Sustainable processess

The objective of environmental sustainability is to preserve natural resources, reduce pollution and develop alternative sources of energy. There are different requirements that a process must fulfil to be considered sustainable, and include reducing the resources used in terms of products, water and power, reducing residues and air emissions, using manageable and non-toxic products and using renewable raw materials. With these requirements in mind, Cromogenia Units, S.A offers a variety of sustainable processes for unhairing and tanning.

During the tanning process, large volumes of water and chemicals are used. Some of these chemicals can be harmful to the environment and people's health should they be misused; therefore, water pollution must be controlled. The most significant loads in each stage are shown in *Table 1* (BAT, 2013).

*Table 1: Polluting loads in each stage**

	Stage			
	Unhairing	Tanning	Retanning	Finishing
COD	70%	9%	17%	4%
BOD5	70%	8%	17%	5%
SS	77%	6,5%	13%	3%
Cr3+	-	71%	28%	-
S2-	100%	-	-	-
TKN	82%	6%	12%	-
Cl-	68%	27%	4,5%	-
SO42-	18%	45%	36%	-

** salted bovine without hair recovery.*

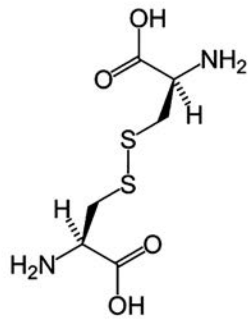
Unhairing is the most polluting stage of the tanning process, as shown in *Table 1*. Sulfide will be determined by the percentage of Na_2S used. Hide and solubilised hair proteins are responsible for COD, BOD, SS and TKN. Strong reducing agents, such as Na_2S, are used in this stage to destroy keratin. In acidic conditions Na_2S can react to produce H2S, which is a an extremely irritating and toxic gas that may cause death at very low concentrations.

ECO UNHAIRING

One of the main objectives of unhairing is the removal of hair, with Keratin being the main component, and to remove hair it must be destroyed. Keratin is a fibrous structural protein, insoluble in water, organic solvents or salt solutions. Keratin has a high cystine content and its high stability is due to disulfide bonds.

The cystine structure with disulfide bond is shown in *Figure 1*.

Figure 1: Cystine structure.



To eliminate hair there are several options:

- Reducing agents such as sodium sulfide or sodium hydrosulfide: these products break disulfide bonds and form thiosulfate and thiol derivatives. Although this process is widely used, it must be taken into account that sodium sulfide in acidic conditions can form hydrogen sulfide which is lethal at very low concentrations.
- Oxidative unhairing with hydrogen peroxide: this process is not used because sodium hydroxide is required, and in combination with hydrogen peroxide an exothermic reaction can result and wooden drums can be damaged.
- Enzymatic processes: keratinase enzymes can be used to eliminate keratin.

ECO UNHAIRING with RIBERZYM ECO C

ECO Unhairing is a process where a minimum quantity of sodium sulfide/sodium hydrosulfide is used in combination with an enzymatic product. In this case, Riberzym ECO C. Reduction of sulfide addition avoids unpleasant odours in production plants and in resultant leathers. Additionally there is also a reduced possibility for hydrogen sulfide formation. Moreover, the ECO Unhairing process generates waste-waters with lower sulfide content, lower BOD/COD, and lower sludge production. This process uses manageable and non-toxic products and uses renewable resources, enzymes, thus contributing to the sustainability of the process.

Table 2: Percentage variation for COD, BOD and sulfide.

Properties	Percentage variation with respect to standard process
COD	-50%
BOD	-40%
Sulfide	-50%

Table 2 shows COD, BOD and sulfide analysis of the residual baths of a standard unhairing process with sodium sulfide as compared to ECO Unhairing. Sulfide analysis showed a 50% reduction in ECO C wastewater when compared to the standard process.

Final evaluation of the leathers showed a better control of swelling, less appearance of veins with cleaner and more open skins with fewer visible wrinkles.

PICKLING with RETANAL SCT

As represented in *Table 1*, the most important polluting loads in the tanning stage are chromium, chlorides and sulfates. Chromium comes from the non-fixed chromium salts and chlorides come from the salt used in the pickling stage to counteract acid swelling. Sulfates come from the non-fixed chromium salts, and to a much lesser extent to sulfuric acid.

There are several ways to reduce pollution in the pickling stage:

- Bath recirculation: modifying acidity or chromium if needed. These processes may cause stains on the leather because of the remaining residues in the baths, e.g. fat.
- A process without pickling: tanning simultaneously with a slight acidification to avoid swelling. This process may work for sheepskin, but for cattle hide it is not feasible.
- Processes with high exhaustion: with lower chromium salts offer, with higher pH at the end of basification or with high temperature.
- Processes with sulfonic acid derivatives that allows reduced use of salt and acids.

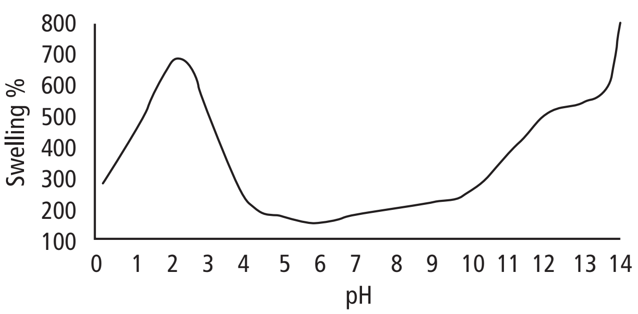
Collagen swelling is shown is *Graph 1*, where a drastic swelling is observed at pickling pH=3.0 if salt is not added.

The addition of Retanal SCT (non-swelling organic acid) allows for a reduction in salt content, totally removes sulfuric acid and also affords a reduction in processing time by up to 50%, contributing to the sustainability of the process. This process also provides greater chromium oxide fixation in the hide and lower chromium oxide in the residual baths. Furthermore, in some instances a loss of collagen may occur during the pickling stage due to the pelt heating caused by the acids used and mechanical action. This loss of collagen may lead to decreased physical properties, fullness and grain firmness and integrity.

Graph 2: If temperature is increased from 32° to 38°C, the loss of collagen increases drastically.

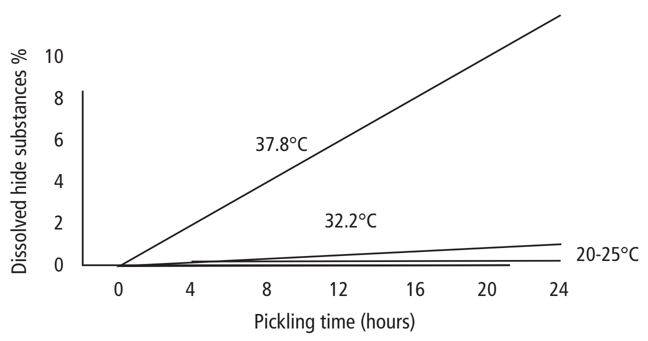
Collagen loss can be determined by hydroxyproline analysis. Hydroxyproline is a non-essential amino acid specific to collagen, that is, it is found in greater proportion in

Graph 1: Collagen swelling with pH.



Source: Covington, Anthony. (2009). Tanning Chemistry: The Science of Leather. RSC, 180.

Graph 2: Collagen loss with temperature and pickling time.



Source: O'Flaherty, Fred; Roody, William; Lollar, Robert. (1978). The Chemistry and Technology of Leather. Krieger, (1) 448.

collagen than in any other protein and therefore its determination can serve as a basis for determining collagen loss. Conductivity, as quantified with a conductivity meter (µS/cm), is a measure of dissolved salts in the bath.

Percentage variation for chromium oxide, hydroxyproline and conductivity of a Retanal SCT process compared to standard process is shown in *Table 3*.

Tensile strength, tear load and grain burst of the leathers after retanning and fatliquoring are shown in *Table 4*. Process with Retanal SCT obtains better resistances than a standard process.

In *Table 5* a standard formulation for Retanal SCT process is shown. This is a suggested formulation and it must be adjusted depending on the customer.

Table 3: Percentage variation for Cr_2O_3, hydroxyproline in hide and conductivity.

Properties	Percentage variation with respect to standard process
Cr_2O_3 in hide	+15%
Cr_2O_3 in bath	-84%
Hydroxyproline in bath	-10%
Conductivity	-170%

Table 4. Percentage variation for tensile strength, tear load and grain burst.

Properties	Percentage variation with respect to standard process
Tensile strength	+35%
Tear load	+15%
Grain burst	+20%

Table 5: Formulation for RETANAL SCT process.

REFERENCE – Standard pickling-tanning	Pickling - tanning RETANAL SCT
80% Water 25ºC, 8 NaCl %, run 10 min. Control 6ºBé	80% Water 25ºC, 4 % NaCl, run 10 min. Control 3-4 ºBé
1% Formic acid, run 30 min	0.5% Formic acid. Run 10 min
1.2% Sulfuric acid, run 3-5h. Control pH=3.0 – crossed section	1.25% RETANAL SCT (1:2), run 30min Control pH=3.5
5.5% Chromium salt 33% Basic, run 2-3h. Crossed section	5.5% Chromium salt 33% Basic, run 2-3h. Crossed section
0.7% Basifying agent PLENATOL HBE, run 8h. Control T=42ºC; pH=3.9; Ts=100ºC	0.4% Basifying agent PLENATOL HBE, run 5-6h. Control T=42ºC; pH=3.9; Ts=100ºC