it being an oxidizing agent, it triggers the following reactions:
1º.- **OXIDATION OF SULFIDE** in waste water under alkaline conditions:

\[
S^2- + \text{DECALIM S/S} \rightarrow \text{SO}_4^{2-} \text{ (solubles)} + H_2O
\]

2º.- **DECREASED pH** of waste water due the replacement of an alkaline product (sulfide) with a neutral salt (sulfate)

3º.- **OXIDATION OF THE ORGANIC MATTER** of waste water by solid protein (solid sediment) degradation to polypeptides, amino acids and finally CO\(_2\) + H\(_2\)O. This results in sedimented solids (solid residues) being significantly decreased.

4º.- **DECREASED final COD and BOD\(_5\)** on account of the greater O\(_2\) supply provided by DECALIM S/S. Waste water treatment plants do not need as much O\(_2\) or as many aeration hours during primary treatment, thus leading to **PURIFICATION SAVINGS**.

5º.- **BETTER BACTERIAL ACTIVITY**, i.e., better biological treatment on account of better treated water during the chemical or primary treatment.

6º.- **REDUCED OR REMOVED ODOR OF SULFIDE**, both at the treatment plant (no more neighbor complaints) and in the finished leather (car upholstery leathers do pass the smell test).

The following photographs show the effect obtained upon primary treatment completion at the treatment plant after using 0.9% DECALIM S/S in the unhairing bath the final water is clearer and more colorless, and three-quarters of solid residues have disappeared.
1 WEEK WITH DECALIM S/S

2 WEEKS WITH DECALIM S/S

3 WEEKS WITH DECALIM S/S

4 WEEKS WITH DECALIM S/S
Once washed after unhairing, leathers are transferred to the fleshing machine, where all fat areas are separated from the flesh.

Leathers are then trimmed (this is key to avoid fat stains in the dyeing and fatliquoring process) to remove fleshing residues dragged towards the leather edges by the fleshing machines.

As stated above, the absence of fat on the leather surface is very important for a correct fleshing without leather slipping in the machine and pieces of flesh left in the flesh side. This is all the more important in continuous fleshing machines.

A correct leather must allow being split directly after fleshing. Otherwise, lay down for some time to allow fat spreading or, better still, use a fat emulsifier in unhairing (CELESAL BE-50).

Leathers can then be introduced in the splitting machine to separate split from grain (pelt splitting); if pelt splitting is not used, proceed with full substance leather until tanning and then split (blue or chrome split).

**Pelt splitting** yields leathers with a more open grain, without wrinkles at the neck, but with a more frayed splitting and less surface yield.

**Wet-Blue splitting** yields a more compact grain (with a possibility of wrinkles) and a more compact split. Because thickness can be better regulated, a better split is obtained.

Once leathers are fleshed and further split (or not split), they undergo the deliming, degreasing and bating processes.
The purpose of deliming is to totally or partially remove the lime present in the leather after the unhairing-liming operation.

The larger the quantity of lime left inside the leather, the longer it will take for pickling acids to penetrate and hence the longer it will take to cross the chrome.

The larger the lime line left in the interior, the harder the leathers and the better their springy touch.

The most frequently used deliming products are:

**AMMONIUM SULFATE** This is the most frequently used deliming agent and the one producing the best results. The calcium sulfate (P.S.= 6.4x10^-5) and ammonia reaction results in:

\[
\text{SO}_4 (\text{NH}_4)_2 + \text{Ca} (\text{OH})_2 \rightarrow \text{SO}_4\text{Ca} + 2 \text{NH}_4\text{OH}
\]

**AMMONIUM CHLORIDE** Much less used in cattle hides on account of producing calcium chloride (peptizing agent) and ammonia in its reaction. Conversely, it is commonly used in goat skin deliming.

Highly convenient in full substance cattle hides on account of its faster penetration rate as compared to ammonium sulfate (lower molecular volume).

\[
2 \text{Cl} (\text{NH}_4) + \text{Ca} (\text{OH})_2 \rightarrow \text{Cl}_2\text{Ca} + 2 \text{NH}_4\text{OH}
\]

**LACTIC ACID** It forms water-soluble calcium lactates in its reaction with lime.

\[
2 \text{CH}_3 - \text{CH(OH)} - \text{COOH} + \text{Ca} (\text{OH})_2 \rightarrow (\text{CH}_3 - \text{CH(OH)} - \text{COO})_2\text{Ca} + 2 \text{H}_2\text{O}
\]

**FORMIC ACID** Can be used in low quantities on account of its pH-lowering effect.

\[
2 \text{H} - \text{COOH} + \text{Ca} (\text{OH})_2 \rightarrow (\text{H-COO})_2\text{Ca} + 2 \text{H}_2\text{O}
\]
DIFFERENT PHASES OF DELIMING with phenolphthalein

**NECK - BUTT COMPARISON**

**NECK:** insufficient deliming

**BUTT = OK**
neck = insufficient

**NECK:** short deliming

**BUTT = OK**
neck = 90% ok

**COMPLETE DELIMING**

60 min.

120 min.

150 min.

180 min.
As a result of their reaction with lime, the above mentioned ammonium salts lead to ammonia detachment which, in aqueous solutions, is in the form of ammonium hydroxide. Ammonium hydroxide is disposed of with the residual bath.

On account of environmental awareness, the legislations of many countries are increasingly limiting the maximum ammonia content in waste waters.

In the area of Valencia (Spain) the ammoniacal nitrogen content is currently limited to:

- **25 mg / l** as a maximum mean daily concentration, and
- **85 mg / l** as a maximum instantaneous concentration.

This means that, in deliming, tanners must complement the use of ammonium salts with deliming products deprived of these salts (or with a poor content thereof).

Cromogenia offers an ammonium salt-free deliming agent: **DESENCALANTE SE - 01**.

Other in-house deliming agents combining dicarboxylic organic acids and ammonium salts at different ratios are:

**DESENCALANTE D - 86** and **DESENCALANTE E - 93**.

Importantly, deliming should be used to remove sodium sulfide residues likely to remain in the hide.

To do so, **SODIUM BISULFITE** (between 0.3 and 1%) is added to the deliming bath to prevent the reaction of sulfide with the pickling acid to form hydrogen sulfide (\(H_2S\)), a colorless gas that leads to respiratory paralysis and death in a few seconds.

As discussed above (pages 11-16), **DERMATAN SULFATE** can be hydrolyzed by using **DECALIM PLUS** in deliming. This product is particularly recommended in full substance leathers larger than 30 Kg., with short beamhouse (24-hour soaking-unhairing), and also in leathers whose tight structure or corneus grain make them prone to wrinkling at the neck, the belly, or the shanks and cheeks.

Dermatan Sulfate should have dissolved completely in leathers undergoing 18 hours under highly alkaline conditions (during liming).

Any undissolved amount of Dermatan Sulfate will remain until the finished leather is obtained.

Because Dermatan Sulfate is a hard and brittle solid, the entire leather is hardened at the final plate operation in finishing, ceases to have a soft and pleasant feel, and becomes harder and brittler.

**DECALIM PLUS** hydrolyzes or dissolves the Dermatan Sulfate that remains in the pelt.

After fleshing and in pelts presenting with neck or shank wrinkles due to the presence of Dermatan Sulfate, the use of **DECALIM PLUS** in the LIMING process is highly recommended.
Its use at this point provides wrinkle-free leathers with a larger area, with a perfectly regular feel in heads and butts and among different batches, and with much leveled dyeing.

If the leather has been received in Wet Blue and has wrinkling problems, the use of a product similar to Decalim PLUS—PLENATOL IS—at 3% in the neutralization process allows obtaining results similar to those of Decalim PLUS in the deliming process.

Its use is highly appropriate in suede splits (mainly those obtained in the beamhouse without unhairing and liming) where darkened areas disappear with sanding, and also in milling articles, where regular milling and uniform grain are obtained.

Also, the deliming and/or bating operation is used to perform DEGREASING.

It is important to remove saturated fats that may lead to the formation of stains in crust leather—and eventually in finished leather.

These stains are caused by the formation of CHROMIUM SOAPS, which in turn originate from their previous formation as CALCIUM SOAPS.

CALCIUM SOAPS

These are chemical barriers added progressively as of leather storage until leather tanning, and result in:

- Dyed stains.
- Untanned lines.
- Non-uniformity of dyeing.

If the leather has fat balls, or the hide is of a very fatty nature, or the preserving product (salt) has not reached the whole hide (or has done so in small amounts), triglycerides break down into saturated fatty acids (SFAs) that, with time, penetrate inside the hide.

In unhairing and due to the action of alkalis, SFAs are neutralized and form calcium soaps. By acid action in pickling, SFAs are again formed and, with the chromium of tanning, form chromium soaps and build “barriers” that prevent the passage of tanning material into these areas, which eventually remain untanned (raw):

<table>
<thead>
<tr>
<th>Time</th>
<th>Unhairing</th>
<th>Pickling</th>
<th>Cr tanning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglycerides</td>
<td>SFA</td>
<td>Ca soaps</td>
<td>SFA</td>
</tr>
</tbody>
</table>

In pelt, calcium soaps appear as white precipitates.
These soaps are purple pink in chrome-tanned hides. During dyeing, the areas with chromium soaps act as barriers that prevent uniformity.

In **VEGETABLE**-tanned hides, two different situations may arise depending on the process:

- **If pickling is performed**, triglycerides become SFAs that remain in the hide and may lead to repousse, but tannin penetration is not hindered.

- **If pickling is not performed**, they remain as calcium soaps. These do hinder tanning penetration and lead to raw areas.

**Preventive action**: Perform excellent degreasing in the deliming phase.

**Cromogenia** offers several degreasing agents (already discussed in the Soaking section) devised to achieve a correct HLB and with very good results at degreasing:

- **CELESAL DL**: Polyglycol ether of fatty alcohols.
- **CELESAL INP**: Ethoxylated fatty alcohol.
- **CELESAL K-6**: Ethoxylated fatty alcohol.
- **CELESAL K-12**: Ethoxylated fatty alcohol.

Leathers insufficiently washed at flaying and with blood residues on their surface will produce grain stains that are already visible in the tanned hide. This defect will be carried over the whole process and may be reduced by using **DECALIM FE** at the beginning of deliming and at the beginning of pickling.

This product also reduces the issue of “nubucking” and coarse grain when lime is present on the surface after unhairing-liming (presence of $\text{CO}_3\text{Ca}$), for example when very hard water is used in deliming.

Once the leathers are degreased and delimed, **BATING** is performed.

**BATING**

The purpose of bating is to hydrolyze the “elastin” protein of the hide.

A correct choice of the type of enzyme is critical to achieve good final leathers:

If a broad spectrum protease is used, hydrolysis is not limited to elastin and also attains part of the collagen, which leads to emptier leathers and looser grain.
Insufficient bating will result in hard, brittle hides with more marked blood veins.

Excessive bating will result in a softer hide, albeit empty and with loose grain.

Marketed enzymatic products range from standard products of approximately 500 LVu (Löhlein-Volhard units) to highly concentrated products of up to 30,000 LVu.

The enzyme activity increases with increasing concentrations, temperatures, and time.

Cromogenia’s enzymatic products belong to the TRIPSOL range and include different concentrations:

TRIPSOL D

TRIPSOL DOBLE

TRIPSOL RSTP – TRIPSOL SQF – VERDITAN EL (pancreatic trypsin). Most appropriate for integral cattle leather and for goat skin. These products act most specifically on elastin and yield more open leathers. They are also most effective to remove loose hair roots that still remain in the dermis and yield cleaner leathers.

TRIPSOL 3D

ENZYMAS 30000

The bating action is paralyzed in the drum by cooling the bath —enzymes lose activity at lower temperatures.

In cooled leathers, hair root extraction is favored by thorough draining with open valves.
A STANDARD DELIMING-DEGREASING-BATING FORMULATION is:

Fleshed, unsplit pelts.
Dose on pelt weight

<table>
<thead>
<tr>
<th>WATER at 30° C</th>
<th>200%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELESAL DL</td>
<td>0.1%</td>
</tr>
<tr>
<td>DESENCALANTE E - 93</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

Run 15 min. Drain 15 min. static.

IN THICK LEATHER

<table>
<thead>
<tr>
<th>WATER at 30° C</th>
<th>30%</th>
<th>30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECALIM FE</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

(in case of iron stains or very hard waters leading to nubucking by CO$_3$Ca)

| DESENCALANTE D - 86 | 0.8% | 1%  |
| DESENCALANTE E - 93 | 1%   | 1.5%|
| SODIUM BISULFITE    | 0.3% | 0.4%|

Run 30 min.

| DECALIM PLUS         | 0.5% | 0.7% |
| DESENCALANTE E - 93 | 0.7%  | 1%   |

Run 120 min. Run 150 min.

Phenolphthalein control
Neck = slight line

| TRIPSOL RSTP | 0.3% | |
| CELESAL DL   | 0.2% | 0.2% |

Run 20 / 30 min. Run 30 / 45 min.

Bating control
Drain 10 min. running

<table>
<thead>
<tr>
<th>COLD WATER</th>
<th>200%</th>
</tr>
</thead>
</table>

Drain running with open valves

<table>
<thead>
<tr>
<th>COLD WATER</th>
<th>200%</th>
</tr>
</thead>
</table>

Drain running with open valves
On the other hand, failing to totally remove elastin will produce the dreaded **BLOOD VEINS**, which:

Are more frequent in **black hair** leather and in **thin** leather.

Are more marked in **fresh leather** than in salted leather, on account of leather non-dehydration.

Are even more marked in **Wet White** tanning than in chrome tanning.

In **milled articles** the presence of blood veins makes milled leather fold at the vein, which becomes even more marked.

The blood vein outline seen in the flesh of pelt leather is maintained up to the finished leather, sometimes more intensely so.

Blood veins have a fibrillary structure that is different from that found in the rest of collagen.

The appearance of blood veins in the finished leather leads to **decreased leather selection** —sometimes a very serious problem.

In mammals, **ELASTIN** is predominantly found where the tissue undergoes repeated extension-relaxation cycles.

Typical examples are arteries, veins, ligaments, lungs, and skin.
BLOOD VEIN STRUCTURE AND COMPOSITION

A cross section of a vein depicts three layers:

- **INNER LAYER** This very fine layer is formed by the endothelium, a baseline layer and a subendothelial conjunctive layer.

- **MIDDLE LAYER** This layer is formed by smooth muscle fibers, elastic fibers and collagen fibers concentrically arranged in varying proportions, depending on the type of vein.

- **OUTER LAYER** This layer is formed by loose conjunctive tissue mainly composed of fibroblasts and collagen.

The middle layer includes elastic fibers composed of a succession of concentric elastic layers between which smooth muscle cells are arranged and where the elastic component is predominant.

**ELASTIN** is a structural protein that confers elasticity to tissues —unlike collagen, which provides resistance.

This monomer has a molecular weight of 70kDa and a large extensibility that vaguely reminds that of a rubber band.

Elastin is formed by an amino acid chain, composed of valine, proline, glycine, lysine and alanine, with alpha helix structures that provide elastin with its characteristic extensibility. It can stretch up to 150% before breaking.
Elastin has different properties according to its state:

1. In the wet state, elastin is elastic, slippery and insoluble in water.
2. In the dry state, elastin is hard, brittle and fragile.

In the finished leather, elastin is in the dry state — hard, brittle and fragile. Therefore, the beamhouse must completely remove the entire amount of elastin present in the leather, in both the veins and the rest of the hide, to obtain a totally elastin-free final leather.

Elastin can be totally removed in two different ways:

1. To make elastin molecules soluble in water and therefore removable from the hide, they must be treated and undergo an enzymatic hydrolysis reaction. The in-process temperature and pH conditions that are best to optimize hydrolysis are found in UNHAIRING and in BATING.

   This hydrolysis must be performed with ELASTASE enzymes, which selectively hydrolyze elastin and leave the other proteins unchanged, including collagen. These enzymes are: RIBERZYM AT (in unhairing) and VERDITAN EL or TRIPSOL RSTP (in bating).

2. Take advantage of swelling in the unhairing process to “expel” unswollen veins on the flesh side and remove them at fleshing.

   Just as important as using the appropriate enzyme is ensuring that the leather does not swell in this process.
If pH > 8.5

--- hide swelling --- vein swelling

**SOLUTION:** Absolute pH control in soaking with:

- **HUMECTOL TPH** (pH buffer at 8.5)
- **VERDITAN CV** (vasoconstrictive wetting agent). When used at 0.6% in soaking and unhairing, it prevents vein swelling even in the case of pH peaks. This is an excellent product to prevent the appearance of blood veins.
- **RIBERSAL LA** (polysaccharide). When used at 0.9% (0.7% + 0.2%) in unhairing, in substitution for the amine.
PROBLEM FOUND WHEN A GENERAL OR BROAD-SPECTRUM PROTEASE IS USED

- Hydrolysis affects “all proteins”, elastin and collagen.

- Because there is a tendency to less bathing to prevent the loss of collagen, undissolved elastin residues remain MARKED VEINS.

- If bathing is increased to dissolve blood veins, excessive bathing will dissolve elastin but also collagen EMPTY HIDE AND LOOSE GRAIN (BELLIES)

- In order to preserve more collagen and prevent loose grain in thin cows and hides, both soaking-unhairing and bathing are usually reduced. The use of a broad-spectrum protease will lead to a HARD, BRITTLE hide due to the presence of non-hydrolyzed elastin.

This problem becomes even more serious in milling articles.

If the elastic tubular structure of the veins remains in the subsequent retanning process, retanning products cannot cross the vein layers and penetrate inside the vein. Consequently, the “venous tubes” remain hollow and are not filled with retanning products.

The hydrolysis or dissolution of the vein structure, or its separation from collagen, allows retanning product penetration to fill the spaces previously occupied by the veins.

Several formulations that vary depending on whether the leather is salted or fresh (pre-fleshing or no pre-fleshing) and with or without hair immunization, are shown below:
**SALTED CATTLE LEATHER BEAMHOUSE FOR BLOOD VEIN REMOVAL WITH DESTRUCTIVE UNHAIRING**

Leather state: **SALTED**  
% on weight: **SALTED SWEEPING**

### PRE SOAKING

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>200%</td>
<td>WATER at 26º C</td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>CELESAL CN</td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>SODIUM CARBONATE</td>
<td></td>
</tr>
<tr>
<td>0.05%</td>
<td>ASEPTANTE DMC</td>
<td></td>
</tr>
</tbody>
</table>

60' T = 22º C ; pH = 8.2; 3.6ºBè  
DRAIN BATH

### SOAKING

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>WATER at 27º C</td>
<td></td>
</tr>
<tr>
<td>0.6%</td>
<td>HUMECTOL RAPID</td>
<td></td>
</tr>
<tr>
<td>0.3%</td>
<td>CELESAL CN</td>
<td></td>
</tr>
<tr>
<td>0.05%</td>
<td>ASEPTANTE DMC</td>
<td></td>
</tr>
<tr>
<td>0.4%</td>
<td>VERDITAN CV</td>
<td></td>
</tr>
</tbody>
</table>

6 - 8 hours. Night in bath. Automatic 5' / 30'  
**Following day:** Run 60'

SOAKING CONTROL: crossed bluish green as per Universal Ind.  
T = 26º C; pH = 8.5/9; 3.5ºBè  
DRAIN BATH

### DESTRUCTIVE UNHAIRING

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>WATER</td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>CELESAL BE - 50</td>
<td></td>
</tr>
<tr>
<td>0.7%</td>
<td>RIBERSAL LA</td>
<td></td>
</tr>
<tr>
<td>0.4%</td>
<td>VERDITAN CV</td>
<td></td>
</tr>
<tr>
<td>0.6%</td>
<td>SODIUM SULFIDE</td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>LIME</td>
<td></td>
</tr>
</tbody>
</table>

Run 45' (1.5 rpm). Stop 15'

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>SODIUM SULFIDE</td>
<td></td>
</tr>
<tr>
<td>0.5%</td>
<td>LIME</td>
<td></td>
</tr>
<tr>
<td>0.05%</td>
<td>RIBERZYM AT</td>
<td></td>
</tr>
</tbody>
</table>

Run 30'. Stop 20'

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>SODIUM SULFIDE</td>
<td></td>
</tr>
<tr>
<td>1%</td>
<td>LIME</td>
<td></td>
</tr>
<tr>
<td>0.05%</td>
<td>RIBERZYM AT</td>
<td></td>
</tr>
<tr>
<td>0.2%</td>
<td>RIBERSAL LA</td>
<td></td>
</tr>
</tbody>
</table>

Run 90'  
KERATIN REMOVAL CONTROL

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3%</td>
<td>LIME</td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>CELESAL BE - 50</td>
<td></td>
</tr>
</tbody>
</table>

Run 90'. Stop 30'. Run 60'

UNHAIRING PENETRATION CONTROL  
If OK, add:

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>80%</td>
<td>WATER 26º C (or better still, hair-save unhairing bath)</td>
<td></td>
</tr>
</tbody>
</table>

Run 30'. Automatic running 5' every hour. Up to minimum 16 hours after starting unhairing.  
CONTINUE AS USUAL

### BATING

<table>
<thead>
<tr>
<th>%</th>
<th>Ingredient</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%</td>
<td>BATH DELIMING. pH = 8.5</td>
<td></td>
</tr>
<tr>
<td>0.6 – 1%</td>
<td>VERDITAN EL</td>
<td></td>
</tr>
</tbody>
</table>

Run 45'- 60'  
BATING CONTROL
SALTED CATTLE LEATHER BEAMHOUSE FOR BLOOD VEIN REMOVAL WITH HAIR-SAVE UNHAIRING

Leather state: **SALTED**
% on weight: **SALTED SWEEPING**

<table>
<thead>
<tr>
<th><strong>PRE SOAKING</strong></th>
<th>200%</th>
<th>WATER at 26°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1%</td>
<td>CELESAL CN</td>
</tr>
<tr>
<td></td>
<td>0.1%</td>
<td>SODIUM CARBONATE</td>
</tr>
<tr>
<td></td>
<td>0.05%</td>
<td>ASEPTANTE DMC</td>
</tr>
</tbody>
</table>

60' T = 22°C; pH = 8.2; 3.6°Bè
DRAIN BATH

<table>
<thead>
<tr>
<th><strong>SOAKING</strong></th>
<th>100%</th>
<th>WATER at 27°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6%</td>
<td>HUMECTOL RAPID</td>
</tr>
<tr>
<td></td>
<td>0.3%</td>
<td>CELESAL CN</td>
</tr>
<tr>
<td></td>
<td>0.05%</td>
<td>ASEPTANTE DMC</td>
</tr>
<tr>
<td></td>
<td>0.4%</td>
<td>VERDITAN CV</td>
</tr>
</tbody>
</table>

6 - 8 hours. Night in bath. Automatic 5' / 30'

**Following day:** Run 60'

SOAKING CONTROL: crossed bluish green as per Universal Ind. T = 26°C; pH = 8.5/9; 3.5°Bè
DRAIN BATH

<table>
<thead>
<tr>
<th><strong>HAIR-SAVE UNHAIRING</strong></th>
<th>40%</th>
<th>WATER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1%</td>
<td>CELESAL BE - 50</td>
</tr>
<tr>
<td></td>
<td>0.7%</td>
<td>RIBERSAL LA</td>
</tr>
<tr>
<td></td>
<td>0.4%</td>
<td>VERDITAN CV</td>
</tr>
<tr>
<td></td>
<td>0.1%</td>
<td>SODIUM SULFHYDRATE</td>
</tr>
</tbody>
</table>

Run 60' (3 rpm). pH = 9.5
1.3% LIME
Run 20' (1.5 rpm). Stop 15'. Run 15'. Stop 10'.
Lime penetration control with phenolphthalein up to hair root. pH = 12.5

<table>
<thead>
<tr>
<th></th>
<th>0.8%</th>
<th>SODIUM SULFIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.8%</td>
<td>SODIUM SULFHYDRATE</td>
</tr>
</tbody>
</table>

Run 20'. Stop 20'. Run 20'. Stop 30'. Run 3'. Stop 30'. Run 3'. Stop 30'. Filter 60' – 90'

<table>
<thead>
<tr>
<th></th>
<th>0.3%</th>
<th>SODIUM SULFIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1%</td>
<td>RIBERZYM AT</td>
</tr>
</tbody>
</table>

Run 30'

KERATIN REMOVAL CONTROL

<table>
<thead>
<tr>
<th></th>
<th>2%</th>
<th>LIME</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1%</td>
<td>CELESAL BE - 50</td>
</tr>
</tbody>
</table>

Run 15'. Stop 30'. Run 15'

UNHAIRING PENETRATION CONTROL
If OK, add:

|                | 80%  | WATER 25°C (or better still, hair-save unhairing bath) |

Run 30'. Automatic running 5' every hour. Up to minimum 16 hours after starting unhairing. CONTINUE AS USUAL

**BATING**

<table>
<thead>
<tr>
<th></th>
<th>70%</th>
<th>BATH DELIMING. pH = 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6 – 1%</td>
<td>VERDITAN EL</td>
</tr>
</tbody>
</table>

Run 45'- 60'
BATING CONTROL
**FRESH CATTLE LEATHER BEAMHOUSE NO PREFLESHING FOR BLOOD VEIN REMOVAL WITH DESTRUCTIVE UNHAIRING**

**Leather state:** REFRIGERATION CHAMBER T = 5º C  
**% on weight:** FRESH. PREFLESHING IN HAIR

**PRE SOAKING**

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 200% | WATER 30º C (*)  
| 0.05% | ASEPTANTE DMC  
| 30' Tª = 26º C; pH = 7 | DRAIN BATH |

**SOAKING**

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 50% | WATER 30º C (*)  
| 0.35% | HUMECTOL RAPID  
| 0.05% | ASEPTANTE DMC  
| 0.5% | VERDITAN CV  
| 3 hours. SOAKING CONTROL: crossed bluish green as per Universal Ind. | T = 27º C; pH = 8.5 |

(*) If from refrigeration chamber. If recently dead, lower temp. to 26º C

**DESTRUCTIVE UNHAIRING**

*Add:*

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 0.1% | CELESAL BE - 50  
| 0.7% | RIBERSAL LA  
| 0.3% | VERDITAN CV  
| 0.6% | SODIUM SULFIDE  
| 0.5% | LIME  
| Run 45' (1.5 rpm). Stop 15' |

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 0.5% | SODIUM SULFIDE  
| 0.5% | LIME  
| 0.05% | RIBERZYM AT  
| Run 30'. Stop 20' |

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 0.5% | SODIUM SULFIDE  
| 1% | LIME  
| 0.05% | RIBERZYM AT  
| 0.2% | RIBERSAL LA  
| Run 90'  
| KERATIN REMOVAL CONTROL |

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 1.3% | LIME  
| 0.1% | CELESAL BE - 50  
| Run 90'. Stop 30'. Run 60'  
| UNHAIRING PENETRATION CONTROL |

*If OK, add:*

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 40% | WATER 26º C (or better still, hair-save unhairing bath)  
| Run 30' |
| 40% | WATER 26º C (or better still, hair-save unhairing bath)  
 | Run 30'. Automatic running 5' every hour. Up to minimum 16 hours after starting unhairing.  
| CONTINUE AS USUAL |

**BATING**

<table>
<thead>
<tr>
<th>(%)</th>
<th>Solution</th>
</tr>
</thead>
</table>
| 70% | BATH DELIMING. pH = 8.5  
| 0.6 – 1% | VERDITAN EL  
| Run 45'- 60'  
| BATING CONTROL |
**FRESH CATTLE LEATHER BEAMHOUSE NO PREFLESHING FOR BLOOD VEIN REMOVAL WITH HAIR-SAVE UNHAIRING**

Leather state: **REFRIGERATION CHAMBER T = 5º C**
% on weight: **FRESH. NO PREFLESHING IN HAIR**

<table>
<thead>
<tr>
<th><strong>PRE SOAKING</strong></th>
<th><strong>200%</strong></th>
<th><strong>WATER 30º C (*)</strong></th>
<th><strong>0.05%</strong></th>
<th><strong>ASEPTANTE DMC</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30’ T = 26º C; pH = 7</td>
<td>DRAIN BATH</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>SOAKING</strong></th>
<th><strong>100%</strong></th>
<th><strong>WATER 30º C (*)</strong></th>
<th><strong>0.35%</strong></th>
<th><strong>HUMECTOL RAPID</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>0.05%</strong></td>
<td><strong>ASEPTANTE DMC</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>0.5%</strong></td>
<td><strong>VERDITAN CV</strong></td>
</tr>
</tbody>
</table>

3 - 5 hours. **SOAKING CONTROL**: crossed bluish green as per Universal Ind.
T = 26º C; pH = 8.5 / 9

(*) If from refrigeration chamber. If recently dead, lower temp. to 26º C

<table>
<thead>
<tr>
<th><strong>HAIR-SAVE UNHAIRING</strong></th>
<th><strong>Add:</strong></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>0.2%</strong></td>
<td><strong>CELESAL BE - 50</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>0.7%</strong></td>
<td><strong>RIBERSAL LA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>0.3%</strong></td>
<td><strong>VERDITAN CV</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>0.1%</strong></td>
<td><strong>SODIUM SULFHYDRATE</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 60’ (3 rpm). pH = 9.5

<table>
<thead>
<tr>
<th><strong>LIME</strong></th>
<th><strong>1.2%</strong></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 20’ (1.5 rpm). Stop 15’. Run 15’. Stop 10’.
Lime penetration control with phenolphthalein up to hair root. pH = 12.5

<table>
<thead>
<tr>
<th></th>
<th><strong>0.8%</strong></th>
<th><strong>SODIUM SULFIDE</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>0.8%</strong></td>
<td><strong>SODIUM SULFHYDRATE</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th></th>
<th><strong>0.3%</strong></th>
<th><strong>SODIUM SULFIDE</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>0.2%</strong></td>
<td><strong>RIBERSAL LA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>0.1%</strong></td>
<td><strong>RIBERZYM AT</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 30’
**KERATIN REMOVAL CONTROL**

<table>
<thead>
<tr>
<th></th>
<th><strong>2%</strong></th>
<th><strong>LIME</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>0.1%</strong></td>
<td><strong>CELESAL BE - 50</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 15’. Stop 30’.
**UNHAIRING PENETRATION CONTROL**
If OK, add:

<table>
<thead>
<tr>
<th></th>
<th><strong>80%</strong></th>
<th><strong>WATER 26º C</strong></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

Run 30’. Automatic running 5’ every hour. Up to minimum 16 hours after starting unhairing.
**CONTINUE AS USUAL**

<table>
<thead>
<tr>
<th><strong>BATING</strong></th>
<th><strong>70%</strong></th>
<th><strong>BATH DELIMING. pH = 8.5</strong></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>0.6 – 1%</strong></td>
<td><strong>VERDITAN EL</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Run 45’- 60’
**CONTROL BATING**
# FRESH CATTLE LEATHER BEAMHOUSE PREFLESHING FOR BLOOD VEIN REMOVAL WITH DESTRUCTIVE UNHAIRING

**Leather state:** REFRIGERATION CHAMBER T = 5º C  
**% on weight:** FRESH. PREFLESHING IN HAIR

### PRE SOAKING

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>200%</td>
<td>WATER 30º C (*)</td>
</tr>
<tr>
<td>0.05%</td>
<td>ASEPTANTE DMC</td>
</tr>
<tr>
<td>30' T = 26º C; pH = 7</td>
<td>DRAIN BATH</td>
</tr>
</tbody>
</table>

### SOAKING

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>WATER 30º C (*)</td>
</tr>
<tr>
<td>0.35%</td>
<td>HUMECTOL RAPID</td>
</tr>
<tr>
<td>0.05%</td>
<td>ASEPTANTE DMC</td>
</tr>
<tr>
<td>0.3%</td>
<td>VERDITAN CV</td>
</tr>
</tbody>
</table>

3 hours. SOAKING CONTROL: crossed bluish green as per Universal Ind.  
T = 27º C; pH = 8.5  
(*) If from refrigeration chamber. If recently dead, lower temp. to 26º C

### DESTRUCTIVE UNHAIRING

Add:

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%</td>
<td>CELESAL BE - 50</td>
</tr>
<tr>
<td>0.7%</td>
<td>RIBERSAL LA</td>
</tr>
<tr>
<td>0.2%</td>
<td>VERDITAN CV</td>
</tr>
<tr>
<td>0.6%</td>
<td>SODIUM SULFIDE</td>
</tr>
<tr>
<td>0.5%</td>
<td>LIME</td>
</tr>
</tbody>
</table>

Run 45' (1.5 rpm). Stop 15'  
<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>SODIUM SULFIDE</td>
</tr>
<tr>
<td>0.5%</td>
<td>LIME</td>
</tr>
<tr>
<td>0.05%</td>
<td>RIBERZYM AT</td>
</tr>
</tbody>
</table>

Run 30'. Stop 20'

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5%</td>
<td>SODIUM SULFIDE</td>
</tr>
<tr>
<td>1%</td>
<td>LIME</td>
</tr>
<tr>
<td>0.05%</td>
<td>RIBERZYM AT</td>
</tr>
<tr>
<td>0.2%</td>
<td>RIBERSAL LA</td>
</tr>
</tbody>
</table>

Run 90'

Keratin Removal Control

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3%</td>
<td>LIME</td>
</tr>
<tr>
<td>0.1%</td>
<td>CELESAL BE - 50</td>
</tr>
</tbody>
</table>

Run 90'. Stop 30'. Run 60'

Unhairing Penetration Control  
If OK, add:

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>WATER 26º C (or better still, hair-save unhairing bath)</td>
</tr>
</tbody>
</table>

Run 30'

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>WATER 26º C (or better still, hair-save unhairing bath)</td>
</tr>
</tbody>
</table>

Run 30'. Automatic running 5' every hour. Up to minimum 16 hours after starting unhairing.  
CONTINUE AS USUAL

### BATING

<table>
<thead>
<tr>
<th>%</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>70%</td>
<td>BATH DELIMING. pH = 8.5</td>
</tr>
<tr>
<td>0.6 – 1%</td>
<td>VERDITAN EL</td>
</tr>
</tbody>
</table>

Run 45'- 60'

Bating Control
# FRESH CATTLE LEATHER BEAMHOUSE PREFLESHING FOR BLOOD VEIN REMOVAL WITH HAIR-SAVE UNHAIRING

Leather state: **REFRIGERATION CHAMBER T = 5º C**  
% on weight: **FRESH. NO PREFLESHING IN HAIR**

## PRE SOAKING
- **200%** WATER 30º C (*)  
  - **0.05%** ASEPANTE DMC  
  - 30' T = 26º C; pH = 7  
  - DRAIN BATH

## SOAKING
- **100%** WATER 30º C (*)  
  - **0.35%** HUMECTOL RAPID  
  - **0.15%** ASEPANTE DMC  
  - **0.3%** VERDITAN CV  
  - 3 - 5 hours. SOAKING CONTROL: crossed bluish green as per Universal Ind.  
  - T = 26º C; pH = 8.5 / 9  
  - (*) If from refrigeration chamber. If recently dead, lower temp. to 26º C

## HAIR-SAVE UNHAIRING
- **Add:** CELESAL BE - 50  
  - **0.2%** RIBERSAL LA  
  - **0.2%** VERDITAN CV  
  - **0.1%** SODIUM SULFHYDRATE  
  - Run 60' (3 rpm). pH = 9.5
  
  **1.2%** LIME  
  - Run 20’ (1.5 rpm). Stop15’. Run 15’. Stop 10’.  
  - Lime penetration control with phenolphthalein up to hair root. pH = 12.5
  
  - **0.8%** SODIUM SULFIDE  
  - **0.8%** SODIUM SULFHYDRATE  
  
  - **0.3%** SODIUM SULFIDE  
  - **0.1%** RIBERZYM AT  
  - Run 30’

## KERATIN REMOVAL CONTROL
- **2%** LIME  
  - **0.2%** RIBERSAL LA  
  - **0.1%** CELESAL BE - 50  
  - Run 15’. Stop 30’.  

## UNHAIRING PENETRATION CONTROL
- If OK, add:  
  - **80%** WATER 26º C  
  - Run 30’. Automatic running 5’ every hour. Up to minimum 16 hours after starting unhairing.

## BATING
- **70%** BATH DELIMING. pH = 8.5  
  - **0.6 – 1%** VERDITAN EL  
  - Run 45’- 60’

CONTINUE AS USUAL
PICKLING

Swelling and unswelling

The large number of electrically charged groups in collagen makes collagen have an amphoteric behavior (that of a molecule with positive and negative charges).

A low pHs, collagen behaves like a cation. At high pHs, collagen behaves like an anion.

\[ \text{Anion} \quad \rightarrow \quad +H_3N-R-COO^- \quad \text{Isoelectric point} \quad \rightarrow \quad +H_3N-R-COO^- + H_2O \]

Starting at the isoelectric point, carboxyl groups lose their charge if pH is lowered by adding acid (H$^+$), while amine groups remain positively charged.

Because the carboxyl groups are neutralized, repulsive forces start developing on account of excess positive charges in the amine groups of the neighboring chains. These repulsive forces are the basis of acid swelling.

The contrary occurs in the alkaline region. The amine groups are neutralized by the addition of alkali (OH$^-$). Then, negatively charged carboxyl groups prevail and repulsive forces are also created. Charge repulsion is the basis of alkaline swelling.

Acid swelling is stronger than alkaline swelling because carboxyl groups are uncharged only within a small pH range —the range where amine groups are charged. Maximum swelling is achieved at pH = 3.5.
Unswelling action of salts

The ability of a salt to prevent swelling in strongly acidic solutions is directly related to the concentration and ionic dissociation of the salt. **Concentrations of 4% of sodium chloride totally inhibit swelling.** In industrial practice, however, 6% is customarily used as a precautionary measure.

The addition of sodium chloride in solution (Cl−, Na+), where chloride and sodium ions are ionized, makes chloride pass from the solution (bath) to the hide (fibers) by the effect of osmosis, thereby neutralizing the positive charges of the amine groups (NH₃⁺), preventing their repulsion and thus preventing swelling.

The leather must be adjusted at the entry and penetration of chromium.

In order to prevent internal tensions and wrinkles, **the leather must have an appropriate pH through its entire thickness before chromium addition.**

That is why the running time of pickling must be long enough to ensure uniform acid penetration.

This is checked with bromocresol green and must appear yellow through the entire section.

In pelt split, correctly delimed leather, 3 to 4 hours are enough for full penetration.

Non-splitted hides require more time, or better still, one night in bath.

In full substance leathers, it is very important to bear in mind that, even at pH = 3 in the pickling bath, the inner pH of the leather may be higher than 4. When confronted to this high pH, the entering chromium will abruptly increase its particle size and lead to internal tensions leading to wrinkling at neck and bellies, and mesh at legs and dewlap.

Because the dissolution of SO₄H₂ is an exothermic reaction, it should be left dissolved beforehand so that it is cold when added to the drum, and also to prevent burn marks and bath temperature increases.
The temperature of the pickling bath must never exceed 27º C. Indeed, as shown in the graph below, the solubilization of collagen increases with increasing temperatures:

*Influence of *Time *and Temperature* *on protein dissolution*

*(2.5% *Sulfuric Acid* *and 3% *Salt)*

*Beginning of pickling (30min)*
Pickling at ½ penetration (120 min.)
Pickling at \( \frac{3}{4} \) penetration (3 hours)

CORRECT PENETRATION

Pickling correct total penetration (4 hours and night in bath)

Bath pH = 2.5
THE PURPOSE OF CHROME TANNING

The purpose of chrome tanning is to obtain deep tanning with the minimum possible offer of chromium salt, and to reduce wastewater pollution.

- A short bath (max 70%) is preferred to improve chromium diffusion (stronger mechanical effect and weaker effect of hydrolysis).

- Temperature must be raised gradually, starting at 20 / 25º C and finally exceeding 40º C.

- Choose slow-reacting basifying agents that reach a final pH between 3.7 and 3.9.

- Use well-chosen masking agents that ensure grain fineness at the beginning of tanning. These agents increase the stability of the chromium complex and thereby are less astringent and more resistant to olation. Also, a much more stable and uniform binding to collagen is obtained.

Cromogenia’s basifying-masking agents are, among others:

- PLENATOL HBE or PLENATOL 88 BASE (in furriery), to be used when temperatures higher than 30 / 35º C at the end of tanning cannot be reached.

- PLENATOL SRB/2 and BASIFICANTE 2MP, which fix greater percentages of chromium at final temperatures exceeding 40º C.

As discussed in the presentation of DERMATAN SULFATE (pages 13 - 17), partial hydrolysis can be obtained by using PLENATOL IS in tanning. This product is particularly recommended in leathers heavier than 30 Kg, in leathers undergoing a short beamhouse (24-hour soaking-unhairing), and in full substance leathers.

It is also recommended in leathers which, on account of their tight structure or corneous grain, have a tendency to cause wrinkling at the neck, the belly, or the shanks and cheeks.
A STANDARD PICKLING–TANNING FORMULATION FOR FULL SUBSTANCE LEATHER is:

**PICKLING**

- COLD WATER 22° C 50%
- SALT 5.5%
- SODIUM FORMATE 0.6%
- DECALIM FE 0.2% (in leathers with Fe stains)
- CELESAL BE - 50 0.1% (in leathers with fattening line)

  Run 15 min. Control Dens = 7º Bé

- FORMIC ACID (1:5) 0.6%
  Run 40 min.

- SULFURIC ACID (1:10) 1.6% (1:10 dissolved and cold)
  2 x 15 min.

- ASEPTANTE WB 0.03%
  Run 180 min. (or better still, night in bath)

  Pickling penetration control: yellow section; pH = 2.5 / 2.7

**TANNING**

- CHROME 33 Sch 3%
  Run 30 min.

- UNIX P 48 (AUT C8) 0.2 – 0.5%

- ASEPTANTE WB 0.05% (if wet-blue is for storage over several months, increase to 0.15% total)
  Run 30 min.

- CHROME 33 Sch 4%
- SODIUM FORMATE 0.7% (only in integral and heavy leathers)
  Run 120 min. Penetration control

- PLENATOL HBE 0.4%
- PLENATOL IS 0.6% (only in thick and > 30 Kg leathers)
  Run 30 min.

- PLENATOL HBE 0.4%
  Run 7 hours. Boiling, temp. and pH control

WASH WITH COLD WATER WITH 0.1% FORMIC ACID

The outer pH must never exceed 4
SIMPLE CALCULATION OF THE SHRINKING DEGREE OF A WET-BLUE LEATHER

PROCEDURE:

- Cut a stretch of butt at the sampling area.
- Mark it from 0 to 10 cm.
- Place it in water at 100° C for 2 minutes.
- The difference in the marked length must be lower than 0.5 cm.

in cm.
ASPECTS TO BE CONSIDERED IN GOOD TANNING

Three aspects should be considered:

1. The temperature of tanning.
2. The presence of Dermatan Sulfate.
3. The lubrication of fibers.
4. Stratigraphic distribution of chromium.

The use of chromium basifying and self-basifying agents that require a high temperature (above 40°C) at the end of tanning to achieve a good chromium salt exhaustion makes the leather more astringent and more “shrunk”, that is, its surface is decreased.

The use of magnesium oxide as a basifying agent in chrome tanning is fairly widespread. This product—a correct agent both in terms of price and low offer percentage—has a lower area yield because it needs a high final temperature to reach good exhaustions. Even so, the stratigraphic distribution of chromium in the different layers is quite irregular, with less chromium being left at the center of the leather.

The greater the final temperature of tanning, the greater the astringency, the greater the shrinking, the smaller the surface, and the lesser the yield.
2 Should Dermatan Sulfate be still present in the leather at this stage of the process, hydrolyzation can be continued in tanning.

PLENATOL IS at 0.6% is added together with self-basifying agent. This product:

- Improves wrinkle opening at the neck and the belly, yielding more open leathers with increased surface.
- Improves wet-blue selection.
- Increases regularity between batches.
- Highly recommended in heavy leathers and in all leathers whose structure has a tendency to form wrinkles at the neck (full substance leathers and 24 h soaking-unhairing processes).
- Great uniformity in milled leathers.

3 Fiber lubrication.

In tanning, using a small quantity of a special chromium/electrolyte-stable oil favors fiber lubrication and diminishes fiber astringency, yielding a more relaxed leather.

Most importantly, the fatliquor of choice must have a high lubrication power, however low its softening power may be.

UNIX P48 for footwear and FOSFOL AUT C8 for car upholstery are excellent choices.

Using these oils in tanning:

- Favors shaving by softening the blade cut and by passing the leather through the shaving machine without yanks or fiber rupture.
- Keeps the leather wet for a longer time; even if it dries, moistening is rapidly favored.
The stratigraphic distribution of chromium should be as homogeneous as possible in the entire leather so that the rest of reactive products (retanning agents, dyes, fatliquoring agents, resins, etc.) are also homogenously distributed.

Uneven distribution of chromium will result in uneven distribution of the next products (retanning agents, dyes, fatliquoring agents, etc.).

A correct stratigraphic distribution is ensured by using basifying agents and self-basifying agents correctly. The graph below shows the amount of chromium oxide (%) in the three areas of the hide (Grain, Middle and Flesh). The more horizontal the line, the better the distribution of chromium:

As shown, BAS.MG (Magnesium Oxide) provides maximum unevenness (4.3% in Grain, 3.9% in Middle and 4% in Flesh). The best distribution is provided by PLENATOL HBE (4.06% in Grain, 4% in Middle and 4.02% in Flesh). PLENATOL SRB/2 also provides a very good distribution of chromium oxide.
USE OF PLENATOL IS IN NEUTRALIZATION

Tanneies are increasingly working with leathers purchased in Wet-Blue, where the content of Dermatan Sulfate in beamhouse processes cannot be modified.

In these cases, using Plenatol IS in neutralization can help dissolve Dermatan Sulfate.

Empirically, the action of Plenatol IS in the neutralization process has shown the same properties as when used in the beamhouse —while also proving less effective. This is made up for with a higher offer of product.

At the 3% dose, add PLENATOL IS together with alkalis in the first addition.

The results obtained in production are:

- **Grain:**
  - Better wrinkle opening at heads and bellies.
  - In milled leathers it provides excellent grain regularity over the entire surface.
  - Improves touch levelness between heads and butts.

- **Split:**
  - Better opening of tight areas (butts and backbone).
  - Improves nap levelness between center and bellies.
  - Improves color levelness between center and bellies.
In full grain milled articles, the addition of 3% Plenatol IS together with neutralizing salts or retanning agents provides a uniform, regular grain over the entire hide, and levels the grain between heads, bellies and butts.

In neutralization of splits with gloss problems at the tighter parts (backbone and butt), this product is used at 3% after running 30 minutes with the alkalis, and continuing with a running time of 90 minutes.

This product dissolves the cementing substances that form the tight structure of these areas and allows the rest of products to penetrate —thus preventing gloss when sanding is performed, should these products remain on the surface.

The result is total color and nap levelness between the most open areas of the butt and the tightest areas.

THE ISSUE OF MOLD

Mold appears in wet piled hides and at pH ≥ 4 (tanned hide storage conditions).

Mold production increases with increasing temperatures.

It develops in colonies and reyields by sending spores into the air.

Red and green molds are most commonly found.

The most effective antifungal agent is Ticyanomethyl-Thiobenzotiazole (TCMTB): ASEPTANTE WB.
Experiments have shown that a **Minimum Inhibitory Concentration (MIC)** is necessary for TCMTB to exert its antifungal action. In a product with 30% of active ingredient, the minimum dose must be 0.08% on pelt weight.

For long-term storage, the dose should be increased to 0.1 – 0.15%.

A pH higher than 4 degrades the product; the higher the pH, the more and the faster the degradation.

In order to prevent TCMTB degradation:

- Add the emulsified product together with the chromium salt, or in pickling.
- Ensure that the emulsion is stable (always add the product in water at 1:3).
- Prepare the emulsion immediately before its addition to the process.
- At the end of tanning, wash with 0.1% formic acid for 10 min. up to surface pH = 3.6 / 3.7.
- Do not store the product at temperatures above 40º C to avoid possible degradation.

If the product is incorrectly added it may cause whitish stains on the grain —barely visible in Wet-Blue but very apparent in dyeing (more gradient colors).
Mold development in palletized wet-blue leather

Mold in the folds of palletized leathers

Mold on the surface

Chrome-tanned leather after treatment with Formic Acid

pH = 3.8 / 3.9

pH < 3.6 / 3.7
Among the problems evidenced in the final article, some have had their origin at the soaking-unhazing process for a number of reasons.

The most commonly found problems are:

A **Loose grain and empty hides.**

B **Wrinkles at:**

1 Neck.
2 Bellies.
3 Cheeks and shanks.
4 Backbone.

C **Dye-related defects:**

1 Fattening line.
2 Lime stains.
3 Gypsum stains.
4 Iron stains.
5 Keratin stains.
6 Whitish, blurred stains.

D **Hair root.**
A **Loose grain**

Loose grain can be influenced by many factors, and decisively so by the beamhouse process.

The junction of the **papillary area or grain and the reticular area** has been shown to be very prone to damage. Indeed, that is where the fibers of the collagen fibrous tissue are much finer and shorter than in the deeper reticular layer.

That is where the hair roots and the secreting part of the sweat glands are located. In the beamhouse process they will empty their content and leave hollow spaces.

Bacteria can also develop on account of collagen degradation in unprotected areas.

All causes share a common element: **fiber degradation (or even rupture) at the junction of the papillary area and the reticular area.**
These causes may have different physical or chemical explanations, including:

- Leather storage at a temperature above 18º C. Due to bacteria.
- Excessive soaking: in time or due to emptying of the fat present in the leather.
- Soaking with pH peaks higher than 10.5. Due to fiber rupture.
- Excessively attacked or loosened unhairing, temperature higher than 25º C., excessive loosening time, excess lime, etc.
- Unhairing with swelling occurring too quickly. Due to fiber rupture.
- Unhairing with excessive mechanical effect. Due to fiber rupture.
- Fleshed leathers with excessive pressure in the fleshing machine (may be due to excess fat on the surface of the pelt leather. Due to fiber rupture.
- Excessive deliming due to excess time or excess product. Due to fiber loosening.
- Excessive bating due to excess time or excess product. Due to fiber loosening.
- pH at end of tanning higher than 4.5. Due to fiber rupture.
- Unbalanced fatliquoring (dried-out grain). Due to fiber rupture.
- Drastic drying or drying using fasteners, leading to fiber rupture.
B Wrinkling

B – 1
NECK WRINKLES

B – 2
BELLY WRINKLES

B – 3
MESH GRID IN CHEEKS

B – 3
MESH GRID IN SHANKS

B – 4
CENTER WRINKLES
NECK WRINKLES

**Causes** of NECK WRINKLES:

- Insufficient soaking.
- Excessively swollen unhairing with little loosening effect.
- Unhairing with excessively fast swelling.
- Presence of cementing products (Dermatan Sulfate) upon the completion of liming.
- Water addition in liming without full penetration.
- Insufficient or inappropriate bating.
- Pickling with a high pH and/or not crossed.

**Possible SOLUTIONS:**

- Improve soaking.
- Do not over-swell the leather in unhairing, and swell slowly.
- Increase structural loosening in unhairing.
- Use RIBERSAL LA together with lime to accelerate penetration.
- Always swell the leather after full penetration of lime.
- Totally remove Dermatan Sulfate from the leather by using DECALIM PLUS in deliming.
- Bate with appropriate enzymes, pickle at a lower pH, and check total penetration.
Belly Wrinkles

Causes of BELLY WRINKLES:

- Insufficient soaking.
- Insufficient or inappropriate bating (presence of elastin in the leather after bating).
- pH of non-crossed pickling (mainly in full substance leathers).
- Presence of cementing products (Dermatan Sulfate) upon the completion of liming.

Possible SOLUTIONS:

- Improve Soaking.
- Bate with appropriate elastase enzymes, such as TRIPSOL RSTP / VERDITAN EL.
- Thoroughly cross pickling up to pH < 2.5.
- Totally remove Dermatan Sulfate from the leather by using DECALIM PLUS in deliming.
MESH GRID IN CHEEKS AND SHANKS

Causes of MESH GRID IN CHEEKS AND SHANKS:

■ Insufficient soaking.
■ Unhairing with little loosening effect.
■ Unhairing with excessively fast swelling.
■ Swelling with unhairing not fully penetrated.
■ Presence of cementing products (Dermatan Sulfate) upon the completion of liming.

Possible SOLUTIONS:

■ Improve soaking.
■ Increase structural loosening in unhairing-liming.
■ Always swell the leather after full penetration of lime.
■ Totally remove Dermatan Sulfate from the leather by using DECALIM PLUS in deliming.
B - 4 CENTER WRINKLES (AT THE BACKBONE)

Causes of CENTER WRINKLES:

- Insufficient soaking.
- Presence of cementing products (Dermatan Sulfate) upon the completion of liming.

Possible SOLUTIONS:

- Improve soaking with wetting products (CELESAL CN) or enzymes (HUMECTOL ULTRA).
- Totally remove Dermatan Sulfate from the leather by using DECALIM PLUS in deliming.

C Dyeing defects

C - 1 FATTENING LINES
These are cross-cutting stains where more dyestuff is attached, yielding a more intense color.

While they are already visible in wet-blue, they become much more apparent when dyeing is performed.

Its (non-embossed) outline can be seen.

**Causes** of FATTENING LINES: Chromium soaps formed in tanning.

<table>
<thead>
<tr>
<th>Time</th>
<th>Unharing</th>
<th>Pickling</th>
<th>Cr tanning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglycerides</td>
<td>SFA</td>
<td>Ca soaps</td>
<td>SFA</td>
</tr>
</tbody>
</table>

**Possible SOLUTIONS:**

- Degreasing with **CELESAL DL** in deliming – bating.
- Use of lipase (**DEFAT 50**) and of emulsifier (**CELESAL BE-50**) in unhairing.
- Use of emulsifier (**CELESAL BE-50**) in pickling.

**C - 2** LIME STAINS (**CO₃Ca**)
Causes of LIME STAINS:

- Any limed hide area left outside the bath during laying down will remain in contact with the air, and the OH\(^{-}\) groups located on the surface will react with air CO\(_2\) and generate CO\(_3\)\(^{\equiv}\) which, with the Ca\(^{++}\) ions of the hide, will result in CO\(_3\)Ca precipitation in the hide (P.S. = 0.87 x 10\(^{-8}\)).

  This defect occurs when the pH of the hide starts approaching neutral pH (around 9) and not its drying pH.

- Using **water** with a high CO\(_3\)H\(^{-}\) concentration (high temporary hardness) —which becomes CO\(_3\)\(^{\equiv}\) on account of pH and results in CO\(_3\)Ca precipitation in the hide.

- Using a calcium salt anytime during the process after deliming —Ca\(^{++}\) ions are delivered.

Lime stains in limed hides have a rough appearance and a sandy touch.

In VEGETABLE-tanned hides, these calcium carbonate precipitates prevent tannin penetration and leave raw areas.

The grain then turns brittle and dark, and the color is irregular.

In CHROME-tanned leathers, they block chrome penetration and yield chrome-poor, light areas that will absorb less dyestuff at dyeing.

They can be partially removed by washing before deliming with acetic acid and hydrochloric acid. The grain, though, will remain rough and rugged, with a sandy touch.

Preventive action:

- Avoid drafts likely to dry the surface.

- Prevent hides from floating in the bath; run frequently.

- Leave hides in bath after fleshing or splitting if they are to be left unprocessed for a long time.

- In the last unhairing wash, use 0.2% of DESENCALANTE SE - 01 or of RETANAL SF. These will also facilitate the passage of the leather through the fleshing machine.

- The addition of 0.2% of DECALIM FE in main deliming and of another 0.2% together with sodium chloride in pickling favors the removal of lime and stains caused by it.
The predecessor of a gypsum stain is usually a lime stain on the hide. That is, we already have a CO₃Ca precipitate which, by reacting with SO₄(NH₄)₂ in deliming, or with SO₄H₂ in pickling, leads to a SO₄Ca precipitate.

In deliming:

\[
\text{CO}_3\text{Ca} + \text{SO}_4(\text{NH}_4)_2 \rightarrow \text{SO}_4\text{Ca}.2\text{H}_2\text{O}
\]

In pickling:

\[
\text{CO}_3\text{Ca} + \text{SO}_4\text{H}_2 \rightarrow \text{SO}_4\text{Ca}.2\text{H}_2\text{O}
\]

However, gypsum stains can also be caused by:

- Using CO₃Na₂ directly on the hides in liming or in reliming.
- Using calcium formate directly on the pickled hide.
- Using dolomite (calcium and magnesium carbonate) in basification.
- Using water with high temporary hardness in unhairing, on account of its CO₃H⁻ content.
C - 4  IRON STAINS

Causes of IRON STAINS:

- Iron stains are caused in the slaughterhouse by the iron contained in the hemoglobin of the blood spilled on the leather surface. These stains become dry before washing.

Corrective action: Iron stains are removed with:

- 0,2% of DECALIM FE at the beginning of main deliming, after draining the first bath.
- 0,2% of DECALIM FE at the beginning of pickling, together with the salt.

The grain becomes very smooth and less astringent, mainly in very hard waters, thus preventing possible blind grain from increasing.

C - 5  KERATIN STAINS

These are brown epidermis residues not removed in unhairing.

Caused by:

- Insufficient soaking.
- Insufficient unhairing (insufficient time or insufficient product concentration).
- Presence of fat on the hair surface at the beginning of unhairing.

Possible SOLUTIONS:

- Increase soaking.
- Increase unhairing (in time or in product concentration) and/or use an enzyme of the RIBERZYM AT type.
- Increase degreasing agent CELESAL DL in soaking.
- Use emulsifier CELESAL BE - 50 at the beginning of unhairing.
C - 6  WHITISH STAINS

These are blurred whitish stains.

**Causes** of the PROBLEM:

- Whitish, blurred stains are caused by irregular distribution and fixation of the antifungal agent on the leather surface, particularly when the product has a low stability at low pH or when the solution has been prepared too soon and the product has come to decant and separate from water.

**Possible solutions** of the PROBLEM: To avoid antifungal agent decanting and separation:

- Use an antifungal agent that is stable at acid pHs and that has a very good solubility in water (those presented in aqueous solutions are preferred to those presented in alcohol solutions).
- Add the emulsified product together with chromium addition, or in pickling.
- Ensure that the emulsion is stable (always add the product to water at 1:3).
- Prepare the emulsion immediately before adding to drum.
- Always add using a funnel and with the drum running.
- Do not store the product at a temperature above 40° C to avoid product degradation.

D  Hair roots

Hair root residues not sufficiently attacked in unhairing may be found. These may be visible to the naked eye or when sanding the leather surface (nobuk).

**Caused by:**

- Insufficient soaking.
- Excessively high pH peak in soaking.
- Insufficient initial concentration of SH\(^-\) ions.
- Excessive immunization with lime (in time or in percentage).
- Presence of fat on the hair surface at the beginning of unhairing.
Possible SOLUTIONS:

- Perform longer, more energetic soaking.
- Control pH in soaking, particularly when alkalis are added (the use of buffering agent HUMECTOL TPH is preferred).
- Increase the concentration of $\text{SH}^-$ ions and/or unhairing time.
- Control lime penetration in the processes involving hair immunization.
- Increase CELESAL DL in soaking.
- Use CELESAL BE - 50 at the beginning of unhairing.
- Use unhairing enzymes RIBERZYMP MPX / RIBERZYMP AT.
- Use DEFAT 50 at the beginning of unhairing.
- In the last unhairing wash, use 0.2% of DESENCALANTE SE - 01 to unswell the grain and help the hair root be expelled by the pressure exerted by the fleshing machine, thereby facilitating its passage through it.
- Add a small quantity of salt (ClNa) to the first bating wash to unswell the grain a little and gain mechanical effect on a grain that no longer oppresses the hair root.

Let me close by saying that I hope you will find the above concepts useful whenever appropriate.

Enrique Comes

Barcelona, March, 2017
CATTLE HIDE IN THE BEAMHOUSE
Enrique Comes
BARCELONA 2017