PECULIARITIES OF NEUTRALIZATION OF LIME-FREE PELT OBTAINED USING SODIUM ALUMINATE

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Sodium aluminate can be used as an alternative to calcium hydroxide for qualitative unhairing of hide. Due to the absence of calcium compounds in the derma of the unhaired pelt, less-ammonia and non-ammonia methods of pelt neutralizations were tested. The experiments have shown the possibility to use almost two times less ammonia sulphate than conventionally or boric acid for qualitative neutralization of the pelt obtained using sodium aluminate. The pelts neutralized by both methods can be pickled and chromed conventionally, and properties of these pelts after chroming are close to the chromed leather produces by control method.

.Keywords: unhairing, sodium aluminate, neutralization.

INTRODUCTION

A major contributor to the pollution from the tanning industry is conventional unhairing using sodium sulphide and lime. Huge amounts of lime sludge and total solids formation are the main drawbacks of lime (Thanikaivelan *et al*., 2001). Herewith, the cleaning of unhairing solutions, polluted with lime, sulphides and products of protein degradation remains as very difficult and expensive. For this reason, the development of new and cleaner liming methods is perhaps the most urgent, compared with the perfection of other leather producing processes.

The use of lime-sulphide process remains as mostly applied unhairing-opening up of derma method in leather industry (Fennen *et al*., 2014). On the other hand, such process can be improveed as more clean and environment friendly as well.

The way to avoid the formation of solid lime sludge polluted by sulphides, protein degradation products, detergents etc. is replacement of lime by other soluble in water strong alkalis. Lime can be successfully replaced by sodium hydroxide. The developed lime-free method of unhairing-dermal opening up allows diminishing of consumption of sulphides and reaching of properties of chromium tanned leather not worse than those of leather produced using conventional method (Valeika *et al*., 2000; Kazlauskaite *et al*., 2002).

Thanikaivelan *et al*. (2001) proposed the method of hide unhairing-dermal opening up method which employs enzyme, low amount of sodium sulphide and sodium hydroxide. Later, a new hair saving unhairing method using a system containing enzyme preparation, sodium hydroxide, sodium sulphide, and disodium hydrophosphate was developed (Valeika *et al*., 2009).

Munz and Sonleitner (2005) report about developed methods of unhairing applying sodium silicate as lime substitute. They state that lime in the unhairing process can be substituted by sodium silicate without problems. As a result, effluent loading is reduced and so also sludge volumes from effluent treatment decreases.

Saravanabhavan *et al*. (2005) investigated a lime and sulphide-free unhairing process using a commercial enzyme with the activation using sodium metasilicate. The

process led to significant reduction in chemical oxygen demand and total solids by 53 and 26%, respectively. Liu et al. (2009) developed novel lime-free unhairing method based on system containing sodium silicate, enzyme, surfactant and urea. The environmental factors were all superior to the conventional liming process.

There is one more interesting material having strongly alkaline properties, good solubility in water and, comparatively, low price. This material is sodium aluminate, which is an important commercial inorganic chemical for various industrial technical applications (Sirvaityte *et al*., 2015).

It is very important that avoiding of the lime allows an improvement of deliming (or just neutralization) because there is not lime in the unhaired pelt. Since Helsinki convention (Helcom Recommendation, 1995) recommends refusing of ammonium compounds for the deliming, the serious attempts to replace the ammonia salts by other materials are done during these two decades.

Firstly, the use of carbon dioxide for the deliming could be mentioned. The method is investigated enough widely, and it is adopted for the practical use (Deng *et al*., 2015). Carbon dioxide can be used in solid state (dry-ice) as well. The option of using dry ice for deliming would be effective for cleaner leather manufacture (Sathish *et al*., 2013).

Zeng *et al.* (2011) report about deliming with a composite of sodium hexametaphosphate and boric acid. An analysis indicated that the deliming by sodium hexametaphosphate and boric acid produced clearer grain with less calcium salts.

Crudu *et al.* (2012) investigated deliming process based on a use of new multifunctional products based on maleic copolymers. The significant reduction in ammonium salts (up to 66%) and sulphates (78%) was reached in such case.

Weak acids such as lactic, boric, formic, citric and acetic acids or esters of organic acids can be used to substitute for ammonium salts. The investigations have shown that leather quality specifications obtained using different acids and ammonium sulphate were close to each other (Colak and Kilic, 2008). Peracetic acid acts as qualitative deliming agent as well (Sirvaityte *et al*., 2007; Sirvaityte *et al*., 2009). The treatment of limed pelt by peracetic acid allows removing not less calcium compounds than while using ammonium sulphate, qualitative deswelling of pelt. The use of peracetic acid entirely eliminates the emission of H_2S.

Therefore, the literature data suggest application of various materials instead of ammonia compounds for deliming process.

The main aim of the present research was to investigate neutralization of hide unhaired using sodium aluminate reaching to reduce ammonia compounds use or to replace them by other more environmentally friendly materials.

EXPERIMENTAL

Salted cowhide was used as raw material for this study. The soaked and washed hide was cut into pieces 5x10 cm and experimental series were prepared from these pieces. An unhairing-opening (experimental) up of derma structure of samples was carried out as follows: H_2O - 100%, temperature 25^oC, $NaAlO_2$ 2%, Na_2S (100%) 1.5%, 2 hours run continuously, NaOH 0.5%, 2 hours run continuously, later 5 minutes every 4 hours, total duration 24 hours (analytical grade sodium aluminate ($NaAlO_2$) containing Na_2O 40-45% and Al_2O_3 50-56% was used in this study). The liming-unhairing using lime and sodium sulphide was used as control method. The pickling and chroming of neutralised-bated samples were carried out accordingly to conventional technology.

The enzyme preparation (EP) *OROPON ON2* „TFL“ (Switzerland) was employed for the bating process.

The amount of collagen protein was estimated from the amount of hydroxyproline in the solution, and the amount of hydroxyproline was determined using a photo colorimetric method (Zaides *et al*., 1964).

The shrinkage temperature of hide samples, the pH of pelt and chromed leather, and the amount of chrome compounds in leather were determined according to standards (Standard ISO, 2002; Standard ISO, 1977; Standard ISO, 2009). Shrinkage temperature of chromed leather samples (wet-blue) was determined as described in the literature using special equipment and replacing the distilled water with glycerol (Golovteeva *et al*., 1982). The concentration of chromium in solution was determined according to the method described in the literature (Golovteeva *et al*., 1982).

RESULTS AND DISCUSSION

Two directions of the unhaired hide neutralization have been chosen: a) neutralization with decreased amounts of ammonium compounds, and b) neutralization with non-ammonia compounds. As non-ammonia compounds were tested lactic acid, boric acid and buffer containing acetic acid with sodium acetate. After preliminary investigation the most auspicious methods were found: a use of almost two times decreased amount of ammonia sulphate comparing as conventionally, and a use of boric acid.

Results of the neutralization are presented in Table 1.

Table 1. Methods of pelt neutralization-bating and process run quality indexes

Indexes	Pelt obtained by variant			
	1	2	3	4
	Unhairing-derma opening up method			
	Control	Experimental		
	Neutralization			
	H_2O – 40%, temperature 34-36°C, a) $(NH_4)_2SO_4$ – 2.2%, 30 min.; b) $(NH_4)_2SO_4$ –1.5%, 30 min.		H_2O – 40%, temperature 34-36°C, $(NH_4)_2SO_4$ – 2%, 1 hour	H_2O – 40%, temperature 34-36°C, a) boric acid 1.5%, 30 min.; b) boric acid 1.5%, 30 min.
	Bating (in neutralization solution)			
	H_2O – 100%, EP *OROPON ON2* – 0.15%, 1 hour			
Solution pH after process	8.97	8.76	9.04	8.10
pH of pelt	8.98	8.96	9.12	8.58
Shrinkage temperature, °C	64.0	65.3	65.2	66.0
Removed collagen proteins, g/kg of hide	0.42	0.34	0.33	0.41

Note. Shrinkage temperature of pelt after unhairing: control 56.3°C; experimental 57.3°C.

After the neutralization adding almost two times less amount of ammonia sulphate (variant 3), about 10-15% of thickness of the pelts' cross-section was coloured into

slight pink when phenolphthalein had been dropped onto it. The pelt neutralized by boric acid after phenolphthalein test was very similar to the previous mentioned one. The control pelt (1 variant) and the pelt obtained by the use of sodium aluminate but neutralized conventionally (2 variant) had no pink colour after phenolphthalein test.

Other qualitative indexes after neutralization were close for the pelt obtained following all four variants. On the other hand, the less effect on collagenous proteins during the neutralization of the experimental pelt by the use of ammonia sulphate was observed.

The neutralized and bated pelts were washed, pickled and chromed. The indexes showing quality of chroming process and of chromed leather are presented in Table 2.

Table 2. Indexes of chroming and chromed leather

Indexes	Pelt obtained by variant			
	1	2	3	4
Solution pH after process	3.91	3.94	3.78	3.84
pH of leather	3.61	3.78	3.89	4.08
Shrinkage temperature, °C	109.3	111.0	110.6	109.6
Cr_2O_3 content in leather, %	4.91	4.23	4.18	3.87
Exhaustion of Cr_2O_3, %	80.3	79.0	78.7	75.4

The analysis of the chromed leather allows supposition that leather treated with sodium aluminate bounds less chromium compounds comparing with conventional one. This index slightly depends on the neutralization method as well. The exhaustion of the chromium compounds has similar trend of course: more chromium in a leather means less amount in the used chroming solution. The most interesting thing in this situation is that chromium content in the leather had not direct influence on the shrinkage temperature of it. All samples had almost the same shrinkage temperature. It can be supposed that in control sample not all chromium compounds are bound by two links. Therefore, they are joined in the leathers' structure but do not increase the thermostability of the leather.

CONCLUSSIONS

The pelt unhaired and opened up using sodium aluminate, sodium sulphide and sodium alkali due to the absence of calcium compounds in the derma can be neutralized using 2% of ammonia sulphate or 3% of boric acid. The pelt after neutralization-bating, and had similar properties as conventionally neutralised one. Accordingly, after chroming these pelts were also very close in their properties. On the other hand, they characterised by less chromium content comparing with control leather.

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