Environment Protection Engineering

Vol. 14 1988 No. 2

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TANNERY AND POLLUTION CONTROL: A NEW PROCESS FOR SKIN DEGREASING USING 1,1,2-TRICHLORO 1,2,2-TRIFLUOROETHAN. A CLEAN TECHNIQUE

A new degreasing process is proposed for the leather industry [1] and more particulary for fellmongery (small skin processing). It can solve both a precise technical problem (effeciency in degreasing pickled skins) and an important water pollution problem due to techniques used up to now.

This new process proposed here deals with pollution while it originates and not afterwards. Effluents are completely eliminated at degreasing stage.

1. INTRODUCTION

Future development of leather industry, and more particulary of tannery, depends on the improvements of manufacturing techniques. Quality leathers will be then marketed due to these techniques.

On the other hand, laws concerning waste water are becoming more and more drastic and during leather processing the impact of tannery discharges on the environment must be taken into account.

The new process proposed here deals with skin degreasing, an important stage in the leather manufacture on which depends the quality of the final products.

2. THE DEGREASING STAGE IN LEATHER PROCESSING

Tannery manufacturing consists in the transformation of hides (sheep, goats, pigs) in leather owing to various physical and chemical operations.

Skin degreasing must take place before tanning. At this stage, most skins are pickled. Pickling is a process in which hides are acidified in order to make it possible:

the penetration of tanning material,

skin preservation and storage,

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an easier degreasing through the decomposition of protoplasmic membranes of cellular fats.

The hides contain a fairly high percentage of water (about 65%). Skin degreasing is not a very easy operation in itself. We must keep in mind the conditions that must be fulfilled in order to obtain a good quality leather [2], [3], i.e.:

1. Removal of natural fat in excess. Fats must be uniformly dispersed. Some parts of a hide have a high percentage of fatty substances (neck, backbone) and other parts have not (bellies).

2. Not complete removal of fats (the skin would then be of irremediably bad quality).

3. Adequate elimination of all fatty substances; fats are composed of a mixture of chemicals, i.e., glycerides, phospholipides, waxes, sterols, free fatty acids. The presence of fatty acids in the hides can cause the formation of fatty spews on the final product which will be of bad quality.

4. The operation must take place at normal or not very high temperatures consistent with the heat resistance of hides before tanning.

5. The operation must be compatible with later treatments (tanning, dyeing).

2.1. TRADITIONAL DEGREASING PROCESS

Many papers are dealing with degreasing techniques, especially of pickled skins. Main degreasing processes, their advantages and drawbacks are presented in tab. 1.

Table 1

Different techniques for degreasing pickled skins

Degreasing process	References	Principle	Advantages	Drawbacks
Aqueous phase and surface active agents	[2], [4]–[7]	Fats are emulsified with cationic or preferably nonionic surface active agents in bath of water and salt (NaCl)	No organic solvent in waste waters	Not efficient for skins with high percentage of fats. Effluents (pollutant loads). Quantity of water in relation to weight of pickled skins is at least 250%
Aqueous phase and surface active agent and organic solvent	[2], [5], [8]–[10]	The principle is the same as above but an organic solvent (petroleum, white spirit, perchloroethylene) is added to increase solubility of fats	Degreasing is usually efficient	Sometimes for very fatty hides two degreasing stages are needed. Solvent is present in hides (influence on tanning). Effluents (pollutant loads)
Enzymatic process	[11]–[13]	Hydrolysis of fats by a lipase	No organic solvent in waste waters	Difficult to realize actually. Skins are often of poor quality. Effluents (polutant loads)

Degreasing in aqueous phase in the presence of a surface active agent and a solvent (light petroleum rich in hexane) is the method mostly used in industry at the moment.

Drying the skins cannot be realized at this stage of manufacturing: drying is expensive, requires a lot of energy and furthermore skins can be damaged because of cristallization of salts.

A single stage is not generally sufficient to obtain high efficiency. The solvent in which fats are dissolved is extracted from skins by several rinsing operations.

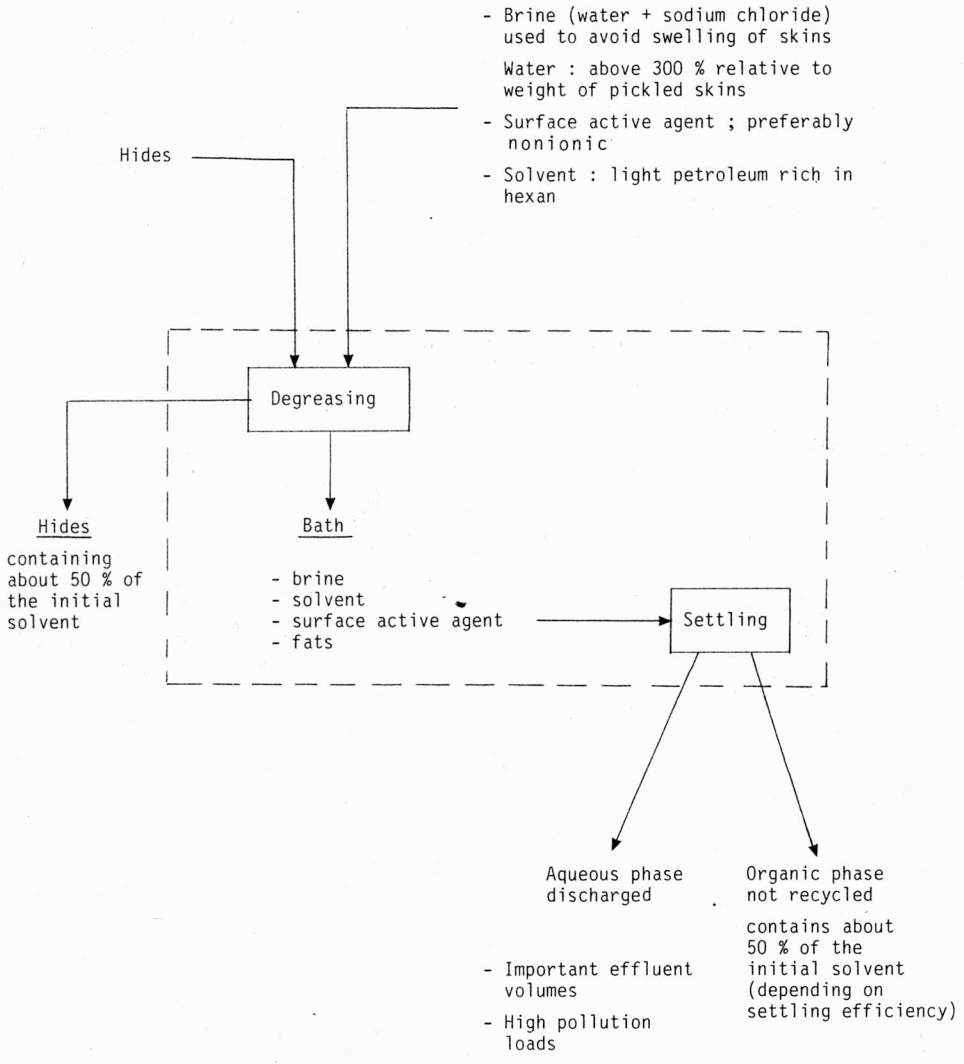

Fig. 1. Diagram of traditional degreasing process

The recovery is not complete since about 50% of the solvent is absorbed by skins. All the residual baths are settled (settling is not complete) after which the aqueous phase is discharged. The organic phase cannot be used again. It contains 25 to 50% of the initial solvent. A diagram of this operation is presented in fig. 1.

2.2. NEW PROCESS PROPOSED

This new proces [1] deals with pollution while it originates and not afterwards. It is a clean technology. Because of its properties and especially its low superficial tension and its high degreasing capacity, the solvent, i.e., 1,1,2-trichloro 1,2,2-trifluoroethan, is efficient for wet pickled skins without any surface active agent.

No rinsing operation is required and, consequently, both consumption and discharge of water can be avoided. The solvent is easily regenerated by distillation and can be used for many operations. Moreover, the residual bath can be reused for several degreasing stages without regeneration.

Furthermore extracted fatty substances, considered up to now as waste, can be utilized:

1. By direct marketing (lubricants industry, surfactants, cosmetology and so on).
2. In a much more original and interesting economical way for the stage of fat liquoring. Fats are then used in the leather industry itself.

Two stages are involved in this process:

a degreasing stage itself,

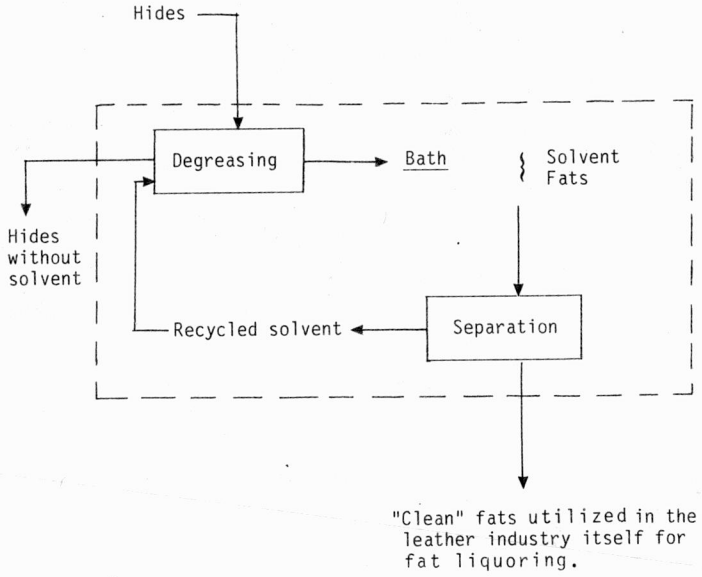

Fig. 2. Diagram of a new clean degreasing process

a complementary recovery of the solvent absorbed by the skins. Skins are free from solvent at the end of the operation. Degreasing takes place at atmospheric pressure and at room temperature in the presence of 2 to 5 dm^3 of solvent per 10 kg of pickled skins (for example). The study and knowledge of operating parameters permits the control of this process.

Many tests (laboratory and on pilote scale) lead to the conclusion that the quality of the obtained skins is good and slightly better than those obtained in the traditional process (slightly brighter colours). This operation is then perfectly consistent with the subsequent treatment of the skins (tanning, dyeing). A diagram describes this process in fig. 2.

3. POLLUTION BALANCE

A few examples of pollution balance are shown in tab. 2. They are representative of effluents in fellmongery. On the basis of these results the following conclusions can be drawn:

high values of parameters show a high pollutant load,

the effluent volume is important in relation to the weight of pickled skins.

Table 2

Pollution parameters of degreasing baths (traditional process)

		BOD_5 mg/dm^3	COD mg/dm^3	pH	SS mg/dm^3	Quantity of water in relation to weight of pickled skins %
(1)	Mixture	not measurable	100–120000	2.3	20000	200–400
	Aqueous phase		30–40000	2.3	–	
	Solvent phase		78–80000	2.6	–	
(2)	Mixture	not measurable	45–60000	2.3	8800	250–1300
	Aqueous phase		15000	2.2	–	
	Solvent phase		300000	2.6	12500	
(3)	Mixture	not measurable	193000	–	5000	250
	Aqueous phase	2300	4700–6700	–	2000	

(1) and (2): examples found in the literature [5], [15].
(3): example given by the Agence de Bassin Adour – Garonne.

The volume of waste waters discharged is at least of 1600 m^3 per 600 tons of pickled skins.

Pollutant loads per day are given in tab. 3 (for a particular plant where the industrial prototype is located). These results concern the lower aqueous phase of

Table 3

Pollutant loads per day in the case of particular plant

Parameters		Traditional process	Clean technology
Effluent volume	(m^3/day)	7.3	No waste waters
SS	(kg/day)	14.6	
COD	(kg/day)	33	
BOD_5	(kg/day)	14.6	
pH		~2.2	
Equitox/day		~124.1	

Given for a production of 60000 dozens of pickled skins per year.

settled effluents. Therefore minimum values are given in the table. Furthermore, COD values can be significantly higher if the recovery of baths is not correctly done. The interest of such a new process is obvious and allows us to define this technique as a clean technology.

It must be mentioned that the main advantages of this process are relative to the pollution aspect and waste utilization, i.e.,

1. The complete elimination of aqueous effluents and then the complete purification (no more brine discharge, no more surface active agent and no more corresponding taxes).

2. In this process, operating conditions do not induce another form of pollution.

3. Natural fats, considered up to now as a waste, are utilized and then used in the industrial plant in another operation of leather processing (fat liquoring).

4. The solvent is safe and the main advantages during its industrial use can be defined as follows: it is fireproof, it cannot explode and is considered one of the less toxic among commonly used solvents (average exposition value, 1000 ppm, identical to that of ethanol).

4. CONCLUSIONS

1. It must be said that the main advantage of the method consists in solving both a precise technical problem and an important waste water problem in the idea of the process itself.

2. Effluents are completely eliminated at degreasing stage.

3. Fats that were considered up to now a waste are utilized.

4. The economical advantage of the process is obvious as the high cost of investment can be repaid in the period shorter than two years.

ACKNOWLEDGMENT

This work was financed by:

"Chambres Syndicales des Patrons Mégissiers de Graulhet–Mazamet et de l'Industrie du Cuir de Mazamet".

"Ministère de l' Environement" and particularly by "Service des Technologies Propres".

The study was conducted in collaboration with:

SOCOP Tannery in Graulhet.

Ets Julie Frères, Mechanical construction plant in Graulhet.

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GARBARNIE A OCHRONA ŚRODOWISKA: NOWA BEZODPADOWA TECHNOLOGIA ODTŁUSZCZANIA SKÓR Z ZASTOSOWANIEM 1,1,2-TRÓJCHLORO 1,2,2-TRÓJFLUORETANU

Zaproponowano nową technologię odtłuszczania skór w przemyśle skórzanym, w szczególności podczas procesu obróbki skór surowych. W porównaniu z metodami stosowanymi dotychczas zaproponowana technologia rozwiązuje zarówno problemy techniczne (zwiększenie efektywności odtłuszczania piklowanych skór), jak i zanieczyszczania wód. Ścieki są całkowicie eliminowane już w czasie procesu odtłuszczania.

КОЖЕВЕННЫЕ ЗАВОДЫ И ОХРАНА СРЕДЫ: НОВАЯ БЕЗОТБРОСНАЯ ТЕХНОЛОГИЯ ОБЕЗЖИРИВАНИЯ КОЖ С ПРИМЕНЕНИЕМ 1,1,2-ТРИХЛОР 1,2,2-ТРИФТОРЭТАНА

Предложена новая технология обезжиривания кож в кожевенной промышленности, особенно во время процесса обработки сырых кож. По сравнению с применяемыми до сих пор методами, предлагаемая технология решает как технические проблемы (повышение эффективности обезжиривания соленых кож), так и проблемы загрязнения вод. Сточные воды полностью исключаются уже во время процесса обезжиривания.