



In 2014, two of the biggest tanners in the Arzignano cluster, Gruppo Dani and Gruppo Mastrotto, formally launched a joint project called Green Leather Industry for the Environment (greenLIFE), on which they have worked with three technical partners: chemical supplier Ikem, biotechnology firm Ilsa and the cluster's wastewater treatment service provider, Acque del Chiampo. It has the aim of promoting sustainability in the tanning industry. Half of the funding for greenLIFE came from the European Union, which has asked the project partners to share their findings with the wider leather industry. The partners have picked World Leather as the ideal platform on which to publish the results of greenLIFE. This paper, the first of six World Leather will publish in the course of 2017, kicks the series off.

greenLIFE 1: Oxidative liming

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greenLIFE overview

The greenLIFE project has set out to develop a new oxidative liming and bath reuse and new enzymatic liming and chrome-free tanning processes. In addition, the project partners aim to improve the collection and reuse of hide and leather by-products in the industrial, agricultural and energy sectors, and evaluate the impact on wastewater treatment of the new technologies and analyse their wider environmental and socio-economic impacts.

Its main goals are to achieve a 20% reduction in water consumption and in the chemicals used at the beamhouse stage, a 20% reduction in solid waste, a large reduction in sulfides at the hair-removal stage, 15% recovery and reuse of by-products with industrial value, and the creation of a new knowledge hub to share ideas and technologies.

Started in 2014, the project is due to end in May 2017, and has required €2.3 million in investment, with half the amount financed by the EU through its LIFE Programme, a wider financial plan to support environmental, conservation and climate action projects.

GreenLIFE is sponsored by five Italian companies based in the Vicenza tanning cluster, including rival companies that have, nevertheless, worked closely together on this. These five partners will use this new series of papers in *World Leather* to share the main results of the research activities they have carried out over the last three years.

1. Gruppo Dani research Project aims

Development of oxidative hair removal, by using water hydrogen, and the subsequent reuse and treatments of the liming baths, with the following aims:

- Reduction of polluting load in the tannery wastewater, in terms of reduction of sulfides and sulfates
- Recovery and reuse of non-sulfide contaminated by-products
- Reduction in use of water consumption and chemicals during the liming phase
- Production of finished leather of good quality and free of odours
- Adoption of a technical and plant set-up similar to the present, with timeline processes comparable to the actual ones.

2. The utilised technology and plant design (PP drum)

For the experiments a drum made of polypropylene was used, a material that has a high chemical resistance to strong acids and hydrogen peroxide based solutions, which are the most widely used chemicals in oxidative liming.



It is also equipped with:

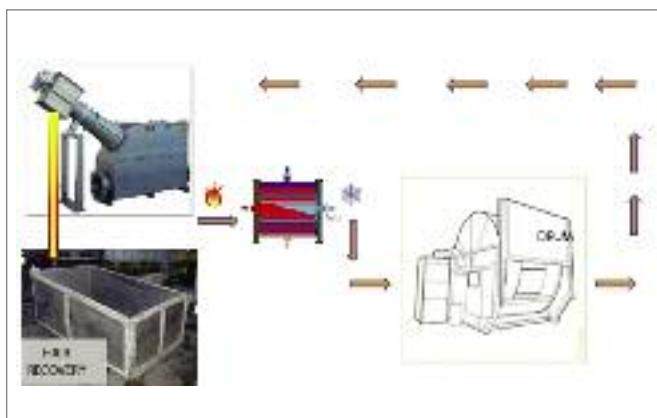
- a computerised system for the programming of automatic recipes and the automatic and gradual dosage of chemicals
- a recycling system that, at each rotation, conveys a determined quantity of bath in a side pan, which allows the measurement in real time of pH and temperature without stopping the machine; this pan is also used for the heating of the bath through a steam jet.
- two cooling systems, an external heat exchanger and an internal wall through which a liquid cooled by a chiller (internal cooling system) passes.

At each turn of the drum, the bath is collected in a side tank through internal channels and subsequently passes through a filter that serves to trap the hair; subsequently the bath goes through a heat exchanger that cools it and it is then pushed back inside the drum by a closing pump.

From now on, the main issues of the research programme will be briefly described and the main experimental results achieved will be presented.

3. The analysed variables for the development and optimisation of the recipe

In the course of the research we tested and evaluated several parameters that can be divided into two main categories:



Dani's research, as part of the greenLIFE project, included the development of a new hair-recovery system.

- chemical variables (use of new chemicals, changes in dose percentages)
- operational variables (change in rotation times, temperature variations during the various phases of the recipe).

Hides were evaluated visually by the team during the various stages of production, from raw to finished leather. During tests, important features were discussed such as washing the hide, smoothing out wrinkles, swelling and evaluation of semi-finished and finished leather.

The information has been used to refine the recipe and improve the quality of the finished product.

4. Hair-recovery system

Beside the new hair-removal technology, we have seen various hair-recovery methods, in order to separate and enhance keratins rich in protein content, little affected by the action of the depilatory oxidative mixture.

We first tested a grill master disc that has not been successful because the depilatory mixture affects the hair and makes it difficult to pass it to the outside of the grill master. Subsequently a 'filter-cochlea' was tested. It operated continuously during the course of the depilatory liming step; this type of machine combines both hair-screening and drainage.

Tests have shown that the structure of the filtered hair changes as liming proceeds; in the first hour the hair comes out well drained, while during the next hour of extraction, probably because of the prolonged attack by the oxidant mixture, the hair loses consistency and becomes a "pulp" that traditional machines can barely lift.

Even with this machine, after about two hours, it is not possible to extract hair because of excessive deterioration.

With the tested systems, the results obtained until now are insufficient when compared to the percentage of hair recovery that can be achieved by conventional liming.

5. Drum cooling system

The tests carried out in the course of the research have shown that the temperature of the bath during the liming phase is the most critical parameter as it affects both the speed of the reaction on the hide and the structure of the hide itself (we noticed an increased presence of swelling in the sides of the hides, which had undergone a temperature in the liming stage of between 30°C and 32°C).



In tests, Gruppo Dani found oxidative liming to give reduced odour, greater dyeing consistency and water-savings.

It is difficult to control the temperature with only the internal cooling system of the drum, in particular during the summer season, and it was necessary to use an external heat exchanger (installed downstream of the filter-cochlea) in particular in the first two hours of liming, the time in which the reaction develops its maximum exothermic rate.

As a result, the temperature inside the drum was easily lowered to the desired level, although we must not exaggerate cooling because we have also noticed that at a temperature below 27°C the kinetic reaction slows down and, in the usual processing times, hides obtained are less clean on average.

6. End-of-liming bath treatments

Downstream of the process, in order to separate as much solid material as possible, the end-of-liming baths were treated with a vertical centrifuge. The bath was discharged from the drum, transferred to a reservoir and treated with phosphoric acid (H_3PO_4) until the pH reached 4; subsequently this liquid was processed with the centrifuge to obtain a "clarified" bath and a semi-solid sludge.

6.1. Sludge resulting from centrifugation

The sludge obtained by centrifugation has been analysed to quantify the content of carbon, nitrogen and sulfates, which are the main parameters used to make an initial screening to see if the sample is potentially interesting from an agronomic point of view. The results are reported in *Table 1*.

The nitrogen and carbon values are interesting and this sample has been subjected to further studies and laboratory tests, which will be discussed in a subsequent article in this greenLIFE series.

Table 1: Nitrogen, carbon and sulphates in centrifuged sludge

	Total N (%)	Total C (%)	Total SO_3 (%)
Trial n°1	9.4	37.0	2.7
Trial n°2	8.3	38.9	2.0
Trial n°3	9.1	38.3	2.4

**Table 2: Results of different intermediate bath steps in liming process**

Parameter	Measure unit	Liming bath	After acidification bath	After centrifugation bath	Neutralisation bath
Chlorides	mg/L	16.700	11.620	11.905	9.745
Total sulfur	mg/L SO ₄	2.630	2.310	1.950	1.590
Total suspended solids	mg/L	22.915	26.035	1.655	1.205
Total nitrogen on filtrate	mg/L N	4.134	2.254	2.137	1.769
COD on filtrate	mg/L O ₂	46.750	20.240	17.205	20.280
TOC on filtrate	mg/L	16.083	6.756	6.649	5.687
Calcium	mg/L	355	1.536	1.537	18
Sodium	mg/L N	20.760	15.830	15.430	17.000
Total phosphorus on filtrate	mg/L P	183	11.080	11.380	6.708
Total phosphorus	mg/L O ₂	1.035	11.770	11.480	7.862

Table 3: Comparison traditional and oxidative liming

	Chlorides	Sulphates	Sulfides	Sulfur	TN	SST	COD	TOC	Ca	Na	Alkalinity	Total P	Total P on filtrate
	g	g	g	g	g N	g	g	g	g	g	g CaCO ₃	g	g
Conventional Liming	5.074	90	651	2.589	586	3.852	7.663	2.121	83	4.742	2.308	98	15
Oxidative Liming	5.009	139	0	458	555	4.675	6.933	2.290	38	5.061	2.446	87	43
Change	-1%	53%	-100%	-82%	-5%	21%	-10%	8%	-54%	7%	6%	-11%	187%

Table 4: Traditions vs. oxidative liming and bath reuse

	Chlorides	Sulphates	Sulfides	Sulfur	TN	SST	COD	TOC	Ca	Na	Alkalinity	Total P	Total P on filtrate
	g	g	g	g	g N	g	g	g	g	g	g CaCO ₃	g	g
Conventional Liming	5.074	90	651	2.589	586	3.852	7.663	2.121	83	4.742	2.308	98	15
Oxidative Liming / Water recovery	5.392	128	0	288	323	2.629	4.355	1.229	22	5.143	1.946	419	334
Change	6%	42%	-100%	-89%	-45%	-32%	-43%	-42%	-73%	8%	-16%	328%	2127%

6.2. Liquid resulting from centrifugation

The centrifuged bath was used after neutralisation with 30% of caustic soda (NaOH) for soaking in a subsequent liming; *Table 2* shows the analytical results of the various intermediate steps of processing the liming bath.

The analysis shows a clear reduction of the COD and suspended solids, confirming that the spin-drying has taken solid substance from the bath, and shows a phosphorus enrichment in the bath, an element useful for the growth of plants.

We have calculated that the recovery of end-of-liming baths gives us a water-saving of about 18% for each of the following liming baths. We trust that the iteration of this process can go on for a long time.

7. A comparison between traditional and oxidative liming

In conclusion, we report some analytical comparisons between possible scenarios with oxidative liming and traditional liming with sulfide.

7.1. Traditional liming versus oxidative

At first, we see an analytical comparison between traditional and oxidative liming (*Table 3*).

The most interesting parameter is the total sulfur which decreases drastically, as well as many other analysed parameters. In contrast the TOC value is increased because it evaluates the rate of oxidability of carbon only.

After the analytical verification of a normal oxidative liming, we have

considered two scenarios which could lead to further improvements.

7.2. Traditional vs oxidative liming and reuse

The liming bath at the end of liming is not discharged but after an appropriate treatment (acidification with H₃PO₄ + centrifugation + neutralisation) it goes back into the next liming; in this case, a further step allows us to avoid sending the solid waste separated during centrifugation to the purification plant and the clarified bath can be reused with a dramatic saving of water.

The liming recipes have been kept the same to check the effects that the inclusion of the recovery bath can have on the entire phase of the process (then monitoring the total wastewater). The analytical data of the main parameters used in the monitoring of part of the sewage treatment waters are reported in *Table 4*.

The comparison shows a reduction in the pollution load, synthesised by variations of suspended solids and COD.

The raising of phosphorus values (as a result of the bath treatment) can be seen in positive terms as this element is useful for bacteria to survive inside the purifier.

The reuse of liming baths also saves about 18% of water used in the beamhouse process.

8. Conclusions

These tests, aimed at improving the liming recipe, have allowed us to achieve medium-to-good quality hides showing three improvements in comparison to hides processed with traditional liming:

- A much more uniform dyeing
- Increased consistency in printability
- A significant decrease in odour.

Despite the progress, we have to work on smoothing out hides which sometimes show unwanted stretches on the sides.

In the last test with the comparison between traditional and oxidative liming plus reuse, we achieved our objective of a substantial water saving from stage to stage.

The tests made on a semi-industrial scale have allowed us to collect a series of chemical and operational data and information allowing us to industrialise the process and bring oxidative liming into an industrial environment.

Obviously, some adjustments to the recipe have been required, but they did not damage the quality achieved in removing hair from the hide. 🌱

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