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STORAGE AND PROCESSING OF AGRICULTURAL PRODUCTS

Use of a Chloroform By-Product in Raw Fur and Hide Dressing Processes

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Abstract—It has been established that granulated preparations from a chloroform synthesis by-product with an acid, neutral, and alkaline pH containing sodium formate have antiseptic, wetting, and leather-forming properties and should be used in fur and hide dressing processes.

Keywords: dressing hides and fur pelts, chloroform by-product, formate, antiseptic

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INTRODUCTION

The shortage of antiseptic agents intended for disinfecting, primary treating, curing, and processes of dressing raw hides and fur pelts. Most foreign chemicals used in the fur and hide industry are expensive. Furthermore, many chemical materials are toxic and belong to hazard classes 1 and 2. Even the traditional antiseptic sodium silicofluoride widely used in typical methods is characterized by a high toxicity and low bacteriostatic properties.

In connection with this, the problem of finding cheap, effective, and environmentally clean agents for producing antiseptics is urgent. Compounds containing formates can be promising agents. Specialists at the Fur Industry Research Institute and All-Russian Veterinary Sanitation, Hygiene, and Ecology Research Institute have developed a preparation having antiseptic and bactericidal properties. This is an environmentally clean product far surpassing in efficacy the action of the widely known traditional antiseptic hexafluorosilicate (sodium silicofluoride). The preparation contains a mixture of carboxylic acids with 33% sodium formate in it. It is used in the process of soaking various fur pelts and sheepskin at a concentration of 0.1–0.5 mL/g [1, 2]. Preparations containing sodium formate have clearly expressed antibacterial properties, are not toxic, dissolve well in water, and are relatively cheap. Formates are obtained at chemical plants during production of chloroform after appropriate treatment and purification from chloroacetic compounds [3]. The chloroform by-product is an odorless gray powder. According to the certificate, it contains at least 70% sodium formate and 15% sodium chloride. The solubility of the powder in 100 mL cold water is 71.8 g and in hot water 200 g. The chloroform by-product contains (mass fraction, %): 1.6×10^{-2} iron, 2.7×10^{-4} copper, 0.7×10^{-3} zinc, $<5.0 \times 10^{-4}$ cadmium, $<1.0 \times 10^{-4}$ arsenic, 4.0×10^{-5} mercury, and $<1.0 \times 10^{-4}$ lead.

The researchers of the Pharmacology, Chemotherapy, and Toxicology Laboratory of the All-Russian Experimental Veterinary Institute have established the nontoxicity of the chloroform by-product for white mice, guinea pigs, rabbits, and chickens. The preparation is not mutagenic for yeast strains and doesn't have a recombinant effect [4]. Moreover, it is a large-tonnage and transportable product. The use of this product in technological operations of fur and hide dressing can broaden the assortment of ecological agents having antiseptic properties.

The purpose of the present work was to use this preparation based on the by-product in rabbit pelt and cattle hide dressing processes.

MATERIALS AND METHODS

The experiments were conducted at the enterprises in the Kirov oblast. At the Slobodskii Fur Association Belka, we studied the possibility of using preparations based on the chloroform synthesis by-product with an acid, neutral, and alkaline pH in the rabbit pelt dressing process as an antiseptic instead of the traditional sodium silicofluoride. Powdered and granulated preparations were used. The dressing experiments were carried out in the following variants: in a single technology with sodium silicofluoride in a dose of 1 g/L; experimental, with preparations with an acid (pH 5.6), neutral (pH 7.0), and alkaline (pH 12.5) reaction with the use of various doses (1, 5, 8, and 15 g/L).

At the Arteks and Vakhrushi-Yuft' farms, the granulated alkaline (pH 12.5) preparations containing sodium formate and sodium chloride were used in typical cattle hide dressing technologies as an antiseptic during soaking as well as during pickling. Soaking was carried out with use of the preparation in doses of 0.7, 2.0, and 3.0%. In the control variant, 0.7% calcined soda was added to the water. Sodium sulfide was used as a sharpening agent, and surface-active agents (0.2%) were added to intensify soaking. Soaking time was 16 h in both variants.

During the experiment, standard liming of the unhaired hide was carried out with the use of sodium sulfate in a dose of 2% and lime 3.5% (control variant) and without them (experimental variant). Pickling was done with minimum concentrations of sodium chloride, 50 g/L (control variant) and 45 g/L (experimental variant), with the use of a granulated preparation containing sodium formate and sodium chloride in 0.7, 2.0, and 3.0% doses. Sulfuric acid was used in both variants.

During the experiments we studied the antiseptic, wetting, and leather-forming properties of the fur pelts. The soaking process was checked from the results of bacteriostatic investigations.

RESULTS AND DISCUSSION

Testing of the preparations with active acidity (pH 5.6) showed the possibility of using them as an antiseptic when soaking rabbit pelts. When using this preparation, the pH value of the soaking bath was 6.04 at the start and 6.44 at the end, and in the control variant respectively 4.67 and 5.80. After the soaking process, the leather was well soaked uniformly throughout the entire thickness and density. Pelts of all specimens after soaking were soft over the entire area, dull white in cross section, and contained 68–71% moisture and 1.95–2.0% sodium chloride. The total number of microorganisms in 1 g of leather was: with treatment by the existing technology in the presence of sodium silicofluoride 8.0×10^6 and with the use of preparations with pH 5.6, 6.8×10^6, and with pH 7.0, 8.4×10^6 microbial bodies. With the use of the alkaline (pH 12.5) granulated preparation in a concentration of 1, 8, and 15 g/L during soaking, the pH value of the bath was from 7.9 to 7.3, and in the control variant with a sodium silicofluoride solution, 5.8. In all variants the pelts were well soaked; weakening of the bond of hair with the leather was not observed. A substantial difference between variants was not noted in an organoleptic evaluation of the soaked leather or upon removing the muscle and adipose layer during fleshing. A microscopic analysis of the soak liquor and leather after soaking didn't reveal significant differences in any variants. Bacteria were absent within the dermis; loosening of the leather and thin splitting of the collagen fibers, which were covered by a uniform thin adipose layer, was observed in all variants on pelt specimens after tanning. Penetration of the tanning compounds into the leather was uniform in all specimens. The chemical and physicochemical indices of pelts of the control and experimental specimens corresponded to State Standard GOST-2974: all pelts withstood tensile stress >50 N; the hydrogen ion concentration of a water extract of the leather (pH) was 5.5; according to the organoleptic evaluation, leather of the finished intermediate product didn't have significant differences in any variants.

According to fur dressing technology, the pH value of the soak liquor should be not more than 6.5; its higher value promotes hair slip. According to the test report, preparations containing sodium formate with an acid pH can be used as an antiseptic in a concentration of 2–3 g/L when soaking fur pelts.

At the Arteks farm, soaking of cattle hides in accordance with the established technology with the use of the chloroform by-product in a dose of 2% of the raw material weight promoted uniform soaking of the leather throughout the layers and over the entire surface. Macrosalted hides reached maximum absorption during 8-h soaking. The rate of absorption by the experimental specimens at various stages was slightly higher than that of the control specimens. After soaking, the hides were soft, contained 67.0 and 67.5% moisture, the pH of the water in all specimens at the start of soaking was 9.5 and at the end 8.4.

Indicators of the sanitary and hygienic safety of the hide and fur raw materials are the degree of their biological damage as a result of microbiological contamination. About 20 species of various microorganisms, including putrefactive, having pronounced proteolytic capacity, can be found on fresh hides after flaying [5]. Bacterial damage was not noted in a histological bacteriological examination of the control and experimental hide specimens; there was no chafe marks on leather of the experimental specimen. The total number of microorganisms in 1 g of leather in the control variant was 14×10^6 and in the experimental, 2.3×10^6 microbial bodies. The bacteriostatic effect from using the chloroform by-product was 6 times higher than with the use of calcined soda.

At the Vakhrushi-Yuft' farm, the soaking time during dressing of cattle hide was 16 h in the experimental and control variants. At the start and end of the process, the pH of the soak liquor in the control variant was 10 and 9 and in the experimental, with the addition to the liquor, of the tested alkaline liquor (pH 12.5) in a dose of 0.7% it was respectively 7.8 and 7.0; in a 2% dose, 8.7 and 7.2; and in 3% dose, 9.3 and 7.8. Soaking with the use of both calcined soda and the chloroform by-product provided sufficient and uniform soaking of the raw material throughout the entire thickness and over the area. The degree of soaking of the hide in the control variant was 65% and in the experimental, 66–68%. The presence of sodium formate in the liquor provided considerable protection of

Chemical and physicomechanical indices of cattle leather

Index	Variants			
	control	experimental (preparation doses)		
		0.7%	2%	3%
Shrinkage temperature, °C	70	68	73	75
pH of water extract	4.25	4.40	4.80	5.50
Tensile stress, N	47.5	50.0	52.0	52.4
State of collagen structure	Uniform distribution of collagen bundles	Uniform thin separation of collagen bundles		

the raw material from bacterial action. In 1 g of leather, in the control variant were found 12.4×10^6 microbial bodies; in the experimental variant at a minimum dose of the preparation, 7.6×10^6; and at an increased dose, 4.7×10^6 microbial bodies. Lime penetration of the dermis of the hides occurred in an optimal time. The duration of liming in the control variants was 56 min and in the experimental, 55–56 min.

It is known that organic acids (formic, acetic, or lactic) are used for pickling unhaired hides. Formic acid in the pickle has a positive effect on the chrome tanning process and promotes a more uniform distribution of the chrome tanning salts over the thickness of the hide and their stronger binding by collagen. The data of the experiments indicate the possibility of using the preparation containing sodium formate and sodium chlorine during treatment of bated hides (pickling). The use of this preparation allows a slight reduction of the content of sodium chloride in the pickle of the experimental variant (by 0.5%). It is necessary to note that the addition of sodium formate to the pickle in doses of 2 and 3% promoted a more even distribution of the chromium complex throughout the thickness of the dermis and an increase in the content of chromic oxide content in it. The chrome tanned intermediate products of the control and experimental variants met the standard technological conditions with respect to quality (table).

The thermal stability of the leather in the experimental and control specimens met the requirements of the GOSTs. The elastoplastic properties of the hides weren't inferior to the control ones.

Thus, experiments revealed the possibility of using a chloroform by-product freed from chloroacetic compounds—sodium formate—in preparatory operations of dressing hides as an antiseptic during soaking as well as in the pickling of the intermediate product. Investigations showed that preparations with both an alkaline and acid pH have antiseptic, wetting, and leather-forming properties,

It is recommended to use preparations containing sodium formate and sodium chloride in preparatory processes of dressing hides in the following doses: during soaking 0.7% and during pickling 2% of the raw material weight.

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