

## **LAYMAN'S REPORT**

Actual project is based on the aqueous degreasing of sheepskins through the replacement of ethoxylated nonylphenol by biodegradable ethoxylated alcohols and further recycling.

Several companies of the leather sector have been involved in the development of the whole project:

- Cognis Iberia: manufacturer of chemicals for the leather industry
- Hellenic Tanneries: belongs the Colomer Group and are specialised on sheepskins and goatskins production.
- Curtidos Gregori: company specialised on sheepskins production.
- AIICA: Spanish leather technology centre that provides quality services to the leather sector. It is the project co-ordinator and beneficiary.

Main objectives to obtain in the project can be schematised into five points that are:

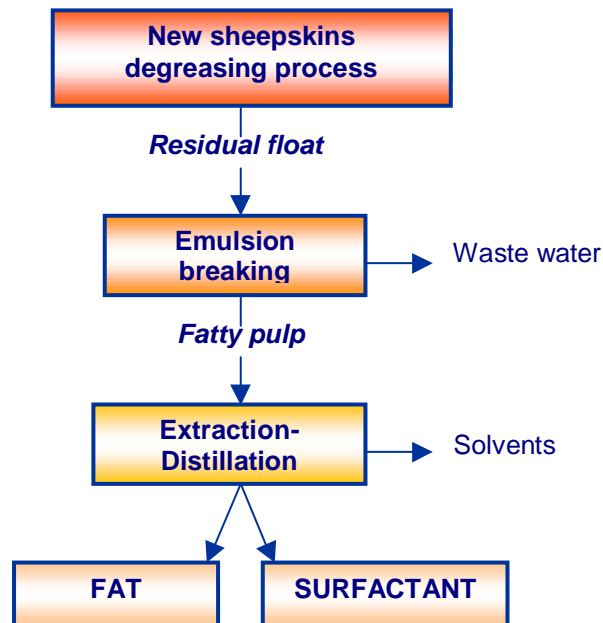
- The industrial implementation of a sheepskin degreasing process replacing ethoxylated nonylphenol.
- The recovered surfactant recycling for sheepskins degreasing
- The reduction of waste water pollution and the generation of solid wastes.
- The fat revalorisation as an industrial by-product.
- And the demonstration and dissemination of the results of the project to the leather industry, to other related industrial sectors and to the general public.

To achieve these objectives, work project has been separated into five tasks:

The three first tasks made the experimental and technical part of the project:

- Degreasing process evaluation (task 2106)
- Prototype build-up (task 2462)
- Industrial process implementation (task 2521)

Technical part of the project can be summarised by means of the following schema, as introduction.



A new sheepskin degreasing process was implemented, using a new biodegradable surfactant. Following, experimental plant for the emulsion breaking of degreasing residual float was designed. A fatty pulp, composed by surfactant, fat, part of water and salts, was separated. Waste water was also separated. Finally, an extraction - distillation prototype was build-up. Through an extraction of the fatty pulp obtained with solvents, surfactant and fat were recovered.

The two remaining tasks, also important, consisted of:

- Management and information to the EC, periodically (task 2524)
- Dissemination of the obtained results through different ways to the general public and specially to the leather sector (task 2525)

The first task (task 2106) consisted of the degreasing process evaluation. And, what is degreasing process? Consists on sheepskins natural fat removal in order to avoid irregular accumulations of it, that is incompatible for the high quality articles manufacturing. At present, degreasing process is carried out by the use of biodegradable surfactants, normally nonylphenol. The objective of this task was the replacement of ethoxylated nonylphenols currently used by ethoxylated alyphatic alcohols, due to the need to replace nonylphenols, that have been included in the list of Priority Substances under the Water framework Directive. Another objective was to establish a protocol for the suitable surfactant recovery.



As result, the satisfactory nonylphenol substitution was obtained with a good degreasing process efficiency, avoiding a lot of modifications in the degreasing process that apply every company. Method for the surfactant recovery based on a previous emulsion breaking and a subsequent surfactant extraction through the use of solvents was also established.

Second task (task 2462) consisted of design and build-up of surfactant recovery prototype. Both emulsion breaking prototype and extraction-distillation prototype were designed and build-up.



Prototype for emulsion breaking of degreasing residual floats was basically made of a tank provided of heater and agitator systems.

Extraction-distillation prototype consists of a reactor and a distillator. On the left, reactor to do the extraction process is located. Reactor is provided of heater and agitator systems, although the first one is not necessary in our case because the extraction process is carried out at room temperature. On the right, distillator is located, it is provided of a conventional system and also a vacuum distillation system.



Once prototypes build-up, following task was the industrial process implementation (task 2521) The objectives were the industrial sheepskins degreasing using the new surfactant, the surfactant recovery from the residual floats by the use of the prototypes build-up and finally, the re-use of the recovered surfactant for new degreasing processes.

Emulsion breaking process consisted of heat the fatty emulsion (water from the degreasing float) at 90°C during 2h with a discontinuous shaking. Rest during 6-8 hours for the following decantation of the two-formed phases. Lower phase composed by water and salts was discharged to the treatment plant. The top phase composed by fat, surfactant, part of water and salts was recovered.

Surfactant and fat were recovered by extraction process with heptane and ethanol and following solvents distillation. Fatty pulp, heptane and ethanol were added into a tank with an agitator system. The ratio fat:solvent was 1:3 in both solvents, previous adjustment of the mix water (30%). This mix was shaken at room temperature for 2 hours. After 4-6 hours of rest, the two phases formed were separated and recuperated. Lower phase, hydroalcoholic, contained the surfactant and the top phase, heptanic, contained the fat. Through a conventional distillation system, that also allows a vacuum distillation, solvents were recovered and the fat and surfactant were separated.

Recovering efficiency depended on the type of ethoxylated alyphatic alcohol used. A surfactant with a very high degreasing power (low HLB) presents less recovery efficiency applying the same extraction protocol. From the three surfactants studied at industrial scale, the best recovering degree was the obtained with Surfactant 2 that is around 75%. The remainder surfactant not recovered was contaminating the separated fat.

The surfactants recovered were used in the industrial production of sheepskin leathers applying the new degreasing process. They were applied mixed with 25% of fresh surfactant, obtaining a degreasing process efficiency around 90% and residual fat contents on leather lower than 1% over dry weight, that is a effective degreasing comparable with the conventional ones.

The waste water pollution was reduced applying the new recovered and recycled process, obtaining drops on COD values of 90-94%.Solid waster generation was also avoided saving energy and costs involved with its incineration process. On the other had, it was the possibility of fat valorisation as raw material for the potential manufacturing of fatliquoring products to the leather sector, calcic soaps (mechanical lubricants) and detergent soaps, although this is a subject that need of an exhaustive study. Therefore, new process is evaluated as environmentally viable, while it is not possible to do an economical balance of the whole process due to the lack of information, because it directly depends on is the design of the recovering equipment at industrial level that is linked with the size and productivity of each tannery, therefore it is necessary to do a personalised study. Moreover, it exists the possibility to study the viability to build-up a common facility that will undertake the emulsion breaking and surfactant recovery process for all the companies located at the area, avoiding thus the individual investment of each company and improving the tanneries competitiveness.

Concluding, we have an open way for the whole replacement of nonylphenols by alyphatic ethoxylated alcohols and a suitable surfactant recovery. However, each one of the alyphatic ethoxylated alcohols has distinct behaviour, which means that the extraction process is not generic and must be adjusted for each type of surfactant.