Lime Free Unhairing: Sodium Aluminate as an Alternative Towards a Cleaner Process

by

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Abstract

Sodium aluminate as an alternative to calcium hydroxide was tested in the hide unhairing process and the possibility of such replacement was confirmed. Qualitative unhairing is achieved using water solution containing sodium aluminate 2–3% and sodium sulphide 1.3–1.5%. The effect on collagen during unhairing using the sodium aluminate is significantly less than that of conventional liming. An addition of 0.5% NaOH allows better opening up of the derma to be obtained. Industrial trials of lime-free unhairing using sodium aluminate have shown that the leather produced meets the quality requirements for shoe upper leathers. Lime-free unhairing using sodium aluminate leads to less pollution of wastewater by TSS, Kjeldhal nitrogen and sulphides.

Introduction

The leather industry is one of the most environmentally polluting branches of industry, especially due to its wastewaters. Huge amounts of lime sludge and total solids formation are the main drawbacks of lime.[1] Herewith, the cleaning of unhairing solutions, polluted with lime, sulphides and the products of protein degradation, remains very difficult and expensive. For this reason, the development of new and cleaner liming methods is perhaps the most urgent requirement, compared with the perfection of other leather production processes.

Of course, readers may at once counter that there are many possibilities to avoid this by using pure enzymatic,[2-6] oxidative unhairing,[7-13] or mixed enzymatic–oxidative methods.[14-17]

Unfortunately, the situation with oxidative unhairing is similar to that with pure enzymatic unhairing. Jenen *et al.* very clearly summarize the situation: "unhairing solely by proteolytic and keratinolytic enzymes has been tried over and over again, but for the lack of selectiveness was difficult in practice to control.[18] A lot of work has also been invested in oxidative unhairing, but until today it is very limited in its use as it is hard to get consistent results. Generally, it is to fair to say that alternatives to sulphide are not widely accepted because they either do not remove the hair completely, or they have a negative impact on leather quality, or the demand for process control is too high, or the costs involved are prohibitive. Sometimes it is a combination of these reasons".

Hence, the use of the lime sulphide process remains the most commonly applied method of unhairing and opening up of the derma in the leather industry. On the other hand, this process can be improved and made cleaner and more environmentally friendly as well. There are a few possible ways to achieve this. The first is to use auxiliary materials, which are less harmful than sulphide, allowing decreased demand for sulphides for unhairing. Once again enzymes are often used as such additives. Proteolytic enzymes in the liming step can accelerate the unhairing.[18] A reliable unhairing process with low sulphide and lime content can achieve an excellent unhairing effect and lead to substantial reduction of the load to the environment of sulphide, nitrogen, COD, and sludge.

Sehgal *et al.* proposed to use nickel carbonate instead of sodium sulphide.[19] The skins were treated with a paste of 1% nickel carbonate, 1% sodium hydroxide, 3% lime and a filler such as kaolin or china clay plus water. The results obtained were comparable with the sulphide lime system in terms of the duration and efficacy of the process.

The next way, which avoids the formation of solid lime sludge polluted by sulphides, protein degradation products, detergents etc., is the replacement of lime by other strong water-soluble alkalis. Lime can be successfully replaced by sodium hydroxide. Since the action of sodium hydroxide on collagen is stronger than that of lime, salts such as sodium chloride or sodium sulphate are added to buffer the effect of the NaOH. The developed lime-free method of unhairing and dermal opening allows a reduction in the consumption of sulphides and enables the properties of chromium-tanned leather to remain as good as those of leather produced using conventional methods.[20] The dermatan sulphate changes and microscopic investigations have confirmed the importance of the added salts for the quality of leather produced by the lime-free method.[21]

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Thanikaivelan *et al.* proposed a hide unhairing and dermal opening up method which employs enzyme, a low amount of sodium sulphide and sodium hydroxide.[1] The performance of the leathers is shown, through physical and hand evaluation, to be on a par with conventionally treated leathers.

Later, a new hair-saving unhairing method using a system containing enzyme preparation, sodium hydroxide, sodium sulphide, and disodium hydrophosphate was developed. The method results in a high quality pelt suitable for leather manufacturing, decreases the pollution caused by sodium sulphide and the other products of hair degradation, and avoids the pollution caused by calcium compounds.[22]

Another alkali investigated as a possible substitute for lime is sodium metasilicate. Munz and Sonleitner report on methods developed for unhairing by applying sodium silicate as a lime substitute.[23] They state that lime in the unhairing process can be substituted by sodium silicate without problems. As a result, the effluent loading is reduced and so also the sludge volumes from effluent treatment decrease. Saravanabhavan *et al.* investigated a lime and sulphide-free unhairing process using a commercial enzyme with the activation using sodium metasilicate. The strength and bulk properties of the experimental leathers after the developed unhairing are comparable to those of control leathers. The process led to a significant reduction in the chemical oxygen demand and total solids by 53 and 26%, respectively.[24]

Liu et al. developed a novel lime-free unhairing method based on a system containing sodium silicate, enzyme, surfactant and urea.[25] This innovative process makes it possible to achieve an equivalent effect on the fiber opening, shrinkage temperature and mechanical properties of crust leather compared with a conventional liming process. The environmental factors were all superior to the conventional liming process.

There is one more interesting material that has strongly alkaline properties, good solubility in water and a comparatively low price. This material is sodium aluminate, which is an important commercial inorganic chemical for various industrial technical applications.

Therefore, the possibility of replacing lime with sodium aluminate in unhairing systems was investigated, and the aim of paper is to introduce readers to the peculiarities of the action of sodium aluminate on hide collagen and its influence on unhairing quality.

Experimental

Raw Material

Salted cowhide was used as the raw material for this study. The soaked and washed hide was cut into pieces 5x10 cm and experimental series were prepared from these pieces. The series were formed in such a way that samples from all hide parts would be presented in each series. A treatment of pieces with chemicals was performed in a laboratory drum with capacity of 3 liters. The rate of rolling was 20±1 revolutions per minute. The samples were soaked and washed according to conventional technology. The parameters of unhairing of the experimental samples were varied according to the conditions of the experiments. The unhairing for the control samples was carried out as follows: H_2O 40%, temperature 20–22°C, $Ca(OH)_2$ 2.3%, Na_2S(100%) 1.2%, 1 h run continuously, $Ca(OH)_2$ 2.3%, 1 h run continuously, H_2O 100%, 2 h run continuously, later 5 min. every 3 h, total duration 24 hours (% are based on hide weight in descriptions of unhairing methods).

Chemical Materials

Analytical sodium aluminate ($NaAlO_2$) containing Na_2O 40-45% and Al_2O_3 50-56% was used in this study. The chemicals used for the technological processes and for the analysis were of analytical grade. Other chemical materials used for technological processes were of commercial grade.

Evaluation of Unhairing Quality

The quality of unhairing was evaluated according to the following scoring system:

1. the hair is affected weakly;
2. the hair is affected strongly but residuals of hair and epidermis remain on the derma and cannot be removed mechanically;
3. residuals of hair and epidermis remain on the hide but can easily be removed mechanically;
4. the hide surface is clean.

Determination of Hide and Leather Properties

The shrinkage temperature of the hide was measured according to the standard.[26]

The swelling was calculated as the ratio of increase in weight of the hide during unhairing and the soaked hide weight, and expressed in percent. The amount of collagen proteins removed was estimated from the amount of hydroxyproline in the treatment solution. The amount of hydroxyproline was determined using a photo colorimetric method.[27] Measurement of samples pH was carried out according to the standard.[28] The amount of non-collagenous proteins removed was calculated as the difference between the total proteins and the collagen proteins in the treatment solutions.

The total proteins were established by Kjeldahl's procedure.[29] The porosity of the hide was determined according to the method described in the literature.[29] Before the evaluation of porosity; the hide samples were dehydrated with acetone.[30] The strength properties, the amount of chrome compounds in the leather, soluble matter in dichloromethane, and volatile matter were determined according to the standards.[31-34] The shrinkage temperature of the chromed leather samples was determined as described in the literature using special equipment and replacing the distilled water with glycerol.[29]

Statistical Analysis

All data were expressed as the average value of triplicate measurements. Standard deviations did not exceed 5% for the values obtained.

Results and Discussion

The unhairing using sodium aluminate was utilized under conditions: H_2O – 100%, temperature 20–22°C, Na_2S - 0.9%(100%), $NaAlO_2$ – 0.5%, 1%, 1.5%, 2%, 3%, 4%, 10% (respectively variants 1, 2, 3, 4, 5, 6 and 7), 8 h run continuously, later 5 min. every 3 h, total duration 24 hours. The qualitative indexes of the process are presented in Table I.

The amount of sodium aluminate added to the solution has an influence on the unhairing quality and unhaired hide properties. The best quality of hair removal is reached using 2–3% of $NaAlO_2$. It should be noted that the control unhairing showed a better unhairing result. Comparison of the indexes indicating the effect of the materials used on treated hide leads to the proposition that the sodium aluminate–sodium sulphide system affects the hide less than the lime–sulphide treatment. The hide unhaired by the control method had the lowest shrinkage temperature and highest swelling. The amount of collagen proteins removed during the process was the highest as well.

It is very interesting that the increase of sodium aluminate content from 0.5 up to 4% has only a negligible influence on the shrinkage temperature and swelling of the hide but increases the amount of collagen proteins removed. On the other hand, the addition of 10% of sodium aluminate leads to the weakest effect on the hide.

Since the unhairing quality thus far did not satisfy the authors, the process was carried out using other amounts of sodium sulphide. 2% of $NaAlO_2$ were used together with 0.9%; 1.1%; 1.3%; 1.5% or 1.8% of Na_2S (100%) and the unhairing effect was determined (Table II). Other process parameters were the same as described in Table I.

Hence, the lime-free process using sodium aluminate requires not less than 1.3% of sodium sulphide to achieve a good unhairing effect.

The next step was to assess the effect of temperature on the qualitative indexes of treated hide when the process was carried out using Na_2S (100%) 0.9% or 1.5% (variants 1 and 2 respectively) and 2% of $NaAlO_2$ at 20 and 30°C (Table III). Other process parameters were the same as described above.

The increase of the lime-free process temperature did not lead to better unhairing when 0.9% Na_2S was used. Herewith, the effect on collagen was significantly stronger than when treating at 20°C. Evidently, the same increase of temperature has the most influence on the properties of hide unhaired according to the control method. It can be supposed that 20°C is the optimum temperature for unhairing with the use of sodium aluminate.

Table I

Sodium aluminate influence on unhairing quality and hide properties.

Unhairing variant	Index			
	Shrinkage temperature, °C	Removed collagen proteins, g/kg of hide	Swelling, %	Unhairing quality, points
1	57.8	0.12	16.9	2
2	58.0	0.13	19.8	2
3	58.3	0.15	18.2	2
4	58.7	0.16	17.6	3
5	58.9	0.18	19.8	3
6	57.3	0.18	18.6	2
7	59.3	0.08	17.9	2
Control	57.0	0.41	20.4	4

Note. Shrinkage temperature of hide after soaking 63.7°C.

Assessing the effect of lime-free unhairing on swelling and the change of hide shrinkage temperature, the next conclusion is that the hide derma is not opened up enough for the subsequent processes, and it should be treated somewhat more strongly to reach a qualitative derma opening level.

Based on the investigation of using sodium silicate for the leather processing, sodium hydroxide has been chosen as auxiliary for better opening up of derma.[35] The unhairing–dermal opening up was carried out as follows: H_2O – 100%, temperature – 20–22°C, $NaAlO_2$ – 2%, Na_2S(100%) – 1.5%, 2 hours run continuously, NaOH – 0; 0.5 or 1% (respectively variants 1, 2 and 3), 2 hours run continuously, later 5 min. every 3 hours, total duration 24 hours. Hide shaved after soaking was used for the experiment so that hair should not have any influence on the results of the totally removed proteins.

Comparison of the properties of hide after treatment by the control method with the properties of hides obtained using sodium aluminate (Table IV) has shown that the hide treated by adding 0.5% NaOH is characterized by the closest indexes to conventional hide. The addition of NaOH 1% leads to a slightly heightened action on collagen and hide overall. One more positive effect is that unhairing with the use of sodium aluminate increases the removal of non-collagenous proteins. Accordingly, better removal of non-collagenous proteins leads to higher porosity of the hide.

On the other hand, it was very clear that the effect of the treatment with sodium aluminate (without NaOH) on collagen was markedly stronger than in the previous experiment (data in Table I or Table II). Moreover, more collagenous proteins are removed during the control treatment of the shaved hide as well (usually the amount of collagenous proteins removed varies in the range 0.2–0.5 g/kg of hide[20, 36] during conventional unhairing–liming). The authors' supposition was that it occurred due to the action of sodium sulphide that, in the case of the absence of hair, enhanced the general effect of alkalis on collagen proteins.

The developed unhairing–dermal opening up method was tested under industrial conditions. Industrial trials to make shoe upper leather were performed in the joint-stock company "Kedainiu Oda" (Lithuania). Five salted cow hides (weight 20–24 kg) were cut along the backbone. The right sides (control) were processed according to the technology valid in the enterprise, according to which the unhairing–dermal opening requires 0.6% NaHS (100%), 1.2 Na_2S (100%), 3.9% $Ca(OH)_2$ and other auxiliary materials.

The technological processes for the left sides (experimental), excepting, of course, the unhairing–dermal opening process, were

Table II
Effect of sodium sulphide amount on lime-free unhairing quality.

Index	Amount of Na_2S used for lime-free unhairing, %					Control unhairing
	0.9	1.1	1.3	1.5	1.8	
Unhairing quality, points	3	3	4	4	4	4

Table III
Influence of unhairing temperature on pelt properties and unhairing quality.

Unhairing temperature, °C	Unhairing variant	Index			
		Shrinkage temperature, °C	Removed collagen proteins, g/kg of hide	Swelling, %	Unhairing quality, points
20	1	60.8	0.17	16.8	3
	2	60.0	0.20	16.3	4
	Control	57.0	0.41	20.8	4
30	1	60.6	0.44	10.9	3
	2	58.0	0.48	2.3	4
	Control	55.0	0.87	0.7	4

carried out according to the same enterprise's technology. The unhairing–dermal opening process was executed as follows: H_2O – 100%, temperature – 20–22°C, $NaAlO_2$ – 2%, Na_2S (100%) – 1.5%, 2 hours run continuously, NaOH – 0.5%, 2 hours run continuously, later 5 min. every 3 hours, total duration 24 hours.

The qualitative properties of the produced leather were determined (Table V).

The solutions used in the industrial trials after the unhairing process were tested to evaluate the indexes of the pollution load. The results are presented in Table VI.

The experimental leather had a somewhat lower chromium content but its shrinkage temperature was almost the same as that of the control. Herewith, the experimental leather contained a smaller amount of matter that was soluble in dichloromethane. The relative elongation values are very close for both leathers, but control leather had a slightly higher tensile strength value. As reported by Aravindhan *et al.*, in order to enable the easy diffusion of chemicals, a series of pre-tanning operations ensure the opening up of the fiber bundles and the removal of the nonfiberous materials, resulting in a loose structure.[37] Chrome tanning provides for good inter and intra networking of fibers, but is unable to replenish the firmness found in the original raw material. Therefore, a lower tensile strength can be caused by a

Table IV
Dependence of properties of pelt on method of unhairing-dermal opening up.

Index	Unhairing-dermal opening up variant			
	1	2	3	Control
Swelling, %	16.3	19.3	23.5	17.4
Shrinkage temperature, °C	59.0	57.3	56.7	57.8
Removed collagen proteins, g/kg of hide	0.38	0.54	0.72	0.56
Removed non-collagenous proteins, g/kg of hide	3.74	4.58	5.20	3.23
pH of pelt after process	11.15	11.22	11.42	11.37
Porosity, %	45.9	49.9	51.8	47.5

Table V
Properties of leather depending on method of unhairing-derma opening up.

Indexes	Unhairing-dermal opening up method	
	experimental	control
Moisture content, %	13.6	13.6
Cr_2O_3 content, %	4.7	4.9
Shrinkage temperature, °C	108.0	108.3
pH of leather	3.61	3.61
Amount of matter soluble in dichloromethane, %	4.2	4.8
Tensile strength of leather, N/mm^2	16.6	17.2
Relative elongation of leather at the strain 10 N/mm^2, %	32.5	32.1
Relative elongation of leather at the break, %	55.3	52.1

higher level of nonfiberous materials removed during the derma opening up process. Despite the mentioned differences, both leathers met the quality requirements for shoe upper leathers.

It is evident that lime-free unhairing leads to less pollution of the wastewater. Unhairing when sodium aluminate is used allows a decrease of the pollution load by TSS, Kjeldahl nitrogen, and especially by sulphides. Meanwhile, it is still not clear why there is such a low amount of sulphides at the end of the experimental unhairing.

Research continues, seeking to reduce the consumption of sulphides incorporating enzymes.

Conclusions

Sodium aluminate can be used instead of lime for lime-free unhairing of hides. The qualitative removal of hair is achieved using a solution containing 2–3% of sodium aluminate and 1.3–1.5% of sodium sulphide. The effect of such a process on collagen is weaker than that of the conventional one. Increase of the temperature up to 30°C does not lead to better hair removal but significantly enhances the effect on collagen.

A qualitative derma opening up level can be reached by adding NaOH 0.5% into the unhairing solution after 2 hours of the process beginning and continuing the process for 22 hours. The addition of NaOH leads to better removal of non-collagen proteins, and, accordingly, to higher porosity.

Industrial trials of lime-free unhairing using sodium aluminate have shown that the leather produced, according to the main qualitative indexes, somewhat yields to conventionally produced leather, but it absolutely meets the quality requirements for shoe upper leathers. The lime-free unhairing when sodium aluminate is used leads to less pollution of wastewater.

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Table VI

Indexes of pollution load (g/kg of hide) and pH of wastewater after unhairing-dermal opening process.

Index	Unhairing-dermal opening up variant	
	experimental	control
Total dissolved solids	81	97
Total suspended solids	4.2	6.4
Na_2S	1.3	13.4
BOD	32.8	25.9
COD	48.0	90.7
Total Kjeldahl nitrogen	14.8	19.9
pH	12.46	12.52

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