Modern Unhairing Technologies for Effective Control of H_2S Release from Beamhouse Operations

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Abstract. The toxicity and obnoxious smell of hydrogen sulphide (H_2S) gas is an issue for the leather industry that has been contained rather than eliminated in tannery practice. Completely eliminating H_2S from tanneries while maintaining practical and economically feasible processing is still a big challenge to be addressed. Significant progress has been made by introducing robust and reliable low sulphide unhairing systems based on selective soaking and specific enzymatic liming auxiliaries. These systems allow the reduction of sodium sulphide offers from the typical 2.5% to 1% of pelt weight. These lower levels reduce the amount of hydrogen sulphide gas released into the environment from the liming float, as well as the amount of sulphide that is carried over in the hide to subsequent processing steps. Overall, the H_2S problem is not eliminated, but significantly reduced with this technology. In a further evolution of the technology, organic thio compounds can be used to fully or partially replace the already low levels of sulphide required, and thus allow to operate with offers well below 1%, or even completely without inorganic sulphide. Alternatively to, or in combination with organic thio compounds, H_2S scavengers can be used to reduce or eliminate hydrogen sulphide released from liming floats. Different types of scavengers are available, but the selection is limited for technical and economic reasons.

1 Introduction

The tanning process aims to transform hides in stable and imputrescible products namely leather using a large amount of chemicals. The complete leather manufacturing process is divided into three fundamental stages: beamhouse, tanning and post tanning, involving each several steps.

The first step is the soaking, which in an optimal way prepares the hide for the liming-unhairing treatment, one of the most important operations in the leather making process. The purpose of liming-unhairing is not only to remove hair, but also interfibrillary components, fatty matter and epidermis and to open up fiber structure.

A conventional hair burn unhairing process uses sulphide to achieve the goal of a fairly complete hair removal. The down-side is a high effluent load caused by the high amounts of chemicals used and the complete liquefying of hair.

The use of sulphide for unhairing has always been problematic. It has made unhairing one of the most investigated areas over the past few decades, where the focus has been to reduce the amount of sulphur-based products, but due to a lack of a workable economic alternative, sodium sulphide and sodium hydrosulphide are still the preferred chemicals used for breaking-down the hair. It results in the effluent being highly loaded with sulphide, with the associated risk of hydrogen sulphide emission from the effluent when the pH drops below 9.5.

This paper on hand shows how the release of hydrogen sulphide from beamhouse operations can be effectively controlled by a combination of technologies involving more effective unhairing with lower amounts of reductive agents, replacement of inorganic sulphide by an organic thio compound and the use of an appropriate H_2S scavenger.

2 Background

2.1 Unhairing effect of sodium sulphide

The traditional reductive liming process employs sodium sulphide in alkaline medium. Sodium sulphide is an effective and economic unhairing agent. The unhairing effect of sodium sulphide is at its maximum when SH^- and OH^- ions in the solution are present in equal quantities:

$$2Na_2S + 2\ H_2O = 2\ NaHS + 2\ NaOH$$

$$2NaSH + Ca(OH)_2 = 2NaOH + Ca(SH)_2$$

Covington has calculated the theoretical required amount of sodium sulphide of industrial grade (60-70%) for a hair burn process to be just 0.6%, relative to hide weight. In practice, the typical amounts employed for a reliable process are much higher, namely 2-3%. The main reason for this is the fact that the rate of unhairing depends on the concentration of sulphide ions (S^{2-}) in the float. Short floats are commonly used to obtain a high concentration of sulphide allowing an easy access of active process chemicals (e.g. lime, sulphide, enzymes etc) to the points of attack of the hair.

In a traditional hair burn process the point of attack of the hair is the keratin in the hair cortex, which is degraded by sulphide due to the breaking-down of cysteine bridges.

In the state-of-the-art hair safe process, where the keratin is protected by an immunisation step, the point of attack is mainly the protein of the hair bulb which is hydrolysed either solely due to the alkaline conditions or by proteolytic enzymes, if present. A second and equally important point of attack is the pre-keratin that is above the hair bulb; it can be degraded by proteolytic hydrolysis combined with the keratolytic effect of sulphide. (**Fig. 1**)

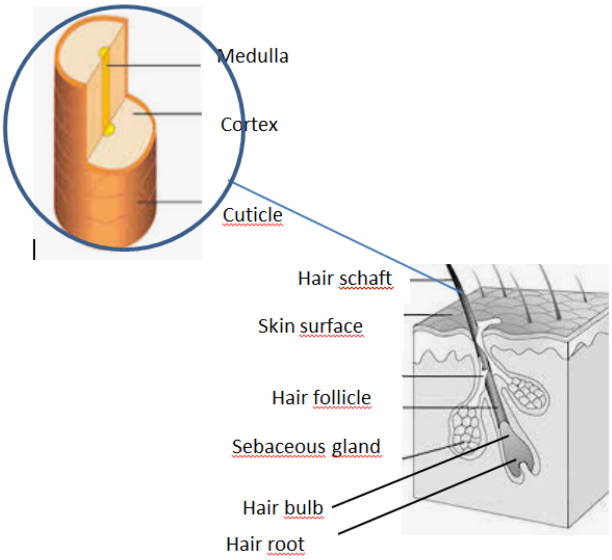

Fig. 1. Layers of the skin and hair structure.

Sodium sulphide used in the unhairing-liming step is one of the most dangerous materials applied in the leather making process. Upon acidification, solutions containing sulphide will release hydrogen sulphide gas into the working place.

Hydrogen sulphide is the reduced form of sulphur which can be formed by the reduction of sulfate (SO_4^{2-}) ions in contact with organic matter according to the following equation:

$$SO_4^{2-} + \text{organic matter} + H_2O + \text{microbial activity} = H_2S + H_2O + 2HCO^{-3}$$

Depending on the pH of the solution, there is an equilibrium between ionic species HS^- and S^{2-} and the neutral H_2S gas as shown in the **Fig. 2** below.

$$S^{2-} + H^+ = HS^-, \text{pka} = 12{,}9$$

$$HS^- + H^+ = H_2S, \text{pKa} = 6{,}97$$

$$H_2S = HS^- + H^+$$

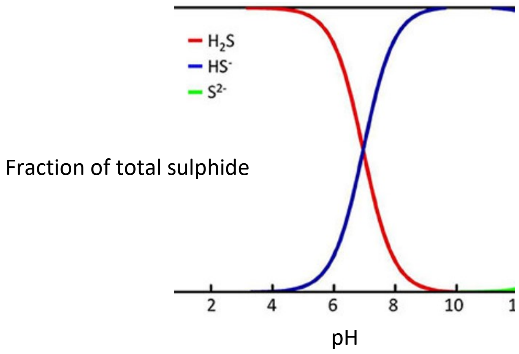

Fig. 2. Dissociation of H_2S with the pH.

2.2 Hydrogen sulphide

Hydrogen sulphide gas is an extremely hazardous gas, colourless, heavier than air, providing a strong and unpleasant odour already at low concentration.

In any tannery using sodium sulphide, the emission of low levels of hydrogen sulphide gas cannot be completely avoided, and the risk to release higher, potentially even lethal doses needs to be controlled very carefully.

Levels as low as 0.2 ppm of H_2S are already unpleasant. The effect on humans who absorb the gas through inhalation ranges from drowsiness to loss of consciousness to death, depending on how much the concentration exceeds the prescribed threshold exposure limits. At a concentration of 100 – 150 ppm the olfactory nerve is paralyzed after a few inhalations, and the sense of smell disappears, often together with the awareness of danger. At a concentration of 0.5% (5000ppm), the toxicity is so pronounced that a single breath is enough to cause immediate death within seconds.

There are legal limits for the concentration of H_2S gas at the workplace. A concentration of 15ppm over 15 minutes is internationally acknowleged as the Short Term Exposure Limit (STEL). Because sodium sulphide is such a highly toxic compound requiring safety precautions and extensive waste water treatment, the substitution of sodium sulphide by a non-hazardous alternative is a long held ambition.

The main challenge for the tanneries is to remove the hair completely with a sulphide offer of 1% or less.

The present work demonstrates the partial or total replacement of sodium sulphide by specific enzymes followed by an organic sulphur compound, matches the effectiveness of a traditional unhairing process.

Within a hair saving unhairing process, the removal of hair takes place by enzymatic hydrolysis of the soft proteins in the hair follicles, keeping the hair shaft intact. The thio compound has the capacity of cleaving the cystine molecule of the keratin protein, making it an excellent unhairing agent in its reduced form.

3 Materials and methods

3.1 Raw hide

Wet salted hides were used in the experiments. Liming experiments with thio compound were performed on a laboratory scale each with ca. 1000 g bovine hide. Formulations based on a thio compound and special additives were prepared in the lab and used as reductive agents. The concentration of the thio compound was varied over a range of 0.5 – 5.0% with 1% lime. All the chemical percentages were based on soaked weight. The unhairing efficiency for each trial was evaluated visually.

3.2 Measuring Hydrogen Sulphide

The measurement of the concentrations of hydrogen sulphide in the air were carried out with a portable hydrogen sulphide detector with a detection range of 0 - 100 ppm.

4 Results and discussion

4.1 Low sulphide enzymatic assisted unhairing

As outlined above, a hair save process requires first an immunisation step that protects the hair from degradation. This is affected by adding lime before any unhairing agents are introduced. Under the influence of the lime the cysteine of the hair is transformed into lanthionine, which can no longer be hydrolysed by reduction.

After the keratin of the hair is protected by immunization, the keratolytic effect of sulphide is directed solely at the pre-keratin above the hair bulb. This explains why, compared to a traditional hair burn process, the enzymatically assisted unhairing allows the reduction of the sulphide offer to levels of only 1% relative to hide weight on bigger bovine hides. The enzyme provides the strong proteolytic effect that is still also required, because the cells in Malpighi's layer and the basal cells of the hair bulb need to be attacked to achieve a good and consistent unhairing effect. In effect, the medulla, but not the cortex of the hair is being degraded. (**Fig. 1**)

The selection of specific proteolitic enzymes ensures that the collagen of the hide and particularly the grain remains undamaged throughout the process.

With the appropriate enzyme, a hair save process can be done without any compromise regarding the rate and effectiveness of unhairing or the cleanliness of the pelt as shown in the **Table 1**. The lower offer of sulphide also results in significantly reduced levels of S^{2-} in the liming float as well as in the hide. This means that later on in deliming and pickling, less H_2S will be released.

Table 1. Unhairing at different dosage of sodium sulphide.

	Condition of limed pelts	
Na_2S dosage (%on salted weight)	**Unhairing degree**	**H_2S gas formation**
2.6% in the lime float	excellent loosening of hair	pH12.6= 0ppm pH11 > 100ppm pH9 > 100ppm
1% in the lime float	excellent loosening of hair	pH12.6= 0ppm pH11= 60ppm pH9= 60ppm
0.6% in the lime float	moderate loosening of hair	pH12.6= 0ppm pH11= 25ppm pH9= 25ppm

The results from the low sulphide enzymatic assisted unhairing show a significant reduction of the main pollution parameters such as COD, TKN Nitrogen and total disolved solids (TDS) when compared with a conventional unhairing system. However, the H_2S gas formation issue is still not completely eliminated.

4.2 Further evolution of the technology, the use of organic sulphur compounds

Organic thio compounds with high reductive potential are effective unhairing agents and can be used as replacements for inorganic sulphide. The expected advantage of the use of the thio compound is the avoidance of H_2S gas formation even at low pH. The selected thio compound was checked at different concentrations and pH values for H_2S formation, and as expected it was confirmed that no H_2S was released at any pH between 12.5 and 3 for concentrations up to 5%. The results are given in **Table 2**.

Table 2. H_2S gas formation with thio compound.

Thio compound dosage	H_2S gas formation (from pH 12,5 to 3,0)
5 g/l	not detectable
15g/l	not detectble
30g/l	not detectable
50g/l	not detectable

The same organic thio compound was then used in an enzymatically assisted hair save unhairing process. The soaked hides were pre-treated in the drum with lime and the thio compound. With a concentration of 3% of thio compound, very satisfactory unhairing results were obtained without any additional offer of inorganic sulphide.

The result of these unhairing trials can be found in **Table 3**. Apart from the convincing unhairing effect, it was however very surprisingly found that some low levels of H_2S were still released from the pelt when the pH was lowered during the deliming stage.

Table 3. Unhairing at different dosage of thio compound used in an enzymatically assisted hair save system.

Thio compound dosage (% base on salted weight)	Unhairing degree	scud presence	H_2S gas formation (from pH 12.5 to 3.0)
0.5%	no loosening of hair	present	not detectable
3.0%	very good loosening of hair	clean pelt with yellowish aspect	pH 12.5= 0ppm pH9 <15ppm pH3 < 10ppm

This apparently seems to contradict the results previously obtained with the organic thio compound alone.

To understand these results, we need to consider that the immunization of the hair against reductive hydrolyses is never complete under practical circumstances. Without a physical elimination of the hair by filtering already at the early stage of unhairing, some reductive degradation of keratin will always happen. It may be assumed that the sulphur containing degradation products are absorbed by the pelt, leading to the formation of H_2S at lower pH during deliming and pickling. The exact mechanism of this conversion still to be elucidated.

4.3 Use of H_2S scavenger

As the previously described work shows, not even the complete removal of sulphide from the unhairing steps will fully avoid the release of H_2S during subsequent operations at lower pH. An effective method to nevertheless completely supress any release of H_2S is the use of oxidative auxiliaries during the relevant steps of the beamhouse process.

The effectiveness of the approach was demonstrated with a test performed in two steps, the first step consisting of an enzymatically assisted unhairing using an organic thio compound and the second consisting of a H_2S scavenging treatment using a formulation of oxidizing agents with additives. The unhairing results and detected H_2S gas formation are summarised in **Table 4.**

Table 4. Results of unhairing followed by H_2S scavenging.

Unhairing process	**Results**
hair save sulphide method	hide completely unhaired but H_2S gas formation
oxidative unhairing method with percarbonate	hide not completely unhaired but no H_2S gas formation
enzymatically assisted unhairing process with reduced sulphide and H_2S scavenger	hide completely unhaired with reduction of H_2S gas formation
enzymatically assisted unhairing process with thio compound and H_2S scavenger	hide completely unhaired without H_2S gas formation

The results indicate that the use of an enzymatically assisted unhairing process with organic thio compounds followed by an oxidative treatment step allows the full elimination of H_2S from beamhouse operations.

5 Conclusion

The objective of the study was to show that evolution of unhairing technologies allows reducing or eliminating hydrogen sulphide released from liming floats and pelts.

The suggested unhairing technology involving the use of an organic thio compound, in combination with oxidative agents with additives as H_2S scavengers in an enzymatically assisted unhairing provided the best available solution to eliminate sulphur in the liming process. The tests performed resulted in a great outcome in terms of cleanliness and complete removal of the hair without damaging the grain of the hide. The possible future studies combined with the obtained results make this process suitable for an industrial application.

The optimized low sulphide hair save liming process offers today the best possible compromise between leather quality, safety and significant reduction of the environmental impact.

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