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Clean Technologies in Soaking & Liming of Leather Manufacture

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Abstract: *Clean technologies are applied for reducing the polluting impact that originates from soaking & liming of leather manufacturing industry. The waste water is treated more easily in the effluent treatment plant. They have also the aim to produce a leather free of harmful substances. This process reduces the consumption of water. Clean technologies can contribute to reduce the sludges volume coming from effluent treatment plant. Moreover, these techniques increase the value of the solid wastes that can be sold in other industrial sectors. This paper is an attempt to make a thorough study of all the clean technologies available in manufacturing leather.*

I. INTRODUCTION

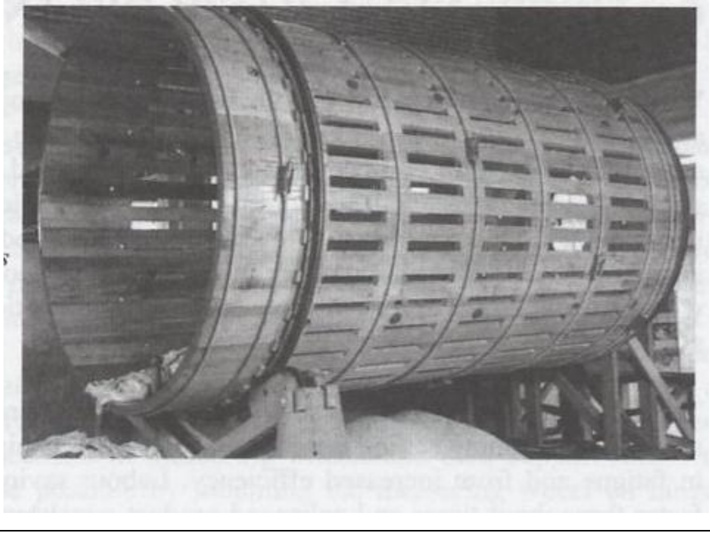
Clean technology, often referred to as cleantech, encompasses processes, products, or services that reduce negative environmental impacts through significant energy efficiency improvements, sustainable resource use, or environmental protection activities. It is primarily designed to mitigate pollution, reduce waste, conserve natural resources, and promote renewable energy and eco-friendly practices.In the context of industries like leather manufacturing, clean technologies aim to minimize pollutants, make wastewater treatment more efficient, and produce goods free of harmful substances, all while reducing water and energy consumption (Muthukrishnan, 2021).

CLEAN TECHNOLOGIES: The techniques are the following.
Systems improving the fixation of chemicals to leather. Use of alternative non toxic and eco-friendly chemicals. Recycling of pollutant baths.

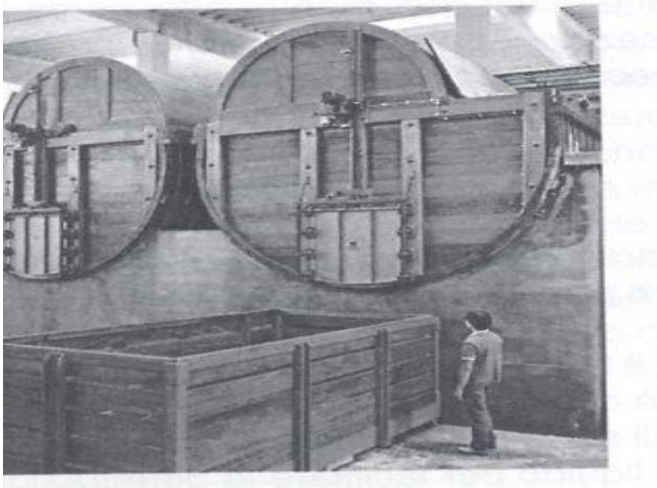
BEAMHOUSE OPERATIONS; SOAKING, UNHAIRING-LIMING, DELIMING-BATING, PICKLING, DEGREASING.

DESALTING BY DRUMMING: The removal of salt is made mechanically by using wooden cage drums (4-5 meters in diameter, 6-7 meters long).When mounted at a slightly inclined horizontal axis, the goods can be loaded at the higher and will drop out at the lower end. The excess salt have dropped out through the drum apertures on the way through. After the weighing, beamhouse operations are carried out.

PICTURE OF A DESALTING DRUM



SOAKING: The raw hides re-absorb the water lost after the curing process, during the transport and a less or more storage before the beginning of work. There is also the removal of salt, dirts, soluble proteins. The absorbed water rehydrates dried interfibrillary protein, loosening its cementing action on the fibres. The collagen fibres and keratin protein of the hair and epidermis also take up water and become more flaccid and flexible. Satisfactory soaking is judged by feel, cleanliness, absence of salt.Soaking may be done in paddle (careful soaking of delicate raw material in long float) and more frequently in a drum.
Picture of paddles



DRIED HIDES SOAKING:-The soaking of dried hides is very difficult and requires more time than wet salted hides.That is due to sticking of collagen fibres , that is caused by sun-drying and coagulation of interfibrillary proteins. Being hard, horny and little flexibile, they cannot be undergone the rotations in the drum. For this reason the hides are pre-soaked in the soaking pit (static conditions)and after 18-24hours ,then they are soaked in the drum. Contrary to the wet salted hides, they do not contain salt, which favoures the interfibrillary proteins solibilization. For this reason it is necessary to add common salt at the beginning of soaking (Berber & Birbir, 2019).

DRIED HIDES SOAKING

Soaking of dried bovine hides - % riferred to dried weight

Phase	+	%	Chemicals	°C	Dil	Time (min.)	pH, remarks
Pre-soaking in pit			Water to cover the hides	20			
		0,3	Biocide (1)		1 : 4		
		0,3	Surfactant (2)		1 : 4	120'	
Drain							
1°Soaking in pit			Water to cover the hides	22			
		0,3	Biocide		1 : 4		
		0,5	Surfactant		1 . 4		
		3,0	NaCl			16 h	
Discharge							
Soaking in drum (2-3 giri/min)		400	Water	22			
		0,2	Biocide		1 : 4		
		0,2	Surfactant		1 : 4		
		0,4	Na_2S				
		1,2	Prod. based on MgO				
		0,4	Na_2CO_3				
		1,0	Enzymatic product(3)			Run.60'-stop 60'-run. 20' every hour x 8 ore	pH= 10,5-10,6
						drain¾ of the float-Run. 4 h	
	+	300	Water	24			
	+	0,2	Surfactant			60'	

Automativ overnight: run 20' every hour x 10 ore. Total timr op process about 48 h.
Checks: the hides must be softy and flaccide, white section. pH at the end of process:tra 9,7- 10,0. Temperature at the end of process:22-23°C.
Notes : (1) biocide is based on dityocarbammate. (2) the wetting agent is a non ionic (80% of active matter). (3) proteolitic enzyme.

FRESH HIDES SOAKING: Contrary to all expectations, the soaking of fresh hides is moreeasy compared with that one of wet salted hides.During the storage of salted hides, sodium chloride attacks the interfibrillary proteins (albumins, globulines etc.). This action makes easier their solubilization and removal from interfibrillary network .Therefore , the use of salt needs during the soaking of fresh hides.

SOAKING OF WET SALTED HIDES

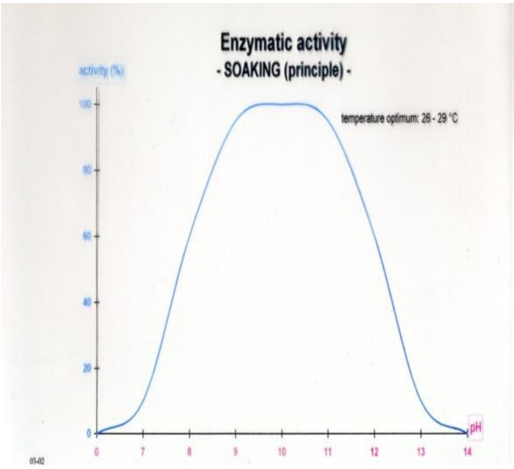
Soaking of wet salted bovine hides (28-30 kg) - % referred on wet salted weight (Drum running . 2-3 rpm)

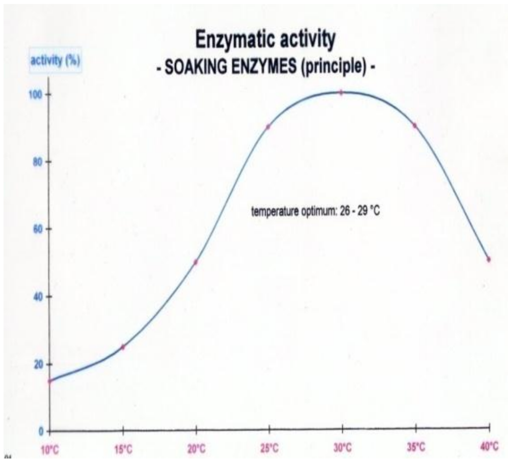
Phase	+	%	Chemical	°C	Dil	Time (min.)	pH, Remarks
Soaking		150	Water	20			
		0,15	Biocide (1)		1 : 4	30	
Drain							
Pre-soakng		150	Water	22			
		0,1	Biocide		1 : 4	60	d = 3-4° Bé
Drain							
Soaking		150	Water	24			
		0,05	Biocide				
		0,15	Wetting agent (2)		1 : 4	10	
	+	0,5	Enzymatic product (3)				
		0,7	Product bas. on MgO				
		0,3	Na_2CO_3			120	pH=10,5-10,6
	+	0,2	Na_2S			300	

Automatic overnight: 10' every hour x 13-14 ore. Total time of process: 22-23 h.
Checks: the hides must be soft and the section of hide white. pH at the end : 9,7 e 10,0.
Bath temperature at the end of process : 22-23°C, density at the end: 3,0-3,5°B .
Notes : (1) biocide is based on dialkyldimethylammonium. (2) the wetting agent is a not-ionogen surfactant (80% of active matter). (3) product based on proteolytic enzyme.

(**By Sarkar, 2005 in Soaking Chapter**)

AIDS TO SOAKING :ENZYMATIC PRODUCTS are based on pancreaticenzymes, those are protease family.They show the best activity at pH between 9 and 11. The ideal temperatura is included between 29 and 35°C.





[Growth response of bacteria community of pH in Soils differing in pH, FEMS Microbiology Ecology, Volume 100,issue 12 Dec 2024 page 06.] [Ref.3]

[Relationship between Temperature & growth rate of bacterial cultures. Journal of bacteriology,vol.149,issue-1 Jan 1982,page.2. [Ref.11]

AIDS TO SOAKING ENZYMATIC PRODUCTS:- The pancreatic enzymes also contain the amylases and the lipases. The Amylases degrade proteoglycans albumins, globulines, that constitute the cementing substance between the collagen fibres. In this way, the hydration of the hide is favoured.The Lipases saponify the natural fat of the hide.The enzymatic products in the soaking make shorter the length of the process. They improve the opening-up of hides. They reduce the wrinkless on the neck and the belly of hides. The finished leather presents finer grain .When the raw stock shows some defects due to a bad curing conditions as hair slip, for example, their use is dangerous. The enzymes can improve the defects of grain (blind grain is the most common defect) (Jianzhong et.al.,2014.)

UNHAIRING-LIMING: The process includes removing of the hair and epidermis , opening-up of the hide structure ,and the increasing of reactivity between collagen and chromium salts and many other chemicals. Chemicals which are employed are Sodium sulphide (Na_2S) and sodium hydrosulphide (NaSH) asunhairingagents.Lime[$Ca(OH)_2$] as opening up of the fibres network. Mercaptans (R-SH) are always more frequently used, as unhairing agents, together sulphideand hydrogen sulphide in ecofriendly systems .The mercaptans allow the reduction of sulphide and hydrosulphide quantities. In this way, the employment of hazardous chemicals can be limited (Dutta, 1985).

MODERN LIMING PROCESS

Hair burn liming, wet salted bovines- % referred on raw hide weight

(drum speed 2-3 rpm)

Pahse	+	%	Chemicals	°C	Dil	Time (min.)	pH, remarks
drain 50% of the soaking float							
	+	35	Water	24		20	
	+	1,2	$Ca(OH)_2$			20	
	+	1,0	NaHS al 70%			30	
		1,0	Na_2S al 60-62%				
		0,15	Surfactant$^{(1)}$		1 : 4	Rot. 20 Stop 20	
	+	1,2	$Ca(OH)_2$				
		1,0	Na_2S al 60-62%			50	
	+	20	Water	24		20	
	+	1,2	$Ca(OH)_2$				
		1,0	Na_2S al 60-62%			60	
	+	15	Water	24		15	
	+	0,15	NaOH al 30%		1 : 10	60	
						Automatic x 16h, run. 10', stop 60'	
Drain							
		150	Water	24			
		0,15	Surfactant$^{1)}$		1 . 4	20	
Scolare							
		150	Water	22			
		0,15	Polyphosphate$^{(2)}$		1 . 4	20	
Discharge, Fleshing							

(1) Surfactant (50% of active matter)
(2) Polyphosphate (65% P_2O_5

(**By Sarkar, 2005 in Liming Chapter)**

ACTION OF UNHAIRING AGENTS:-Unhairing is caused by the breaking of the di-sulphide bridge of cystine that is a component of keratin. The breaking of the S-S bridge can be achieved by reducing chemicals (sulphide, hydrosulphide, mercaptans, etc,) oxidising agents ($NaClO_2$, H_2O_2), enzymatic products or proteolytic bacteria. By using chemicals, the keratin structure may be partially break down forming a pulp or dissolving completely leading to a clean pelt (unhaired skin) surface.

ENVIRONMENTAL IMPACT DUE TO UNHAIRING-LIMING:-

The liming is the process with the higher polluting load. In the waste water coming from liming are dissolved the degradation products of hair, epidermis and interfibrillary proteins. For this reason, the effluent coming from a conventional liming process present high values of COD, BOD, sedimentable solids. In addition, the effluents of liming contain significative amounts of unexhausted sulphide, that is a toxic substance for the mankind and environment (Alemu et.al, 2024).

ENVIRONMENTAL IMPACT DUE TO UNHAIRING-LIMING:
TOXICITY OF SULPHIDE AND SULPHIDRATE.

During the deliming and sometimes pickling, where acidic substances are used, sulphide and sulphidrate can develop sulphuric acid. $Na_2S + 2H^+ = 2\ Na^+ + H_2S$Sulphuric acid can be lethal if it exceeds certain concentration levels. Sulphide is also a problem for waste water because it poisons fish if it reaches the water-courses. Moreover, in certain concentrations inhibits the bio-degrading capacity of bacteria in the biological treatment of waste water. Sulphide forms large quantities of sludges in chemical-physical treatment of effluent (Nazer, et.al. 2006).

ENVIRONMENTAL IMPACT DUE TO UNHAIRING-LIMING:
CLEAN TECHNOLOGIES

i)Reduction of liming pollution is possible to reduce the sulphide and sulphidrate offer
ii) Hair saving unhairing, iii) Recycling and reuse of exhausted liming bath, iv)Recycling of liming bath together the hair saving process and the reduced offer of sulphide system

i)LIMING WITH THE REDUCTION OF SULPHIDE AND SULPHIDRATE OFFER

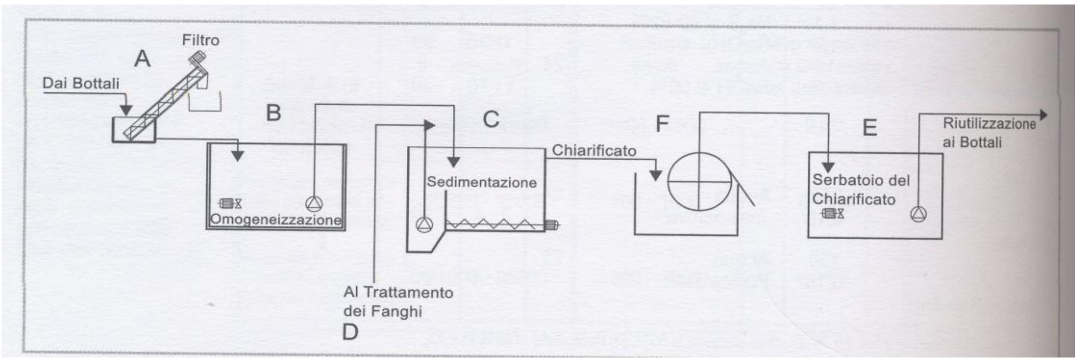
It is not possible to completely replace sulphide at the present time. By combining and employing auxiliary agents of determined chemical nature, it is possible to reduce strongly the quantities used of sulphide and sulphidrate. The employment of Mercaptoethanols contributes to minimize the use of these toxic chemicals.
The reaction mechanism of mercaptoethanols with keratin is similar to that of inorganic sulphide. They show unhairing capacity. These substances are oxidized very easily through the action of oxygen in the air. Their complete oxidation at the end of the unhairing process leads to the formation of non-toxic chemical compounds. Furthermore, they cannot generate sulphuric acid during deliming and/or pickling. Hides obtained using these products are flatter than those ones produced by employment of sulphide (Wu et.al., 2020).

iii)RECYCLING OF LIMING BATH:

The recycling of the bath further cuts down the pollution coming from liming it is possible to save lime and sulphide. By combining recycling and hair recovery, drastic decreases are registered for COD, BOD, TSS and quantities of sulphide in the waste water (Kanagaraj, 2020).

LIMING BATH RECYCLING PLANT -A filtering system (A) which filters large solid particles in suspension - A homogenization basin (B) into which the liquid is pumped - A conical trunk container (C) for the sedimentation of the bath A pumping system (D) for transporting the solids, separated at the bottom of the decanter (3), to the sludge treatment process A rotating filter (F) able to separate even small particles contained in the exhausted liming bath -An accumulation tank (E) from which the bath is sent to the drums

LIMING BATH RECYCLING PLANT



A filtering system (**A**) which filters large solid particles in suspension

- A homogenization basin (**B**) into which the liquid is pumped
- A conical trunk container (**C**) for the sedimentation of the bath
- A pumping system (**D)** for transporting the solids, separated at the bottom of the decanter (**3**), to the sludge treatment process
- A rotating filter **(F)** able to separate even small particles contained in the exhausted liming bath
- An an accumulation tank (**E**) from which the bath is sent to the drums

ECO-FRIENDLY LIMING

Hair-Saving liming with re-cycling of exhausted bath and reduced offer of sulphideCalcinaio- wet salted bovine hides- % referred on raw material weight.

(Drum speed: 3 giri/min)

Phase	+	%	Chemicals	°C	Dil	Time (min.)	pH, remarks
Drain all the bath of soaking							
		70	**Recycled bath**	24			
Penetration of mercaptoethanol	+	1,0	Mercaptoethanol				
		0,2	Surfactant		1 : 4	40	
Immunitation of stem, Activation	+	1,0	$Ca(OH)_2$			Run.20-stop 20	
Hair loosening	+	0,9	NaHS (70-72%)				
		1,0	$Ca(OH)_2$				
		0,2	Mercaptoethanol			40	**Continous filtration for 2 h**
Opening up of hide structure	+	**20**	**Recycled bath**	24		5	
	+	1,0	Na_2S (60-62%)				
		1,0	$Ca(OH)_2$			90	
	+	**18**	**Water**	24		5	
	+	0,2	NaOH (50%)		1 : 10	90	Authomatic x 20h run 10', stop 60'
Drain							
		150	Water	24			
		0,15	Surfactant		1 . 4	20	
Drain							
		150	Water	22		20	
		0,15	Poliphosphate			20	
Discharge, fleshing							

SULPHIDE-FREE LIMING: - In the past, many researches have been carried out about sulphide-free limings. The researchers are studying new systems. At the present, the performances of these technologies have not yet reached, the same results of sulphide liming. The principal systems are: Enzymatic unhairing Oxidative unhairing using sodium chlorine dioxide or hydrogen peroxide (Rao et.al.,2003).

OXIDATIVE UNHAIRING WITH $NaClO_2$:-The system is based on the treatment of soaked hide with sodium Chlorine di oxide in acidic medium. ClO_2 that breaks the disulphide bridge of cystine. The sulphur is oxidized to sulphonic group:

$5 NaClO_2 + 4 HCl = 4 ClO_2 + 5 NaCl + 2 H_2O$

$4 R\text{-}S\text{-}S\text{-}R + 10 ClO_2 + 4H_2O = 8 R\text{-}SO3H + 5 Cl_2$

(**An Introduction of Leather Manufacture by Prof. S.S. Dutta , Page 162)**

This system is not applied because of the ClO_2 development. It is a dangerous product in addition to the fact that opening up of hide structure is not satisfactory

OXIDATIVE UNHAIRING WITH H_2O_2 The unhairing with hydrogen peroxide, in alkaline medium (NaOH), is the most interesting oxidative system.

Advantages: Clean and white pelts are obtained Its a eco-friendly system

Disadvantages: The opening-up of hide structure is excessive, the leather is looser and less close. The higher cost compared with conventional liming. The drum wood is deteriorated in the time by oxidising agents. Drums made on polypropylene should be used.

ENZYMATIC UNHAIRING This system presents many limits and is inapplicable at industrial level.

Problems of this system:

The proteolytic attack of the hair root and the epidermis is effective only after a pre-treatment of hides with alkaline substances. In this way, the enzyme penetration is possible and they are able to degrade the epidermic structure., the enzymes have a long incubation period (about 12 h). During this long time can be attacked also the collagen. Practically, the hydrolysis causes the deterioration of the grain. Unfortunately, very specific enzymes able to disintegrate only the epidermis and the hair root, do not exist today (Durga et.al.,2016).

II. CONCLUSION

Most of the effluents come from beamhouse operation. So, leather industry, especially tanning industry is categorized as a red industry due to pollution of water and careless disposal of solid waste and gaseous emission. For reduction of water pollution, we should adopt modern techniques like recycling of water, after completing the process, use of enzymes wherever applicable, use less chemicals, less wastage of excessive water, checking the chemical absorption after operation is completed and if possible, the bath should be recycled for the next lot. If possible, we should check the solid waste so that it can be utilised for other industry raw materials.

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