



Oxidative unhairing



Hides suspended from conveyor feed to fleshing operations. The photograph shows a comparison between hides from oxidative unhairing and conventional unhairing/liming.

ALL CREDITS: WORLD LEATHER AND GRUPPO DANI, ITALY

The following overview by R.P.Daniels is based on:

- Presentations: G.A.Defero, Ars Tinctoria SRL (Italy), and S.Dani, Italprogetti Engineering (Italy): LGR, Reutlingen 2011 and Freiberg Leather Days April 2012.
- G. Defero, ARL Tinctoria,: SLTC Conference Northampton 2013.
- Information from: Gruppo Dani, Arzignano, Italy 2012 and Italprogetti, Italy 2013.

Oxidative unhairing based on hydrogen peroxide offers the advantages of very clean white pelts and a bleached grain after unhairing, together with an opening of the collagen structure as expected from conventional liming techniques. The hides produced are being tanned as full chrome production, or for wet white processes.

It is stated that when using conventional unhairing techniques based on sulfides and lime that the discharges from these processes generated 83% of the BOD, 73% of the COD, 60% of the suspended solids, and sulfides in the effluent. These can be addressed within effluent treatment, but this is expensive and in particular demands an oxidative step to remove the sulfide.

With oxidative techniques many of these problems can be side-stepped. The effluent is free of sulfide: this means that a major step in effluent treatment is avoided, and the smell of sulfides is completely absent within the plant. Moreover, the final liquors are odour free, and the soluble proteins from the fully solubilised hair can be recovered by simple acid precipitation using either sulfuric or phosphoric acid. This reduces the BOD and COD by 50-60%, thus taking a considerable load off the existing effluent treatment plant in terms of chemical dosing and biological treatment. The precipitates are clean, and can be readily dewatered by pressing and the recovered proteins composted. There is scope for sterilisation to produce clean dried proteins rich in nitrogen for direct agricultural use, or perhaps animal feed supplements. Also, any limed fleshings, limed trimmings, or limed splits are very clean and free of sulfides offering new commercial possibilities.

Although many attempts have been made over the years to manage oxidative unhairing (*Panel 1*) the key to success has been

a combination of good chemical control during the unhairing stage, a careful use of chemicals and auxiliaries, and the advent of the PPE drum as the Ecosmart drum developed by Italprogetti Engineering. Oxidative processes have two major problems when used with traditional wooden drums as the internal structure of the drum deteriorates causing an abrasive surface and a shortened life, and that the process generates heat. The combination of effects rapidly leads to grain losses and abrasion – ultimately a sueded grain surface.

The PPE construction has enabled a jacket or double wall to be constructed within the body of the vessel, and this can be used for water circulation with external cooling - or heating if required - hence very close temperature control. The interior of the drum is not affected by the oxidative process, so the problems of abrasion are avoided together with a long life expectancy. The whole process – particularly drum running times and speeds - can be carefully managed via microprocessor programming and control.

The oxidative unhairing process

The depilation process is carried out using hydrogen peroxide at pH 12.6. A sodium hydroxide solution after cooling is used for swelling; calcium hydroxide must be avoided at this stage as this may produce some immunity to hair breakdown, but, after full hair dissolution, it is possible for some lime to be added. Multi additions of hydrogen peroxide and sodium hydroxide solutions can be controlled precisely by chemical dosing pumps, and the temperature and pH monitored/adjusted using the external feed box that is part of the float recirculation system. The amount of hydrogen peroxide required is dependent on the amount of hair and skin type, and typically takes five hours for hair solution.

**Panel I: Historic**

Oxidative unhairing has been a subject of investigation since the 1960s. The original attempts were drum based and commenced with a basic soaking operation, followed by an addition of sodium chlorite in solution, then glycolic acid. At approximately pH 4.0 chlorine dioxide was generated which dissolved the hair over an 18-hour period. The outcome was very clean bleached hides free of hair and pigmentation. The effluent produced was a clear solution with no remaining hair debris and this was used as a promotional tool.

The mechanism was very different from conventional systems at that time which were mainly paddle based and could easily be observed. In these systems, with a gentle action the hair gradually loosened from the hair root and then, after release, gradually broke down towards the hair tip. The white hair was the first to become released from the grain, followed by brown hair, then black, but mainly with pigmentation remaining in the grain.

Oxidative unhairing worked very differently. The breakdown started from the hair tip, with the hair gradually becoming thinner and weaker until eventually the hair root was dissolved. However, the black hair was the first to dissociate, followed by brown with the white hair the last to dissolve. The skins were very clean and

white, but if the process continued in a normal manner the final leather was always too hard, even if the fatliquors were increased by 20% as advocated at that time. Moreover, the leathers did not lay flat: essentially they needed liming!

It was also a dangerous process as the chlorine dioxide generated within the drum was a serious health hazard as it caused significant lung irritation. The woodwork in the drums also suffered and the process never became a reality, although oxidation using sodium chlorite solution is still reported as a technique used to bleach certain exotic leathers in a pickling process.

Attempts were also made using sodium hypochlorite, but mainly hydrogen peroxide with both lime and sodium hydroxide to provide a liming action and an opening of the structure. These investigations produced leather which were very clean and hair free, but always minus the grain layer.

Since those times various peroxides have been used in different ways without commercial success. But investigations with hydrogen peroxide persisted over the years predominantly at University degli Studi di Pisa, Italy before suitable equipment became available for large scale pilot development and refinements. Now it is possible to produce high quality saleable leathers based on hydrogen peroxide unhairing. R.D.

The steps required in operating this process are conventional and comprise dirt soak, green fleshing, main soak, oxidative unhairing/liming, fleshing, splitting, trimming, deliming/bating, and pickle/tannage. However, the expertise lies in the detail, and for success a holistic approach is required.

First it is essential to remove any salt from the hides, and to green flesh to provide a more uniform substrate and remove fats, followed by a thorough soak in preparation for the unhairing process. Sodium carbonate should be avoided in the soak, and the choice of auxiliaries is very important. Degreasing agents, traditional soaking enzymes and anti-wrinkling auxiliaries should be avoided. If these are introduced into the oxidative stage these just consume oxygen.

It is also important to continue careful attention after the oxidative process. At the deliming stage ammonium sulphate should be avoided, and the temperatures should remain low. Carbon dioxide can be used for deliming, but careful attention should then be given to the selection of enzymes to be used in the bating process. Pickling and tannage may be conventional for either full chrome leather or wet white production.

The advantages offered by oxidative unhairing

- A very clean and white pelt compared to traditional liming/unhairing systems.
- Complete elimination of grain pigmentation.
- A process that is compatible with any tannage.
- Dyeings that can be more intense, but it also offers better scope for pastel shades.
- Opportunities for very clean wet-white leathers.
- Clean sulfide free limed trimmings and splits.
- The avoidance of sulfides within processing and for treatment in effluent processing.
- Offer of easy safe treatment of exhaust liquors from the oxidative process by simple acid precipitation, and reduced load on chemical dosing/biological treatment.
- Opportunities for a new high protein raw material from unhairing/liming as opposed to hair-based sludge. 🌱



Two ton load of hides following oxidative unhairing.



The Ecosmart Drum: This PPE drum has a double skin for a water jacket to enable very close temperature control. Two ton lots of hides for unhairing with hydrogen peroxide can be processed using this equipment.