Oxidative beamhouse processing

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Introduction
The beamhouse process is known to contribute around 75% of the wastewater pollution charge in a typical tanning process. Water consumption from raw to the end of deliming process is about 10-12 litres per kg of salted hide, a value which increases in calves and small skins. This process contributes 87% of BOD, 73% of COD, 60% of suspended solids and 75% of the salinity of the complete process. From the organoleptic point of view the beamhouse processing steps contribute negatively to a tannery’s image, mostly because of sulfides. The ideal of an alternative oxidative beamhouse process is to recover proteins, reduce the environmental impact of the tannery and generate new opportunities of useful by-products, while at the same time reducing the bad smell. This paper considers some practical issues on the industrial implementation of a sulphide free beamhouse process that aims for total water recycling, and the generation of useful by-products.

View of the process
In the leather industry our starting raw material is natural and biodegradable. State of art processes mostly take it to a non-biodegradable product with plenty of non-biodegradable wastes, by means of chemicals which may affect the environment or which implies costly treatments to be removed or neutralised. Sulphide containing waters should be carefully treated by oxidation before any pH reduction to avoid poisonous SH2 (hydrogen sulphide gas) generation.

Several proposals of sulphide elimination by means of oxidative beamhouse processes were presented in the past, showing the advantages of this technology in terms of leather quality and the environment. In several papers it was demonstrated that depilation can be performed safely with less damage than traditional processes.

In our personal experience, oxidative beamhouse processes showed the following advantages:
From the application point of view:
- Pale, even colour, total elimination of scud and pigmentation.
- More intense and even dyeing.
- Does not induce metals oxidation on metal free tannages.
- Compatible with any tannage.
- Deliming and pickling processes does not generate any dangerous gas which means less personal and environmental protection issues or devices.
- Drastic reduction of dangerous emissions in the atmosphere.
- A cleaner working environment.

Process logic
Skins should be pre-soaked and green fleshed, so as to avoid excessive H2O2 consumption. A main soak is done with the scope of removing globular proteins, and thus achieving the necessary liquid diffusion in the skin. Depilation process is carried out with H2O2 at a stable pH12.6 adjusted with NaOH. Considering NaOH dissolution is exothermic, it is advisable to use liquid NaOH 30% concentration. Once the hair is pulped the epidermis is removed easily and a small portion of lime is added running the drum on automatic overnight.

The next morning after draining the float and washing it, is advisable to rinse with an ammonium free deliming agent to pH 9.5-10.

The peels are then fleshed, lime split, trimmed and returned for the deliming and bating processes. No H2S generation is possible, so it is safe to work with ammonium free deliming agents (even acids).

Left: Ecosmart drum by Italprogetti
Right: Oxidative beamhouse colour vs a traditional process
Sulphide free trimmings and splits can be easily used in industrial gelatin production as a by-product of this process.

Hair save vs hair burn
Although hair save systems have been experimented with, from the protein recovery point of view, hair burn systems are more advantageous. Hair save systems move the problem of the hair's BOD and COD contribution to a low biodegradable solid waste which can be disposed of. Hair's high nitrogen content may be used, if dissolved and recovered as protein as a base raw material for fertilizers.

Technical developments for oxidative beamhouse
H₂O₂ is highly corrosive to wood and metal. In this context modern PPE vessels are the best solution in terms of durability. In our practical experience, the best results were achieved by constantly monitoring and adjusting depilation parameters. For this purpose we have prepared a prototype PPE drum with float circulation system through a laboratory box (for taking measurements), and a pH meter connected to a central control system. Two membrane pumps were installed respectively to automatically dose NaOH and H₂O₂, also controlled by the central control system. The vessel has a liquid circulation system which is able to work heated or cooled to control event of temperature increments due to the exothermic reaction of H₂O₂ and warmer climatic conditions.

It is advisable to avoid using degreasing agents, soda ash and traditional soaking enzymes during soaking process. So far in the trials carried out no anti-wrinkle auxiliaries were needed.

Dosing of NaOH and H₂O₂ can be done automatically, setting the desired pH. The system was programmed to dose NaOH to the depletion pH with alternate addition of H₂O₂ in quantities which can be set as desired. The system routinely checks the pH after each H₂O₂ addition. Dosing the required NaOH amount until completion of the cycle.

The temperature is constantly monitored using the float circulation and conditioning system. By means of this technology, and once the correct recipe is defined, which will depend of the weight, conservation, origin and breed of the hides or skins, the process can be performed with the same check points as a traditional beamhouse process.

Environmental waste treatment
The greatest advantage of an oxidative beamhouse process is the generation of a sulphide free highly concentrated protein float. Effluent from an oxidative depilation system may be streamed and treated with sulphuric or phosphoric acid. In this condition proteins can be collapsed with a reduction of over 50% of BODs and COD values. The precipitated proteins can be filter-pressed and after pH conditioning and sterilization as requested by regulations, can be used as a base for fertilizers. The rest of the effluent can be streamed and treated together with the remaining waters in an MBR (Membrane Bio Reactor) where the filtrate can be pH conditioned and reused in the process. MBR technology allows a filtration at microorganism levels.

In our experimental tests we did not find a significant reduction of COD in relation to current modern technology. Traditional beamhouse trials give a COD value in the order of 90–100,000 mg/l, while oxidative beamhouse process gives 75–90,000 mg/l. The advantage of a safe protein flocculation in the oxidative beamhouse by means of acids, allows a quick COD reduction to 5–7,000 mg/l without the addition of auxiliaries.

Retanning trials
Leather articles were made using a titanium tannage (for brilliant colours) in a soft, milled car upholstery leather and a shoe upper nubuck. Other oxidative unhairing hides were sintan pre-tanned, shaved and retanned for white shoe upper (with tara and sintan), light vachetta with traditional tallow fatliquoring, white splits and extremely bright coloured splits. The advantage found in oxidative beamhouse processes is improved colour uniformity and brightness with no sign of hair roots, scud or natural pigmentation.

References
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