Short-term Preservation of Hides and Skins Using Peracetic Acid

by

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Abstract

Treatment with a mixture of sodium hydroxide, hydrogen peroxide and acetic anhydride at 15-20°C during 2 h allows preservation of hide during 20 days at temperature 22±1°C. Prolongation of the treatment duration more than 2 h and increase of the treatment temperature higher than 20°C do not markedly increase the preservation effect but affects hide structure at these higher level. The application of short-term preservation methods leads to substantial decrease of materials consumption. Preserved by oxidative method hide is more sensitive to chemicals during technological processes than ones cured by sodium chloride, and its derma structure is opened in higher level. It binds more chromium compounds during chroming. The crust leather produced from hide preserved by oxidative method characterized by satisfactory strength properties. The use of proposed short-term preservation of hide allows reduction of Cl^- concentration in wastewater more than 11 times.

Introduction

Despite incomes, the leather industry is a high pollutant industry. The reason for this is that leather is not a "friend" of the environment, as it plays a role in the environmental destruction caused by the meat industry as well as the pollution caused by the materials used in leather preservation and processing. For this reason, raw hide preservation has always been a challenge for leather manufacturers.[1]

The raw hides and skins are flayed from the animals and deterioration of the skin starts within 5–6 h after flaying. As the main constituent of raw skins and hides is highly susceptible to bacterial action protein, it is essential to preserve the protein matrix and - temporarily arrest microbial attacks.[2] The preservation has the aim to converse flayed hide/skin into resistant to putrefaction raw material suitable for transportation and storage during particular time. Preservation is accomplished either by destroying active bacteria, by preventing bacterial activity or by preventing bacterial contamination.[3] Wet salting, the conventional method of curing, is followed by most of the tanners because of its practical advantages; employs approximately 40-50% sodium chloride on raw material and is subsequently removed during the soaking operation.[4] The use of the salt causes the significantly higher pollution of tannery effluent, especially by total dissolved solids (TDS) and chlorides (Cl^-).[5] We should not to forget that all chlorides which fall into wastewater of tanneries are not eliminated from it and pass into environment. Therefore, it is very serious reason to develop new and more environmentally friendly preservation methods, which lead to bacteria growing inhibition because sometimes is last 1-2 weeks to gather for processing enough skins or hides. Therefore, such methods are titled as "short-term preservation methods" and allow preservation of hides or skins relatively short time comparing with storage duration after salting.

Short-term preservation method can be divided into physical and chemical ones. The physical methods of short-term preservation are very convenient because any chemical materials are not required for the treatment. The most simple method of physical preservation is cooling of hide/skin at between +2 and +5°C.[6] The hides preserved with this method can be stored until 2 weeks when is kept at 5°C or, accordingly, 3 weeks at 0°C.

The other method of cooling is to add ice. It is possible to cool hides and skins in a continuous way in a mixer by using some ice cubes, cakes or flakes, just after flaying. Within 2 h, the temperature of hides is reduced from 30°C to 10°C. These hides can be stored for 24 h without further treatment.[2] Also, dry ice can be used for this purpose. It gives a uniform cooling and preserves the hides or skins for a minimum of 48 h.[2]

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Radiation processing (irradiation) is a safe method involving systematic exposure of materials to ionising energy to effect specific chemical or biological changes. Despite the fact that sufficiently energetic is used to drive chemical reactions in such case, the obtained emitted by this energy radiation does not induce radioactivity. Consequently exposed products cannot pose any radiation danger. The two principle radiations used by industry are gamma rays and electron beams. For hide processing, for reasons of efficacy, safety, versatility, speed and cost, electron beams are more superior than gamma rays. In electron beam processing, ionizing energy is produced without the use of any radioactive materials.[7, 8]

Overall, the cooling preservation or radiation treatment is not practical because these methods are too complicated for little slaughterhouses. Usually, small suppliers of hides and skins need cheap, simple and fast preservation method.

Therefore, chemical methods of short-term preservation are more convenient than the other methods due to simplicity of use and needless of special equipment. Such materials as neem oil,[9] potassium chloride,[10] polyethylene glycol[4] silica gel,[11] sodium sulphite with acetic acid,[12] acetic acid with benzoic acid,[13] and crude glycerol with polyethylene glycol polymers[14, 15] are investigated as possible preservatives for short term preservation of skins/hides. The main problem of the use of suggested methods is that preservation materials act on collagen, they cause undesirable changes in derma structure and these factors require changes in leather processing technology seeking to produce high quality leather.

Here could be mentioned attempts to use materials having oxidative action for preservation of hides/skins. Sodium chlorite or ozone were employed as preservatives for curing of hides/skins.[16, 17] Ozonized samples kept in open atmosphere gave encouraging results and found to be as effective as control salting method. Unfortunately, the samples kept in the sealed bag were started putrefying in 2 days possibly due to anaerobic microbial activity.

Strong oxidizers are proposed for preservation of raw hides or skins and deliming process. Attempts to use hydrogen peroxide,[18] calcium peroxide[19] for unhairing or peracetic acid for deliming process are attempted.[20, 21]

The main aim of this research was to use peracetic acid (PAA) for short-term preservation of hides and evaluate the impact of preservation on collagen and on processed leather qualitative properties.

EXPERIMENTAL

Raw Material

One fresh cow hide (taken not later than 2 h after flaying) was used for preservation quality evaluation. The cow hide had been cut into pieces 10 x 10 cm and experimental series containing 4 pieces were formed. A treatment of pieces with chemicals was performed in a laboratory drum with capacity of 3liters. After the treatment, each experimental series was stowed into polyethylene box to prevent from desiccation and stored at temperature 22±1°C. The pieces without any treatment were used as control samples.

Next fresh cow hide (taken not later than 2 h after flaying) was used. Firstly, the cow hide was cut along backbone line into two halves: left (experimental) and right (control). The right half was salted using 50% (on fresh hide mass) sodium chloride and left for two weeks of storage. The left half was preserved by oxidative method and left for two weeks of storage as well. Both halves were enveloped into polyethylene film to prevent from desiccation and stored at temperature 22±1°C.

Oxidative Preservation Method Variants

- **Variant A**: H_2O 100% (% based on fresh hide weight), NaOH 0.25%, H_2O_2 0.225%, $(CH_3CO)_2O$ (acetic anhydride) 1%, temperature 20°C, duration 2 h, run continuously;
- **Variant B**: H_2O 100%, NaOH 0.5%, H_2O_2 0.3%, $(CH_3CO)_2O$ 1.5%, temperature 20°C, duration 2 h, run continuously;
- **Variant C**: H_2O 100%, NaOH 1%, H_2O_2 0.45%, $(CH_3CO)_2O$ 2%, temperature 20°C, duration 2 h, run continuously.
- **Variant D**: H_2O 100%, NaOH 2.2%, H_2O_2 1.5%, $(CH_3CO)_2O$ 6%, temperature 20°C, duration 2 h, run continuously.
- Concentration of PAA acid, which forms after mixing of mentioned materials, is accordingly: ~0.4% (**Variant A**), ~0.7% (**B**); ~1.1% (**C**) and ~2.8% (**D**).

Chemical Materials

All chemicals used in experiments were of analytical grade. The commercial chemical materials conventionally used for leather processing were employed as well.

Evaluation of Preservation Quality

Quality of preservation was assessed organoleptically observing any hair slip, appearance of bad odour and appearance of mucous surface of hide. Next method of the preservation quality assessment was to determine the total number of bacteria on hide. The direct method of bacteria amount determination was used.[13]

The sample of hide was considered as deteriorated when any symptom of decay appeared: hair slip, bad odour, or mucous

surface of skin, or the total number of microorganisms on hide exceeded 20×10^6 units per 1 g of hide.[13]

Determination of Hide and Leather Properties

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.[22] The total amount of protein was estimated by employing Kjeldahl's method.[23]

Shrinkage temperature of hide samples was determined as standard.[24] The concentration of chromium in solution was determined using method, which is based on oxidation of the presented in the solution trivalent chromium into hexavalent using hydrogen peroxide, and further iodometric titration.[23]

Strength properties, the amount of chrome compounds in leather, soluble matter in dichloromethane, and volatile matter were detected according to standards.[25-28]

Determination of chromed leather samples shrinkage temperature was carried out using special equipment and method described in the literature when the distilled water is replaced by glycerol.[23]

Statistical Analysis

All data were expressed as the average value of triplicate measurements. Confidence limits were set at $P<0.05$. Standard deviations did not exceed 5% for the values obtained.

RESULTS AND DISCUSSION

Mixture of sodium alkali, hydrogen peroxide and acetic anhydride was used for the preservation of hides. PAA can be produced by few methods. PAA with concentration 15-17% can be produced using hydrogen peroxide and acetic acid (catalyst – H_2SO_4).[10] The produced PAA has pH about 0, so, it is very strong acid, and cannot be directly used for hide preservation.

Other method of PAA production is the reaction using following reactants in the following amounts: (a) an aqueous hydrogen peroxide source to provide in the reaction mixture an active oxygen concentration of 0.8 to 12.0 volumes, (b) acetic anhydride in an amount to provide an acetic anhydride to hydrogen peroxide (calculated as 100%) molar ratio of 1.0 to 1.16 to 1, and (c) an alkaline catalyst compatible with active oxygen in an amount to provide a pH in the reaction mixture of 5.4 to 7.0, and continuously withdrawing an aqueous PAA reaction product at a concentration of about 0.5 to 7% by weight at a rate to provide in the reaction a residence time preferably 1 to 2 minutes.[29]

First step of the investigation was a determination of an influence of the parameters of the treatment (materials concentration, temperature and duration) on the hide preservation time. Evaluating influence of concentrations of materials on preservation time the hide samples were treated according to the variants described in Experimental part. The dependence of the preservation effect on the concentrations of materials used for treatment is presented in Table 1.

The treatment using composition containing sodium alkali, hydrogen peroxide and acetic anhydride depending on their concentrations allow preservation of hide samples without any attributes of deterioration accordingly 15-23 days. So, it can be concluded that oxidative preservation using the presented composition is sufficiently effective comparing with the short term preservation methods presented by other investigators.[17, 30]

The preservation duration is very important factor estimating a preservation method but also it is very important to know how materials used for the treatment act on the treated hide structure. The observation of hide samples after treatment has shown that treatment according to **Variant C** causes slight observable swell of hide sample. So, it can be the symptom of too strong effect of the used materials on the treated hide. The change of hide properties due to preservation can lead to undesirable decrease of produced leather quality.

Therefore, the experiment was repeated treating hide samples under conditions as described in **Variants A, B** and **C**. To set off the effect of materials on the hide, a treatment using increased materials concentrations was carried out (**Variant D**). After treatment a shrinkage temperature of hide samples has been determined during all time of hide samples storage till the signs of deterioration appeared (Figure 1).

The results show that using preservation with lower materials concentrations (**Variants A** and **B**), the shrinkage temperature of hide after the treatment is decreased by 3-4°C (shrinkage temperature of fresh hide was 67°C) and further slightly decreases during first 5-6 days of storage. After that, the

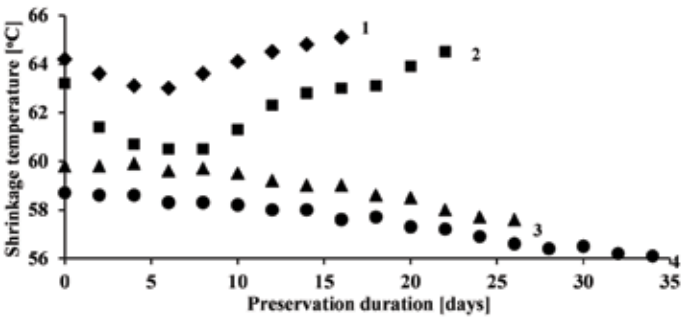

Figure 1. Dependence of hide shrinkage temperature kinetics on duration of preservation when fresh hide treatment is carried out according to variant: 1 – **A**, 2 – **B**, 3 – **C** and 4 – **D**.

shrinkage temperature begins to increase, and, when deterioration features appears, almost reaches the shrinkage temperature of fresh hide: 65°C (**Variant A**) and 64.2°C (**Variant B**).

The increase of materials concentration leads to significant effect on structure of hide samples. The swelling of samples is observable even after treatment according to **Variant C.** During the treatment shrinkage temperature decreases by 8-9°C. During the storage of samples further decrease of shrinkage temperature continues, and both indications decrease of shrinkage temperature and swelling allow a conclusion about serious change of derma structure, which is not desirable effect. Next step was to estimate an influence of treatment duration on hide storage time and shrinkage temperature variations through the storage. The fresh hide samples were treated under conditions described in **Variant B** excepting the treatment duration, which was 0.5, 1, 2 and 3 h.

The prolongation of treatment duration increases the storage time of hide samples (Table 2). On the other hand, the prolongation of treatment duration from 2 up to 3 h has negligible effect on the storage time: it is prolonged only by 1 day.

In Figure 2 are presented results of the determination of hide shrinkage temperature during storage. The character of the curves shows that prolongation of the treatment duration increases the decrease of shrinkage temperature. The prolongation of treatment duration from 2 up to 3 h has negative effect on hide structure: shrinkage temperature of hide samples restores in lower level comparing with samples treated 1 or 2 h.

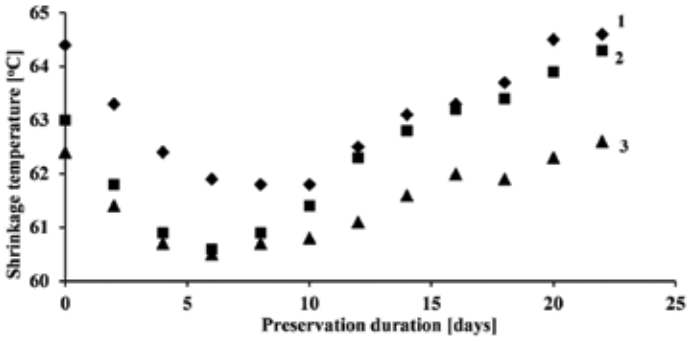

Figure 2. Dependence of hide shrinkage temperature kinetics on duration of preservation when fresh hide treatment duration is: **1** – 1 h, **2** – 2 h and **3** – 3 h.

TABLE I
Effect of concentration of materials used for treatment on on microbial growth.

Hide storage duration, days	Numbers of microorganisms (x 10^{-6}) in 1 g of hide during storage of hide after treatment according to variant		
	A	B	C
3	1.2	0.9	0.4
5	0.9	0.6	0.3
9	1.4	0.8	0.3
11	2.2	0.9	0.4
15	17.6	2.3	0.9
16	29.8	-	-
17	-	4.8	2.1
19	-	10.7	4.9
21	-	24.8	8.7
23	-	-	15.2
24	-	-	26.3

Another parameter, which can have an influence on the hide storage time, is temperature of the treatment. Hide samples were treated under conditions described in **Variant B** excepting the treatment temperature, which was 10, 15, 20 and 30°C (Table 3). The obtained results allow conclusion that treatment temperature in the investigated range has impalpable effect on hide storage duration.

Of course, one or another preservation method can be validated only by checking the quality of the leather processed from hide preserved by this method.[1] The suitability of the preservation method was tested producing leather from the preserved hide, observing the behaviour of the hide during processes, and assessing properties of the leather produced from such hide.

In the first beamhouse process, hides are soaked in water to remove the salt left over from curing and increase the moisture so that the hide or skin can be further treated.[3] Since the hide preserved by oxidative method (OxH) does not lose moisture during storage, it was only washed 2 times in such way: H_2O – 160%, temperature 19-21°C, duration 1h, run continuously. The hide samples cured by sodium chloride (SaltH) were soaked according to conventional soaking method: H_2O – 160%, Na_2CO_3 – 1.4%, temperature 19-21°C, duration 12 h, 1.5 h run continuously, later 5 min every 1 h.

The washing of OxH during 2 h leads to even higher content of moisture in hide comparing with 12 h soaking SaltH samples (Figure 3).

The effect of leather manufacture processes on hide samples was evaluated determining shrinkage temperature of hide and amounts of removed from hide tissue collagen and non-collagenous proteins.

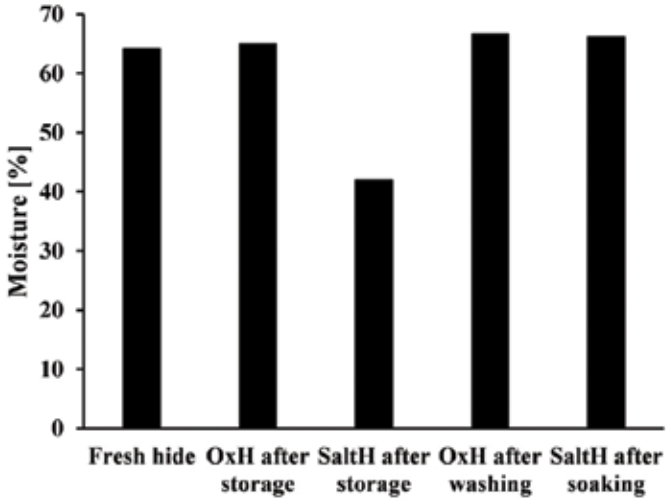

Figure 3. Moisture content in fresh, preserved and soaked hide.

TABLE II
Influence of treatment duration on on microbial growth.

Hide storage duration, days	Numbers of microorganisms (×10⁻⁶) in 1 g of hide during storage of hide after treatment when duration of treatment was			
	0.5 h	1 h	2 h	3 h
1	2.6	2.2	1.4	1.4
3	1.4	1.0	0.8	0.8
7	1.1	0.8	0.7	0.6
11	1.7	1.2	0.8	0.7
17	14.4	5.9	4.5	3.8
18	15.4	-	-	-
19	28.9	15.4	12.0	9.2
20	-	26.3	17.3	12.0
21	-	-	23.1	18.4
22	-	-	-	31.1

TABLE III
Influence of treatment temperature on on microbial growth.

Hide storage duration, days	Numbers of microorganisms (x 10^{-6}) in 1 g of hide during storage of hide after treatment when temperature of treatment is			
	10°C	15°C	20°C	30°C
1	1.7	1.6	1.6	1.4
3	1.0	0.9	0.9	0.9
7	0.8	0.8	0.7	0.6
11	1.0	0.9	0.8	0.7
15	4.8	2.6	2.4	1.9
19	15.4	13.6	11.0	9.8
20	30.0	19.7	16.0	12.0
21	-	24.2	21.8	18.2
22	-	-	-	32.2

TABLE IV
Effect of technological processes on hide shrinkage temperature and proteins removal.

Process	Index and hide preservation method					
	Amount of removed total proteins, [g/kg of hide]		Amount of removed collagenous proteins, [g/kg of hide]		Shrinkage temperature, [°C]	
	OxH	SaltH	OxH	SaltH	OxH	SaltH
Preservation	0.20	–	0.03	–	60.8	62.1
Washing	0.12	–	0.05	–	n.d.	–
Soaking	–	2.72	–	0.07	–	n.d.
Liming-unhairing	9.04	8.12	0.20	0.20	49.4	50.4
Deliming-bating	n.d.	n.d.	0.36	0.21	57.6	60.2
Pickling	3.64	3.93	0.03	0.03	54.8	52.2

**n.d. – not determined.*

The results obtained allows the conclusion that hide preserved by peracetic acid is somewhat more sensitive for chemicals during technological processes and, therefore, it is affected slightly stronger than cured by sodium chloride one. The pickled samples were processed further carrying out chroming and wet finishing operations (including additional chroming), and crust leather was produced form the samples. Qualitative indexes of chroming process and crust leather are presented in Table V and VI.

The higher value of Cr_2O_3 content in leather (accordingly higher exhaustion of chromium compounds during chroming) produced from OxH comparing with the one in obtained from SaltH confirms proposition that OxH during beamhouse processes is affected bit stronger and it's derma is opened more than of salted one (Table V). This fact is the reason, why higher amount of Cr_2O_3 does not lead to higher shrinkage of the leather produced from OxH.

The results obtained show that tendency to bind more chromium compounds remains: difference between values of Cr_2O_3 content increases up to 0.5%. Amount of matter soluble in dichloromethane is almost the same. The crust leather produced from OxH characterizes by slightly lower grain strength and lower tensile strength. On the other hand, the mentioned indexes are absolutely satisfactory for any sort of leather, which can be produced from the crust.

The analysis of waste water after the processing of OxH and SaltH was done to compare the amount of chlorides respective waste water: the received values were accordingly 28.8 and 321.6 Cl^-, kg/t of raw hide. The effect of preservation method is more than demonstrative: the use of short-term preservation of hide allows reduction of Cl^- concentration in wastewater more than 11 times.

TABLE V
Chroming process qualitative indexes.

Index	Chromed leather produced from hide	
	OxH	SaltH
Chromium exhaustion [%]	70.2	65.7
Cr_2O_3 content in leather [%]	3.22	2.79
Shrinkage temperature of leather [°C]	100.2	100.2

CONCLUSIONS

The treatment of fresh hide by a mixture of H_2O100%, sodium hydroxide 0.5%, hydrogen peroxide 0.3% and acetic anhydride 1.5% (% based on fresh hide weight) at 15-20°C during 2 h allows preservation of hide during 20 days at temperature 22±1°C. The prolongation of the treatment duration over 2 h does not increase the preservation effect markedly but affects hide structure at these higher levels. The increase of concentration of materials used for the treatment leads to significant decrease of hide shrinkage temperature, and the shrinkage temperature decrease continues during the all storage time of hide.

Preserved by peracetic acid hide is more sensitive for chemicals during technological processes and, due to this, its derma structure is opened in higher level than derma of cured by sodium chloride control. Herewith, it binds more chromium compounds during main and additional chroming. Leather produced from preserved by oxidative method hide characterizes by slightly lower grain strength and tensile strength comparing with conventionally produced leather. The use of this short-term preservation of hide allows a more than 11 fold reduction of Cl^- concentration in wastewater.

TABLE VI
Crust leather properties.

Index	Crust leather produced from hide	
	OxH	SaltH
Cr_2O_3 content in leather [%]	4.7	4.2
Matter soluble in dichloromethane [%]	10.9	10.8
Volatile matter [%]	10.6	10.5
Tensile strength [N/mm^2]	18.2	18.9
Strain when grain breaks [N/mm^2]	17.4	18.9
Relative elongation at break [%]	68.0	62.5

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