NEUTRALISATION AND BATING OF HIDE UNHAIRED USING SODIUM SILICATE AND SODIUM SULPHIDE

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Various methods of neutralisation of hide unhaired with sodium silicate and sodium sulphide have been investigated seeking to reduce or refuse ammonium sulphate conventionally applied for the neutralisation. Due to the high release of ammonia into the environment, alternative materials are being sought that do not impair the properties of the hide being processed and that a high-quality chromed semi-finished product of leather can be obtained. In the research, different methods of hide neutralisation and their influence on subsequent hide treatment processes qualitative indexes of the obtained leather were analysed and described. It has been found that after unhairing with sodium silicate and sodium sulphide hide, it is appropriate to neutralise and bate the hide by adding 1 % ammonium sulphate, 0.8 % lactic acid and 0.15 % proteolytic enzyme preparation OROPON ON2. To obtain the best quality of chromed semi-finished product of leather, it is advisable to pickle the hide using not more than 1 % sulfuric acid. In this way, neutralised-bated, pickled and chromed leather's quality meets the quality requirements for chromed semi-finished product of leather.

Keywords: unhairing, pelt, neutralisation, ammonia, lactic acid

INTRODUCTION

The leather industry earns special attention because of its strong potential for foreign exchange earnings and employment generation prospects. This industry has developed enormously over the past decades; since then, leather has become a material of choice in the world of fashion. However, this industry, like many others, is facing stringent environmental regulations worldwide, due to vast usage of toxic chemicals and generation of hazardous waste (Khambhaty, 2020).

Despite the fact that liming with sulphides is still the most commonly used process for obtaining unhaired pelts, new methods of hide/skin unhairing-derma opening up are being intensively developed. The main disadvantage of sulphide liming is that the cleaning of unhairing solutions, polluted with lime, sulphides and products of protein degradation remains very difficult and expensive (Sirvaityte *et al*., 2016).

After liming, lime in the unhaired pelt is no longer required, and in most cases, it has a detrimental effect on subsequent tannage. Accordingly, the lime must be removed. Unfortunately, the deliming is not simple neutralisation of lime, and, due to this, only specific chemical materials can be applied. The deliming materials have to have ability to react with lime forming soluble in water compounds; to decrease the pH of the pelt; to remove swelling of the derma tissue (Sivakumar *et al*., 2015).

Removal of the calcium is achieved by decreasing the pH value with acidic chemicals. By acidifying the collagen at pH – 12.5, the amino groups are protonated. Thereby, positive charges neutralise negative charged collagen, and the fibre structure opens, facilitating chemicals to penetrate. In conventional deliming, ammonium salts

https://doi.org/10.24264/icams-2022.III.18

are preferred for this application because they enable comparable short process times and buffer the pH to around 9. When the pH value is not stable, the selection of convenient bating enzymes for the following working step is not possible (Prokein *et al*., 2020; Covington, 2009). Unfortunately, ammonium salts generate considerable amount of ammonia, making tannery environment unhealthy (Sivakumar *et al*., 2015).

Probably, the best way to avoid the pollution caused by the sulphide-lime unhairing is to refuse the employing of lime overall. Many new methods are developed that allow replacing lime with other materials. Firstly, it is enzymatic unhairing. There are a few possible ways to adopt enzymes for the unhairing process. The first one is when the enzymes are applied for a pure enzymatic process, in such a case, the unhairing effect is achieved, owing to the enzyme used (Shrinivas and Naik, 2011; More *et al*., 2017). The next way is to use enzyme and oxidising agents. In such a case, enzymes are used for the main unhairing and oxidisers are used for degrading of hair remnants. Proteases that act in an alkaline or acidic medium are used in such cases (Valeika *et al*., 2012). Unfortunately, so far, such unhairing methods have been applied merely at laboratory scale (Khambhaty, 2020).

The next possibility is to replace lime with other alkalis such as sodium hydroxide (Valeika *et al*., 2000) or sodium aluminate (Sirvaityte *et al*., 2016). In addition, the application of soluble silicates is very promising (Sirvaityte *et al*., 2015).

It is very important that absence of lime in a pelt allows the use of wide spectra of neutralising materials (Zeng *et al*., 2011; Sirvaityte *et al*., 2007; Crudu *et al*., 2012) because there is no lime and there is no possibility to form insoluble calcium compounds.

The main aim of the present research was to investigate neutralisation of unhaired hide using sodium silicate to reduce the use of ammonia compounds or replace them and to assess the influence of the neutralisation on chromed leather properties.

EXPERIMENTAL

Salted cowhide was used as a raw material for this study. The soaked and washed hide was cut into 5x10 cm pieces 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 20-22°C, Na_2SiO_3 2%, 2 hours run continuously, Na_2S (100%) 1%, 2 hours run continuously, H_2O – 50%, NaOH 0.5%, 2 hours run continuously, later 5 minutes every 4 hours, total process duration 24 hours; drain. Washing: H_2O – 100%, temperature 36-38°C, 0.5 hour run continuously, drain; again H_2O – 100%, temperature 36-38°C, 0.5 hour run continuously, drain. 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 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

https://doi.org/10.24264/icams-2022.III.18

in solution was determined according to the method described in the literature (Golovteeva *et al*., 1982).

RESULTS AND DISCUSSION

Twelve compositions were tested to neutralise the pelt after unhairing with sodium silicate and sodium sulphide. For all variants, some of the neutralisation conditions were the same: H_2O 40% (percent are based on pelt weight), temperature 36-38°C, run continuously. Bating (in neutralisation solution) conditions were the same for all variants: H_2O 100%, EP OROPON ON2 0.15%, 1 hour run continuously. Neutralisation variants:

1. $(NH_4)_2SO_4$ 2%, 30 min.; $(NH_4)_2SO_4$ – 2%, 30 min. (control);
2. $(NH_4)_2SO_4$ 2%, 1 hour;
3. $(NH_4)_2SO_4$ 1%, 1 hour;
4. Lactic acid 2.4%, 30 min.; lactic acid 2.4%, 30 min.;
5. $(NH_4)_2SO_4$ 1%, 20 min.; lactic acid 0.8%, 20 min.; lactic acid 0.8%, 20 min.;
6. H_3BO_3 1.5%, 30 min.; H_3BO_3 1.5%, 30 min.;
7. $(NH_4)_2SO_4$ – 1% 20 min.; $NaCH_3COO$ 0.15%, CH_3COOH 1% 20 min.; $NaCH_3COO$ 0.15 %, CH_3COOH 1 % 20 min.;
8. $NaCH_3COO$ 0.2 %, CH_3COOH 1.5% 20 min.; H_3BO_3 1.5%, 20 min.; lactic acid 0.4% 20 min.;
9. $(NH_4)_2SO_4$ – 1%, 20 min.; lactic acid 0.4% 20 min.; lactic acid 0.4% 20 min.;
10. $(NH_4)_2SO_4$ – 1%, 30 min.; lactic acid 0.4% 30 min.;
11. $(NH_4)_2SO_4$ – 1% 10 min.; $NaCH_3COO$ 0.2%, CH_3COOH 0.5% 50 min.;
12. $NaCH_3COO$ 0.2 %, CH_3COOH 0.5% 10 min.; lactic acid 0.4% 50 min.

The quality of neutralisation was assessed determining pH of solution and pelt after process; shrinkage temperature and porosity of pelt; amount of removed collagenous proteins (Table 1) and observing the colouring of cross-section of pelt by phenolphthalein.

Table 1. Indexes of neutralisation process

Neutralisation variant	Index				
	pH of solution	pH of pelt	Shrinkage temperature of pelt, °C	Porosity of pelt, %	Removed collagen proteins, g/kg of pelt
1 (control)	8.52	8.36	63.8	66.5	0.40
2	8.82	8.54	62.7	65.6	0.51
3	9.09	8.83	63.0	64.2	0.42
4	3.01	3.51	47.7	58.2	0.26
5	4.26	6.86	62.5	63.9	0.40
6	8.18	8.59	63.2	59.1	0.77
7	4.51	4.28	57.8	65.3	0.27
8	4.52	4.90	60.3	64.0	0.40
9	8.27	8.37	63.7	65.2	0.09
10	8.92	-	-	-	-
11	8.48	8.31	63.8	67.01	0.11
12	5.95	-	-	-	-

Note: Shrinkage temperature of pelt after unhairing 57.0 °C, porosity 55.8 %.

The pelts were completely neutralised during two hours of treatment with the neutralising materials and the enzyme by almost all neutralisation methods (1-9 and 11),

https://doi.org/10.24264/icams-2022.III.18

with the exception of variants 10 and 12, which resulted in a reddish discolouration of the pelt's cross-section by the application of phenolphthalein.

As the most promising 2nd and 9th variants were chosen for the further experiments. Therefore, the pelt after neutralisation according to 1 (control), 2 and 9 variants was pickled using conventional technology (percent are based on pelt weight): H_2O 100%, NaCl – 5.5%, 15 min.; HCOONa 1%, 20 min.; H_2SO_4 0.5%, 15 min.; H_2SO_4 0.5%, 15 min.; H_2SO_4 0.5%, 5 hours; regime run continuously. The results are presented in Table 2.

Table 2. Indexes of pickling dependently on neutralisation method

Neutralisation variant	Index				
	pH of solution	pH of pelt	Shrinkage temperature of pelt, °C	Porosity of pelt, %	Removed collagen proteins, g/kg of pelt
1 (control)	2.74	2.84	43.0	56.8	0.03
2	2.73	2.78	42.7	64.4	0.04
9	2.70	2.77	40.5	55.8	0.05

The obtained data show similar action of pickling on variously neutralised pelt. Herewith, there are some differences in shrinkage temperature and porosity after pickling.

The pickled samples were chromed according to conventional technology. The results are presented in Table 3.

Table 3. Indexes of chroming dependently on neutralisation method

Neutralisation variant	Index				
	pH of solution	Shrinkage temperature of leather, °C	Cr_2O_3 in leather, %	Exhaustion of Cr_2O_3, %	Porosity of pelt, %
1 (control)	3.23	84.3	2.42	46.9	67.6
2	3.23	86.7	2.32	44.9	68.3
9	3.19	90.0	2.37	51.6	66.9

The chroming was low quality independently on the neutralisation method. The main reason was too low pH after chroming and, accordingly, bad chromium fixation. Since the pH of pickled pelt and chroming solution depends on pH after pickling, presumably, the amount of acid for pickling of such pelt should be reduced.

Therefore, pelt was neutralised according to the 9th method and pickled in three ways: 1 – conventionally (1.5% H_2SO_4); 2 – using 1% H_2SO_4; 3 – using 1% H_2SO_4 and 1% CH_3COOH (other conditions were the same). Conventional chroming was carried out for the pickled pelts. The results are presented in Table 4.

Table 4. Indexes of pickling and chroming dependently on pickling method

Pickling variant	Indexes						
	Pickling			Chroming			
	pH of solution after pickling	pH of pelt after pickling	Shrinkage temperature after pickling, °C	pH of leather after chroming	Exhaustion of Cr_2O_3, %	Cr_2O_3 in leather, %	Shrinkage temperature of leather, °C
1	2.73	2.86	35.7	2.90	63.4	3.43	104.1
2	3.73	3.72	48.7	3.38	76.7	4.61	114.0

https://doi.org/10.24264/icams-2022.III.18

3	3.54	3.21	43.7	3.04	61.4	3.36	101.1

Summarising the results in Table 4 it can be concluded that it is preferable to add 1 % sulphuric acid during pickling to produce qualitative semi-finished chromed product.

CONCLUSIONS

The pelt obtained by unhairing-derma opening up with the use of sodium silicate and sodium sulphide can be qualitative neutralised and bated with 1 % of ammonium sulphate, 0.8 % of lactic acid and adding 0.15 % of the enzymatic preparation OROPON ON2 for the bating. Since the conventional pickling process produces a too acidic pelt, less sulphuric acid (1%) needs to be added to the pickling of such pelt. The chromed semi-finished product obtained after such pickling and chroming had a high shrinkage temperature (114°C), a high content of chromium compounds in the derma (4.6%) and a relatively high exhaustion of chromium compounds during the chroming was reached.

REFERENCES

Covington, A.D. (2009), *Tanning Chemistry: The Science of Leather*, RSC Publishing, Cambridge.

Crudu, M., Gaidau, C., Crudu, A., Popescu, M. and Ionescu, M. (2012), "Innovative Material-Technology System for Reduction of Environmental Pollution with Salts", *Polymer Chemistry and Technology: Proceedings of Scientific Conference Chemistry and Chemical Technology*, Kaunas, Lithuania.

Golovteeva, A.A., Kutsidi, D.A. and Sankin, L.B. (1982), *Laboratornyj praktikum po khimiyi i tekhnologiyi kozhy i mekha*, Legkaiya i Pischevaiya Prom. Moscow (in Russian).

Khambhaty, Y. (2020), "Applications of Enzymes in Leather Processing", *Environmental Chemistry Letters*, 18(3), 747-769, https://doi.org/10.1007/s10311-020-00971-5.

More, S.Y., Bholay, A.D. and Nalawade, P.M. (2017), "Eco-Friendly Applications of Bacterial Extracellular Alkaline Protease", *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 11(4), 81–87, https://doi.org/10.9790/2402-1104018187.

Prokein, M., Chrobot, A., Renner, M. and Weidner, E. (2020), "Free of Salt High-pressure Deliming of Animal Hides", *Environmental Science and Pollution Research*, 27, 35567–35579, https://doi.org/10.1007/s11356-020-09765-2.

Shrinivas, D. and Naik, G.R. (2011), "Characterization of Alkaline Thermostable Keratinolytic Protease from Thermoalkalophilic *Bacillus halodurans* JB 99 Exhibiting Dehairing Activity", *International Biodeterioration and Biodegradation*, 65(1), 29–35, https://doi.org/10.1016/j.ibiod.2010.04.013.

Sirvaitytė, J., Beleska, K. and Valeika, V. (2016), "Lime Free Unhairing: Sodium Aluminate as an Alternative Towards a Cleaner Process", *Journal of the American Leather Chemists Association*, 111(11), 406-412.

Sirvaityte, J., Beleska, K., Valeikiene, V., Plavan, V. and Valeika V. (2015), "Immunization Action of Sodium Silicate on Hair: Part 2 Hair-save Process Based on Lime Substitution by Sodium Silicate", *Journal of the Society of Leather Technologists and Chemists*, 99(5), 231-237.

Sirvaitytė, J., Valeika, V., Beleska, K. and Valeikiene, V. (2007), "Action of Peracetic Acid on Calcium in Limed Pelt", *Journal of the Society of Leather Technologists and Chemists*, 91(3), 123-127.

Sivakumar, V., Ponnusawmy, C., Sudalaimani, K., Rangasamy, T., Muralidharan, C. and Mandal, A.B. (2015), "Ammonia Free Deliming Process in Leather Industry Based on Eco-benign Products", *Journal of Scientific and Industrial Research*, 74(9), 518-521.

Valeika, V., Balciuniene, J., Beleska, K. and Valeikiene, V. (2000), "Lime-free Unhairing: Part 3 Influence of Unhairing Method on Chemical, Physical and Mechanical Properties of Pelt and Leather", *Journal of the Society of Leather Technologists and Chemists*, 84(4), 165-169.

Valeika, V., Beleska, K. and Sirvaityte, J. (2012), "Alkali-free Method of Hide Preparation for Tanning", *Brazilian Journal of Chemical Engineering*, 29(2), 315–323, https://doi.org/10.1590/S0104-66322012000200012.

Zaides, A., Mikhailov, A. and Pushenko, O. (1964), "Modiphitsirovanyi method opredeleniya oksiprolina", *Biokhimiya*, 1, 5-6 (in Russian).

Zeng, Y.H., Lu, J.H., Liao, X.P., He, Q. and Shi, B. (2011), "Non-ammonia Deliming Using Sodium Hexametaphosphate and Boric Acid", *Journal of the American Leather Chemists Association*, 106(1), 257- 263.

*** (1977), Standard ISO 4045:1977. Determination of pH.

https://doi.org/10.24264/icams-2022.III.18

*** (2002), Standard ISO 3380: 2002. Leather – Physical and mechanical tests – Determination of shrinkage temperature up to 100 degrees C.
*** (2009), Standard ISO 5398-2: 2009. Leather - Chemical determination of chromic oxide content - Part 2: Quantification by colorimetric determination.

https://doi.org/10.24264/icams-2022.III.18