Odorless reductive liming, without thiols, thioglycolates and sodium sulphide

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Abstract

The world of industry is increasingly sensitive to production processes with low environmental impact and the tanning industry in particular is following this path, improving every type of processing from wet-end to finishing by choosing ecological products and following the philosophy of saving water, chemicals and energy.
Corichem based this work on the need to have an odorless liming process, especially during the hair removal phase, with less or preferably without use of thiols, thioglycolates and all sodium sulphide added.
Using the experience and a detailed bibliographic research on starches and sugars, studying their reducing power, the research department has formulated a mixture of organic and inorganic substances that enhance the reducing activity of sugars.
The first big problem encountered was the different nature of the hair belonging to various types of skins, for example pig hair is very difficult to remove without sodium sulfide. For this reason, a balanced formulation has been developed that works for every hair type in presence of only a small amount of Sodium hydrogen sulphide. This quantity varies between 0,5%-0,7% for calf hair or cow hair and of 1% for bristles.
The main characteristics of this formulation are the sources found for the organic substances (from food waste or from renewable plant), the power to dissolve the hair, clean the bulbs and remove dirt and keratin on the surface of the skin without sulphur smell.
The process respects the timing and methodology of traditional liming allowing both the recovery of the hair and its complete destruction and does not require the aid of other substances, such as enzymes.
The data collected during our tests will be illustrated and explained during the presentation in which we'll show the content of sulphates in the baths, the value of COD, microscopy studies of the hair degradation and the physical characteristics of the tanned leather.

The products developed in this work are patent pending.

Keywords: sustainable liming; renewable; hair; technical innovation.

1. Introduction

The hair consists of α-keratin a fibrous protein with a helix structure rich in sulfur contained above all in the amino acid cysteine and cystine, which their disulphide bridges make the keratin molecule rot-proof and insoluble in water and organic solvents.

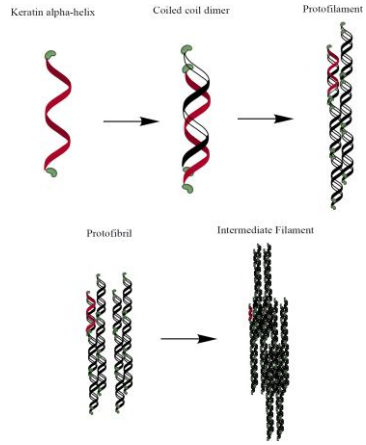


Figure 1: structure of Keratine[1] .

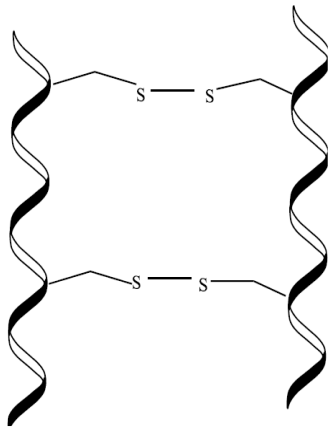
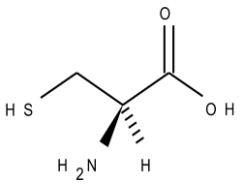
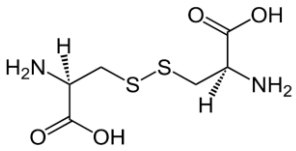


Figure 2: structure of the cystine bridge[2].



cysteine



cystine

The aims of the liming process are:

- open the collagen fibers through alkaline swelling to allow the hydrolysis and the elimination of all polypeptide chains, such as globular proteins and elastin;



Figure 3: fibers of pelt after liming. Magnification 300x

- saponify and emulsify natural fats to facilitate their elimination;
- create interfibrillar spaces through the swelling;
- elimination of hair, keratin and soiled on the surface of the grain and the cleaning of the bulbs.

Classic hair removal involves the use of reducing substances such as the combination of NaHS and Na_2S, in a highly alkaline environment which favors the reduction of the disulphide bridge of cystine as is explained in the following scheme:

$$|S\text{-}S| + 2HS^- \rightarrow 2\,|\text{-}SH + S_2^{2-} \xrightarrow{Ca(OH)_2} |(\text{-}S^-)_2Ca^{2+} + H_2O \qquad [3]$$

Scheme 1 : reduction of sulfur bridge of cistyne

The average content of cystine in the hair is about 120 g/kg and it would require theoretically 1% of sodium sulphide 70% but in the practice during the hair removal much more is used, at least 2-3%.[4]

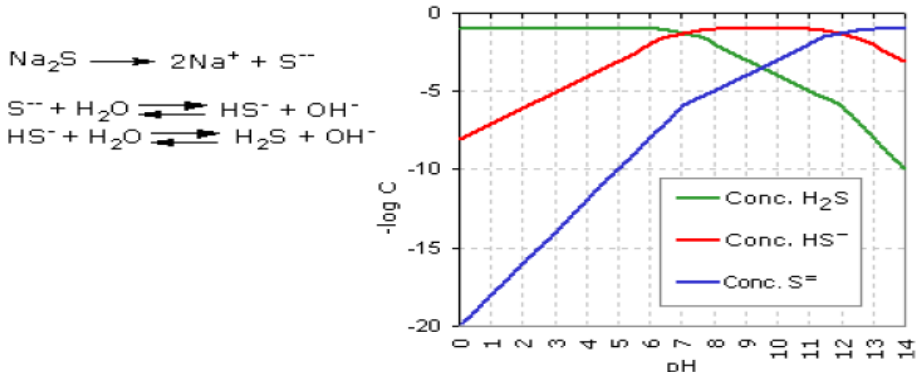


Figure 4: In this diagram is showed the relationship between sulphide species as a function of pH: pH<7 H_2S; 7<pH<12 HS^-; pH>12 S^{2-} . [5]

Corichem with this work has replaced all added sodium sulfide with activated carbohydrates obtaining the same results.

2. Material and Methods

2.1 Material

Carbohydrates aqueous solutions with different formulation of organic and inorganic substances, named: Sample A; Sample B; Sample C; Sample D; Sample E.
Fresh bovine skins with brown coat 100Kg per test

2.2 Instruments

Microscope Keyence VHX-7000
Laboratory drums in stainless steel FER-TI model BRV-S type 1200



Figure 5: Microscope Keyance VHX-7000



Figure 6: drum FER-TI model BRV-S type 1200

2.3 Methods

The work was based on comparing the soaking liming process with activated carbohydrates and the classic soaking liming process. The two processing schemes are shown below

Activated Carbohydrates soaking liming				
Quantity [%]	**Product**	**Temp.[° C]**	**Time [min]**	**Note**
150%	Water	27		
0,1	Preservative agent		run 30 stop 60	
				Drain
150	Water	26		
3,0	NaCl		15	Be°= 1,5
0,4	Phosphated surfactant			
0,1	Sulfated surfactant			
0,2	Preservative agent			
0,15	Liming auxiliary agent			
1,0	Sodium carbonate			
0,5	Sample X		540	Automatic overnight run 10'stop 50' in the morning pH= 9,7 Graminare for 30'
80	Water	26		
1,0	Liming auxiliary agent			
0,7	Sample X			
0,8	Sodium carbonate		30	
2,0	Lime			
0,7	Sodium hydrosulfide		run 60 stop 60	
0,1	Sulfated surfactant			
0,1	Phosphated surfactant			
0,3	Sample X		5	
1	Lime		60	
+				
60	Water	27	30	Automatic overnight run 10' stop 50', in the morning pH = 12,7 Drain
200	Water	27		
0,2	Neutralising/ complexing agent		10	Drain

Scheme2: activated carbohydrates soaking liming process where Sample X indicates the various aqueous solutions of activated carbohydrates reported in point 2.1

Traditional soaking liming				
Quantity [%]	**Product**	**Temp.[° C]**	**Time [min]**	**Note**
150%	Water	27		
0,1	Preservative agent		run 30 stop 60	
				Drain
150	Water	26		
3,0	NaCl		15	Be°= 1,5
0,4	Phosphated surfactant			
0,1	Sulfated surfactant			
0,2	Preservative agent			
0,15	Liming auxiliary agent			
1,0	Sodium carbonate		540	
				Automatic overnight run 10'stop 50' in the morning pH= 9,7 Graminare for 30'
80	Water	26		
1,0	Liming auxiliary agent			
0,6	Sodium hydrosulfide		60	
1,0	Lime		10	
1,0	Lime			
1,1	Sodium sulfide			
0,1	Sulfated surfactant			
0,1	Phosphated surfactant			
1,1	Sodium sulfide		run 20 stop 30	
1	Lime		run 20 stop 30 5 times, Check	
+				
60	Water	27	20	Automatic overnight run 10' stop 50', in the morning pH = 12,6 Drain
200	Water	27		
0,2	Neutralising/ complexing agent		10	Drain

Scheme 3: classic soaking liming process used for the project

3. Results and Discussion

3.1 Results

This paragraph shows the processing phases combined with the microscope images of the carbohydrates soaking liming, where activated carbohydrates work in synergy with NaHS, following the Scheme 2.



Figure 7: soaking

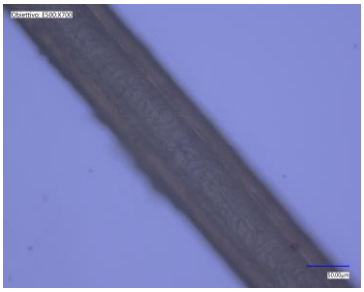


Figure 8: hair after soaking magnification 700x

Figure 9 shows a hair with an intact cortex after the soaking.



Figure 9: pelt after 15min of the add of Sample B and NaHS



Figure10: hair after 15min of the add of Sample B and NaHS; magnification 1000x

In figure 10 we can see that the cortex has a structure slightly opened and the unhairing is not started yet.



Figure11: pelt after 30min of the add of Sample B and NaHS



Figure12: hair after 30min of the add of Sample B and NaHS; magnification 1000x

In figure 11 we can see that the unhairing process has started and in figure 12 is showed how the structure of the hair is corrupted.



Figure13: pelt after 45min of the add of Sample B and NaHS

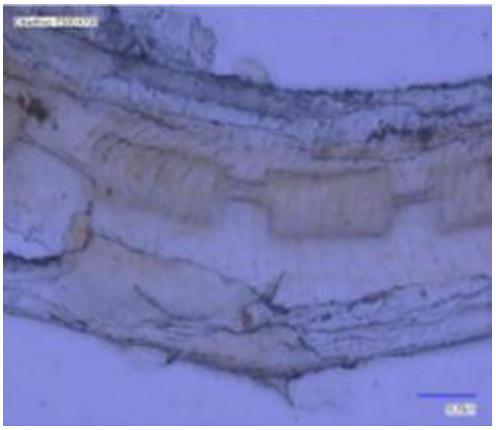


Figure14: hair after 45min of add of Sample B and NaHS; magnification 700x

In figure 13 we can see that the unhairing is almost total while in figure 14 we can see the hair almost dissolved, interesting the detail of the medulla.



Figure15: pelt after 60min of the add of Sample B and NaHS.

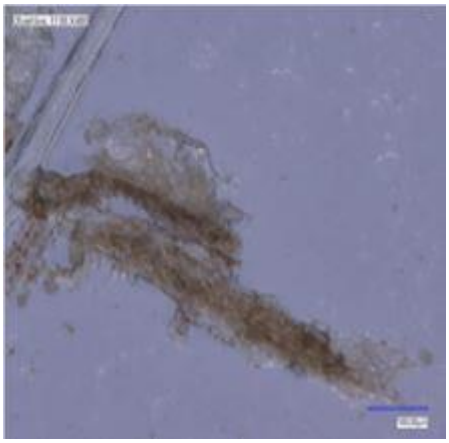


Figure16: hair after 60min of the add of Sample B and NaHS; magnification 400x

In figure 15 we can see a totally unhairing of the pelt an in figure 16 the hair appears broken up.



Figure17: Pelt after the automatic overnight



Figure18: Pelt after activated carbohydrate soaking liming.

In figure 17 and 18 we can see a pelt totally unhaired with grain and bulbs clean.



Figure 19: comparison between pelt from classic soaking liming process and activated carbohydrate soaking liming process; left classic soaking liming process, right activated carbohydrate soaking liming.



Figure 20: Comparison between wet-blue, above chrome tanning from activated carbohydrate soaking liming, under chrome tanning from classic soaking liming.

All the analysis have been done from an external laboratory. The first parameter evaluated was the COD (chemical oxygen demand). For our work it was also important to reduce the polluting load. Each analysis was performed on the bath sample from hair burning liming process, comparing all samples of activated carbohydrates liming with traditional liming. The same procedure was applied also for all the next analysis.

Type of liming	**COD mg/l O_2** (Nanocolor COD 15000)
Traditional	64000
Sample A	52000
Sample B	53000
Sample C	54000
Sample D	56000
Sample E	54000

Table 1 : Chemical oxygen demand in the liming end bath

Type of liming	**Sulfide content mg/l** (Internal method)
Traditional	1910
Sample A	802
Sample B	736
Sample C	787
Sample D	745
Sample E	738

Table 2: sulphide content in the liming end bath

Type of liming	**TKN mg/l** (APAT CNR IRSA 5030 Man 29 2003)
Traditional	4730
Sample A	899
Sample B	965
Sample C	977
Sample D	1002
Sample E	961

Table 3: nitrogen Kjeldahl (TKN) content in the deliming end bath. The deliming agent used for the process was chlorine, sulphate and nitrogen free

Type of liming	Total chrome mg/l (UNI ISO 17294-2:2016)
Traditional	1651
Sample A	1211
Sample B	1185
Sample C	1218
Sample D	1196
Sample E	1167

Table 4: residual total chrome in tanning end bath. Tanning made with 6% of Chrome hydroxysulphate salt 25% in Cr_2O_3

Type of liming	% Cr_2O_3 in wet-blue (UNI ISO 5398-1:2018)	Tg after tanning [C°] (EN ISO 3380)
Traditional	3,3	100
Sample A	3,5	100
Sample B	3,5	100
Sample C	3,5	100
Sample D	3,4	100
Sample E	3,5	100

Table5: Content of Cr_2O_3 in wet-blue. Tanning made with 6% of Chrome hydroxysulphate 25% in Cr_2O_3

3.2 Discussion

Evaluating the analysis data for each sample of Activated carbohydrate, we can see that the new system also brings benefits to the process after soaking and liming, especially for the pollutant load. The data reported in Table 3 are interesting, where we can see a significant reduction of TKN, which can be explained because the pelt after Activated carbohydrate liming have the grain and the bulbs cleaner than the traditional liming. The final choice on the samples tested was made on the quality of the leather, evaluating the color, bulbs cleaning, the degree of depilation and tightening. All the pelts resulted perfectly unhaired and clean, but Sample B was lighter in color and less tight. As we can see in Table 5 the quantity of chrome in wet-blue is perfectly in standard.

4. Conclusion

In conclusion this work proves that is possible to make a reductive odorless liming without the use of thiols, thioglycolate, enzymes and over all sodium sulphide, combining activated carbohydrate with a small amount of sodium hydrogen sulphide obtaining at the same time a technology that is more respectfully of the human health and the environment, able to give a good quality of pelt and wet-blue. We are still working to improve the process decreasing the quantity of sodium hydrogen sulphide. We are testing this process also for metal free tanning while this technology is already applied industrially for chrome tanning.

5. Acknowledgements

We thank the Corichem's WET-END laboratory team for the support during the tests.

6. Reference

1. Figure 1. Wikipedia *Alpha-keratin* 2017
2. Figure 2. Wikipedia *Alpha-keratin* 2017
3. http://www.galileiarzignano.edu.it/wsite/berto/calcinaio.htm
4. Anthony D Covington, *Tanning Chemistry The science of Leather,*120-121. RSCPublishing 2011
5. Figure 4. http://www.galileiarzignano.edu.it/wsite/berto/calcinaio.htm