CHEMICAL ENGINEERING TRANSACTIONS
VOL. 36, 2014
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Valerio Cozzani, Eddy de Rademaeker

ISBN 978-88-95608-27-3; **ISSN** 2283-9216
DOI: 10.3303/CET1436033

DEPOXO Process: Technical and Environmental Study of Hide Oxidative Unhairing

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As an alternative to the traditional process based on the use of sulfides, an unhairing process in drum by hydrogen peroxide, named DEPOXO, was developed for the production of high-quality bovine upper leather. A preliminary investigation at laboratory scale has allowed to set out the optimal process conditions, in terms of H_2O_2 dosage (9 %) and pH (12.5), in order to achieve an effective unhairing and a compatible swelling of hides. The following pilot-scaled runs have assessed the industrial feasibility of the process that allows the production of a versatile base for different final applications of the leather (either chrome or vegetable tanned), and appear practical to implement. The crust leather obtained by the oxidative unhairing process showed good physical-mechanical and technical properties comparable with those obtained by the traditional one, and the leather was technically assessed as satisfactory and suitable according to the market request. The actual reduction of the environmental impact of the novel process, in relation with the traditional one, was evaluated performing a Life Cycle Assesment (LCA) using SimaPro 7.3, one of the most used software for LCA analysis. The results of the life cycle impact assessment underline that damages on main impact categories are greatly reduced through the adoption or the oxidative unhairing. Therefore, the DEPOXO process appears a feasible process, either from the environmental or from the technical point of view, to produce high quality bovine upper leather.

1. Introduction

As a response to the growing concerns about a variety of environmental issues expressed by public opinion and political bodies, the leather industry needs to improve the global sustainability of the tanning process. Among the several phases of the manufacturing process of hides, the beamhouse is responsible for most of the overall impact (76 %), as it generates 83 % of BOD_5, 73 % of COD, 60 % of suspended solids and 68% of salinity (Vuillermet and Aloy, 1977). This is because the traditional unhairing process requires sodium sulphide, and lime in the beamhouse phase. Besides, the fleshing operation that follows the unhairing phase, generates a waste (mainly constituted by collagen) whose reutilization and valorisation, as a valuable protein source, may be precluded by the presence of sulphides. Consequently, the development of an alternative unhairing process, with an environmental impact lower than the traditional one, represents a priority. Prerequisites of any alternative unhairing process are that it must impart to the treated hides at least equivalent properties to those of the traditional, allow the production of a versatile basis for different types of finished product, and the process must be practical, economical to implement as well as compatible with the existing machinery.
In the present work, an unhairing process in drum by hydrogen peroxide, named DEPOXO, was developed for the production of high-quality bovine upper leather. A preliminary investigation at laboratory scale has allowed to set out the optimal process conditions, in terms of H_2O_2 dosage, and pH. The following pilot-scaled runs have assessed the industrial feasibility of the process that allows the production of a versatile base for different final applications of the leather (either chrome or vegetable tanned).
The evident advantages are obviously related to the elimination of the use of sulphides. The consequence is a drastic reduction of the polluting load of the effluents and a significant simplification of the downstream wastewater treatment plants, but, mainly, a impressive improvement of the health and safety of working

Please cite this article as: Puccini M., Seggiani M., Castiello D., Vitolo S., 2014, Depoxo process: technical and environmental study of hide oxidative unhairing, Chemical Engineering Transactions, 36, 193-198 DOI: 10.3303/CET1436033

places by the complete elimination of the likely hazardous event that is the release of hydrogen sulfide gas in the working environment and consequent fatalities or major injuries.
Given the technical feasibility of the oxidative unhairing process, the environmental impacts due to the oxidative unhairing were assessed and compared to the conventional one, according to the Life Cycle Assessment (LCA) methodology. The LCA methodology, described in details by the ISO 14000 series, allows the assessment of the environmental impacts due to products, processes, or services, by the identification of the input (e.g. energy and material consumption) and output (e.g. waste and pollutant production) streams exchanged by the process with the environment (i.e. from raw materials procurement to waste streams disposal). LCA could be used in several contexts. These include use in process design (Mayumi et al., 2010) for comparison (Wibul et al., 2012) and selection of options (Puccini et al., 2013); in business planning for identifying weak links in a processing chain or in comparing processes with those of business competitor; at the research and development phase of a process (Nucci et al., 2013), in guiding process evolution (Puccini et al., 2014).

2. DEPOXO process

2.1 Experimental procedures

The hide samples were supplied by tanneries belonging to the Tuscany (Italy) industrial leather district. The laboratory scale oxidative unhairing tests were conducted on pieces (15x20 cm, average weight 150 g) cut from the butt of heavy cattle skins (32+ kg) supplied by Conceria Volpi S.p.A. tannery. The process runs were conducted in cylindrical stainless steel laboratory drums (35 cm diameter, 20 cm length) rotating in a temperature controlled bath. The effect of the process parameters on the performance of the unhairing process was evaluated by visual observation of the skins (loss of hair, swelling, quality of the grain), and by quantification of the swelling as weight percent increase of the sample. The pilot-scale runs were conducted on medium calfskins (8 - 12 kg) furnished by UPIMAR tannery. The process runs were conducted in a polypropylene-coated pilot-scale drum (1 m diameter, 50 cm length). The industrial-scale runs were conducted on heavy cattle skins (32+ kg) supplied by Conceria Tempesti S.p.A. tannery. In both experimental runs, after soaking (i.e. preparatory operation for tanning) the hides were divided in two sides: a few sides were unhaired and limed traditionally, the corresponding sides were submitted to the oxidative unhairing. After unhairing, the hides followed the traditional pickling/chrome tannage/dyeing-fatliquoring phases currently used to produce upper leathers.
The crust leathers obtained were characterized by their main mechanical properties. Physical tests were conducted according to Italian standards (UNI 10594) for upper leather. The load at tear was determined according to the UNI EN ISO 3377:2 method using an electronic dynamometer (Model Marte, Pegasil®, Zipor, Portugal). The extension at grain crack was determined according to the UNI 11308 method using a lastometer Pegasil® (Mod. EL-51E). The shrinkage temperature was determined according to the UNI-ISO 3380 method using a Giuliani IG/TG/Theiss apparatus. The data reported are the mean of three determinations.

2.2 DEPOXO process development

In the traditional hair destruction (burning) process, breaking down of the -S-S- bonds that characterize the keratin structure of the hair, is obtained by the use of a reducing agent (sodium sulfide or sulfhydrate), accompanied by the use of an alkali to hydrolyse the –SH groups of the reduced proteins and promote their subsequent solubilization. Traditionally, the alkaline hydrolysis is accomplished by the use of lime. A phenomenon named hair immunization can occur due to the application of excessive lime prior to the application of the sulfide. Immunization occurred when the hide was previously treated with calcium hydroxide for a prolonged time, but was not observed when using sodium hydroxide (Castiello et al., 2007). When using H_2O_2 for unhairing, the chemical attack of the –S-S- bond is due to the formation of peroxy anion from H_2O_2 that occurs in highly alkaline medium. The attack of the –S-S- bond by H_2O_2 appears milder and slower in comparison with the reducing agents; H_2O_2 is in fact effective in breaking only the softer keratin present in the root of the hair, while it leaves intact the stronger keratin of the shaft. For this reasons, the use of lime as alkaline agent is not feasible because the immunization process would prevent the desired –S-S- breaking of the hair root proteins. The use of NaOH instead of $Ca(OH)_2$ is however accompanied by a higher degree of swelling of the collagenic structure. The control of the swelling of the hides during the oxidative unhairing, by controlling the pH of the bath, represents a determining factor to obtain a final leather characterized by physical-mechanical properties comparable to those of traditional unhaired leather.

Table 1: pH effect of the oxidative unhairing baths on the unhairing and swelling degree of the hides (offers: 6 wt.% of H_2O_2 based on salted weight).

pH	Unhairing degree	% Swelling
11	ξ	24.6
11.5	ξ	37.6
12	√	52.6
12.5	√	42.4
13	√	39.8

ξ: not satisfactory; √ : good

Table 2: Physical-mechanical properties of the crust leather obtained on pilot scale.

Test	Oxidative unhaired crust leather	Sulfides unhaired crust leather	UNI 10594 guidelines
Tearing load (N) – UNI EN ISO 3377:2 method	58±2	55±2	≥ 50
Grain distension (mm) - UNI 11308 method	9.1±0.2	7.5±0.2	≥ 7
Shrinkage temperature (°C)	99±1	97±1	

A preliminary investigation at laboratory scale has allowed to set out the optimal process conditions, in terms of H_2O_2 dosage and pH, in order to achieve an effective unhairing and a compatible swelling of the hide. As reported in Table 1, unhairing does not occur at pH values below 12, while the swelling degree shows a maximum at pH close to 12. At pH 11-12 an increase of the swelling degree may be explained by the hydrolysis of the carboxylic groups with formation of Na-collagenate and the gradual decrease of the hydrogen inter-fibrillar bondings. The maximum swelling degree at pH 12 may be attributed to the complete hydrolysis. If pH is further increased above 12, the concentration of NaOH in the bath increases and, by osmotic effect, an increasing amount of water is rejected outside the hide, thus explaining the decrease of swelling. These results suggest an operative pH range of 12.5 - 13 as the optimal to conduct the oxidative unhairing. Preliminary runs were also conducted to set out the optimal H_2O_2 dosage, at pH 12.5, by varying the H_2O_2 amount in the range 4.5 - 12 % (on salted hides weight). The experimental results show that an effective unhairing is obtained by using dosages starting from 6 % (on salted hides weight). It must be noted that increasing the dosage of H_2O_2 a higher quantity of NaOH must be dosed to obtain the same pH value. As a result, a slightly higher swelling degree was observed.

The following pilot-scaled runs have assessed the industrial feasibility of the process that allows the production of a versatile base for different final applications of the leather (either chrome or vegetable tanned), and appear practical to implement. The runs were conducted by using the H_2O_2 dosage of 9 % at pH 12.5. The finished leather obtained by the innovative unhairing process showed good physical-mechanical and technical properties comparable with those obtained by the traditional process, and the leather was technically assessed as satisfactory and suitable according to the market request (Table 2).

Finally the industrial runs confirmed the results obtained on pilot scale. The final leather obtained by the novel unhairing process showed good physical-mechanical and technical properties, comparable with those of the traditional, and the leathers were assessed as satisfactory and suitable for their use in the production of high quality upper leathers. Besides, by the oxidative unhairing, the production of a versatile basis for different types of finite products is allowed.

From the experimental investigations on pilot and industrial scale, unhairing by H_2O_2 appears a feasible process, from the technical point of view, to produce high quality bovine upper leathers. The results indicate a dosage of 9% H_2O_2 is the optimal to assure complete unhairing and minimum swelling as well.

Besides, the process is practical, and economical to implement since it is compatible with the existing machinery in tanneries, and the costs of the unhairing phase is comparable with the conventional one (about 7.15 € versus 7.30 per 100 kg of salted hides).

3. LCA analysis

Given the technical feasibility of the DEPOXO process, the novel unhairing procedure was compared to the conventional one from an environmental point of view. The study was performed using a methodological framework based on the International Organization for Standardization (ISO) recommendations (UNI EN ISO 14040 and 14044). The structure of an LCA study is composed of four sequential steps: (1) goal and scope definition; (2) inventory analysis (LCI); (3) impact assessment (LCIA); (4) interpretation, with the discussion of the results and the outcomes of the study.

3.1 Goal and scope definition

Since the objective of the present work consists in an environmental comparison of two alternative processes, LCA have been accomplished in relative terms using a third order approach, and considering only inputs and outputs that change with the alternative. As far as the traditional process is concerned, the unhairing phase requires a system to eliminate H_2S generated during the processing. This step is completely eliminated through the adoption of the oxidative process that uses oxygen peroxide instead of sodium sulfide. The extension of the study (i.e. the system boundaries) includes the production of chemicals used for the unhairing processes, according to the main principles of LCA.

One kg of salted hides was selected as functional unit, i.e. the reference unit to which the inputs and outputs are related.

3.2 Inventory analysis and impact assessment

Input flows and emissions for modeling the processes were collected directly on the field, and are listed in Table 3 (the amount of each pollutant is evaluated per functional unit).

Inventory data for the background system (production of chemicals, electricity, lorry transport, etc.) were based on average technology data from the Ecoinvent 2.2 and Buwal databases, both included in the library of the software Simapro 7.3, which has been used to develop the LCA model.

In order to evaluate the environmental impact of both processes, taking into account the effect on the ecosystem and on the human health, the following impact categories have been considered: (i) global warning, (ii) ozone depletion, (iii) acidification, (iv) eutrophication, (v) photochemical smog, (vi) eco-toxicity water chronic, (vii) eco-toxicity water acute, (viii) eco-toxicity soil chronic, (ix) human toxicity air, (x) human toxicity water, (xi) human toxicity soil, (xii) bulk waste, (xiii) hazardous waste, (xiv) radioactive waste, (xv) slag and ashes, (xvi) non renewable resources. For evaluating contributions to each environmental issue of concern, EDIP 97 impact assessment methodology was used, as this method provides a satisfactory matching between the chemicals included in the LCI of the unhairing processes and the parameters for which EDIP 97 supplies an equivalence factor. The only inconvenient was that, unfortunately, EDIP 97 in its standard way, does not take into account COD as parameters affecting the eutrophication impact category. However, COD is one of the main parameter used to characterize wastewaters of a chemical process, as the one here considered. To fulfil these requirements, a specific equivalence factor was computed in order to express the environmental load of COD in relation to the reference parameter (i.e. nitrates). The equivalence factor was evaluated in 0.23 point, making an interpolation of all parameters that characterize the eutrophication impact category in EDIP 97 and CML 2 impact assessment methodologies.

3.3 LCA results

Results of the impact assessment step are graphically shown in Figure 1. The bar chart shows the relative contribution of the inputs of the traditional unhairing process to each environmental impact category. It is evident that the life cycle of Na_2S accounts for most of the whole environmental impact. Therefore the elimination of Na_2S from the unhairing process appears to be necessary to reduce the environmental impact. Please note that the environmental impact of Na_2S is due to the sulfides released in the wastewaters and also to its productive process.

Figure 2 shows, in relative term, which one of the alternative processes has the greatest impact for each impact category. Take for instance the photochemical smog category. In this case, the oxidative process has an impact 0.9 times lower than the traditional one. As it can be seen, the oxidative unhairing has an environmental impact greater than the traditional one in several impact categories. This is due to the production of oxygen peroxide that accounts for more than the 50 % of the overall environmental impact.

For a fair assessment of results, data must be normalized to express their actual magnitude in relation to a known reference value that is the equivalent impact per person (i.e. the average annual impact generated by the ordinary activities performed by an individual). Normalized data are listed in Table 4.

As shown in Table 4, the impacts categories most significantly affected are “Ecotoxicity water chronic” and “Ecotoxicity water acute”. It is also evident that the adoption of the oxidative process makes it possible to greatly reduce impact in both these environmental impact categories. As far as the other categories are concerned, even if several impacts of the oxidative unhairing are greater than the traditional one, their normalized magnitudes may be considered not significant in terms of effects on the ecosystem and on the human health.

Table 3: Input – Output of the unhairing processes

		Oxidative unhairing	Traditional unhairing
Input	Na_2S	0 [kg]	0.049 [kg]
	$Ca(OH)_2$	0 [kg]	0.04 [kg]
	NaOH (50%)	0.096 [kg]	0 [kg]
	H_2O_2	0.09 [kg]	0 [kg]
Output	COD	0.86 [kg]	1.06 [kg]
	suspended solids	0.59 [kg]	0.60 [kg]
	Nitrogen (as NH_4^+)	0.008 [kg]	0.006 [kg]
	Sulfides (as S^{2-})	0 [kg]	0.046 [kg]

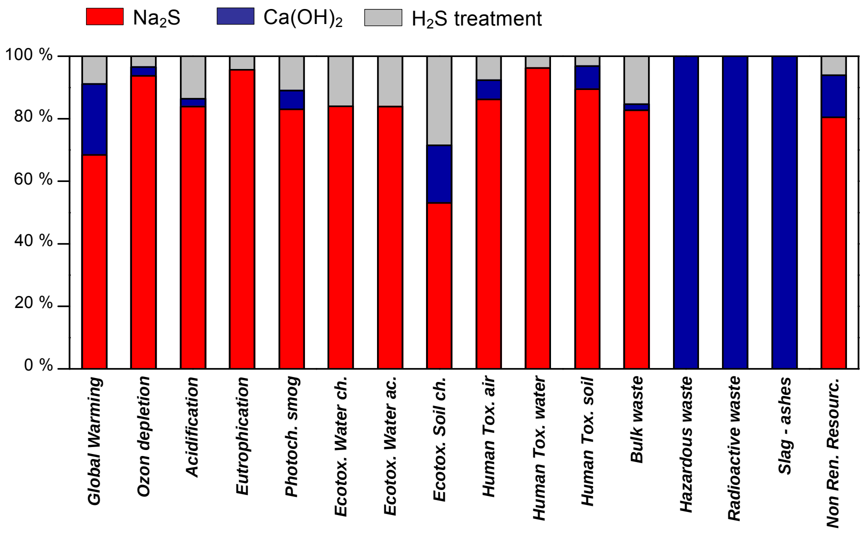

Figure 1: Contribution of the inputs of the traditional unhairing process to each impact category.

4. Conclusions

The oxidative unhairing by hydrogen peroxide to produce high-quality bovine upper leather was first investigated on laboratory scale and validated on pilot and industrial scale. The experimental runs indicate a dosage of 9 % H_2O_2, at pH 12.5, is the optimal to assure complete unhairing and minimum swelling.

The results of the study assess the industrial feasibility of this innovative process, that allows the production of a versatile base for different types of finished products. The finished leathers are comparable to that obtained by the traditional unhairing by sulfides and are characterized by good physical-mechanical and technical properties. The process is practical, economical to implement as well as compatible with the existing machinery. The elimination of sulfides from the beamhouse operations represents a significant improvement of the health and safety of working places by the complete elimination of the likely hazardous event that is the release of hydrogen sulfide gas in the working environment and consequent fatalities or major injuries.

To assess the environmental sustainability of the novel procedure, LCA was used to compare the traditional and the oxidative unhairing process. The life cycle model for both processes has been implemented using the software SimaPro 7.3. Results show that "Ecotoxicity water chronic" and "Ecotoxicity water acute" are the most affected impact categories, and that damages on both these impact categories are greatly reduced through the adoption or the oxidative unhairing process.

At the moment, the process has been investigated leaving the wastewaters treatment out of the boundaries of the system. Considering the obtained results, which reveal that the main impact affect the water's pollution, it seems desirable to extend the systems boundaries to include in the analysis the treatment of the wastewaters too. Further researches are intended to the scope.

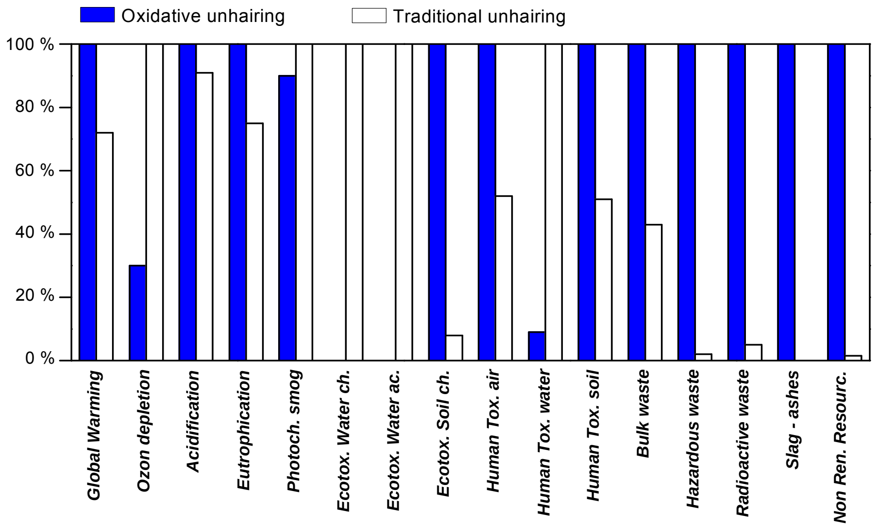

Figure 2: Comparison of the environmental impact associated with the two unhairing process.

Table 4: Normalized results per impact category

Impact Category	Oxidative unhairing	Traditional unhairing
Global warming	1,96E-05	1,43E-05
Ozone depletion	1,08E-07	3,65E-07
Acidification	9,73E-06	8,80E-06
Eutrophication	9,32E-03	6,90E-03
Photochemical smog	7,12E-06	7,69E-06
Eco-toxicity water chronic	3,73E-04	7,00E+01
Eco-toxicity water acute	3,68E-04	3,36E+02
Eco-toxicity soil chronic	6,11E-05	4,34E-06
Human toxicity air	2,46E-06	1,29E-06
Human toxicity water	3,11E-05	3,49E-04
Human toxicity soil	4,77E-05	2,44E-05
Bulk waste	7,91E-06	3,44E-06
Hazardous waste	1,68E-07	1,43E-09
Radioactive waste	1,27E-04	4,78E-06
Slag/ashes	4,38E-06	7,01E-10
Non Renewable Resources	1,00E-08	1,00E-08

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