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Degradation, Hydrolysis, Synthesis and Properties of COLLAGEN from Waste of Chrome Tanning of Tanning Industry

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ABSTRACT: A research of the processes of degradation, hydrolysis, synthesized and studied some of the properties of collagen from waste of chrome tanning of tanning industry. The influence of sodium hydroxide and ethylene glycol on the process of hydrolysis of chrome skin waste is determined. It is shown that the decrease in hydrothermal destruction of chromic leather wastes during sample processing in an alkaline solution occurs within 1-3 hours. Further, with an increase in processing time, the rate of degradation slows down. With the degradation of chrome wastes of leather in ethylene glycol solution, the hydrothermal destruction in the first 3 hours decreases within 56.4-72.3 ° C, and the content of Cr₂O₃ after treatment is 0.8%. The resulting collagen has a high viscosity. The product is recommended to be used as an adhesive or binder in various sectors of the economy.

KEYWORDS: leather waste, collagen, alkali, sodium hydroxide, ethylene glycol, composition, degradation, destruction, hydrolysis.

I.INTRODUCTION

Rational use of waste is an urgent problem, the solution of which will help reduce the cost price of the skin. Possible methods for utilization of non-tanned wastes are to dissolve them in an alkaline, acidic medium or to obtain from them gelatin.

To obtain glue and gelatin, from the tanned production wastes, it is necessary to destroy the bonds formed between the tanning agent and the functional groups of collagen, and also additionally to loosen the structure of the crushed shank. The best results of degradation are obtained when treating leather in solutions of siegnette salt or oxalic acid. The best results of degradation are obtained when treating leather in solutions of siegnette salt or oxalic acid.

An oxidative degradation method has been developed [1-3], based on the conversion of trivalent chromium to hexavalent, whose compounds do not have a tanning effect and are well washed out with water. Perhydrol is used as an oxidizing agent in an alkaline medium. The high effect of degradation by the oxidative method is achieved only after pre-treatment of samples of leather of chrome tanned with solutions of oxalic or sulfuric acid for 3 days. To obtain gelatin from degraded samples, additional ash is still necessary, the duration of which is several days [7].

In the present research, when choosing degrading agents, it was taken into account that, along with the destruction of chromium compounds, simultaneous loosening of the dermis structure should occur and prerequisites for hydrolysis of collagen should be created.

It is known, that in the initial stage of tanning, electroflux bonds play a large part in the binding of chromium to collagen, which over time pass into coordination due to the entry into the internal sphere of the chromium complexes of ionized carboxyl and non-ionized collagen amino groups [6]. And the increase in cross-linking in collagen is greatly influenced by post-bile processes.

In the aquatic environment, the product of the interaction of collagen and tanning chromium compounds is stable in the range of pH 2-7 [8]. When alkalinizing, compounds of trivalent chromium are destroyed, forming chromium hydroxide, and with a significant excess of alkali, water-soluble chromites. Neither chromium hydroxide nor chromites have a tanning effect [9].

II. MATERIALS AND METHODS

For the research of degradation, unpainted chrome waste of leather was used, the physico-chemical characteristics of which are listed in Table 1.

Table 1
Physico-chemical characteristics of unpainted chrome leather waste

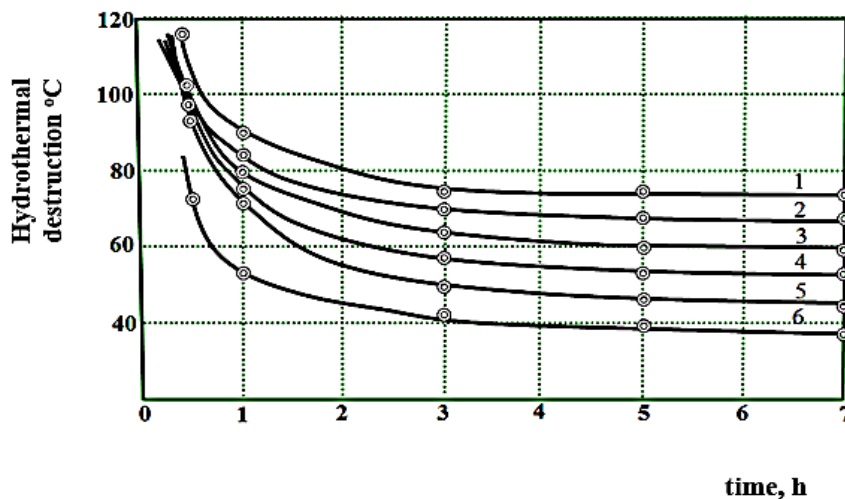
| № | Indicators (on absolutely dry substance) | Unit of measurement | Meanings |
|----|---|---------------------|----------|
| 1. | Moisture | % | 14,6 |
| 2. | Total ash | % | 4,8 |
| 3. | Fatty substances | % | 7,1 |
| 4. | Shank substance,% | % | 76,83 |
| 5. | Chrome oxide | % | 5,2 |
| 6. | Water extractor | pH | 3,2 |
| 7. | Hydrothermal destruction | °C | 92,0 |

For degradation, solutions with different concentrations of NaOH and ethylene glycol are used.

After a certain time interval after the degradation of chrome skin waste in the working solution, neutralization and washing, the hydrothermal destruction and the residual content of chromium oxide were determined.

III. RESULTS AND DISCUSSION

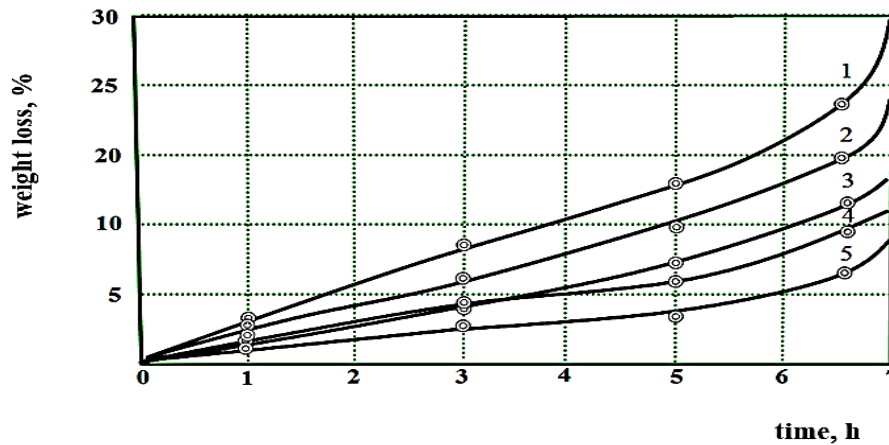
As can be seen from pic. 1, a sharp decrease in hydrothermal destruction of chromic leather wastes when processing samples in an alkaline solution occurs within 1-3 hours.



Pic. 1. The change in the temperature of welding when disintegrating in a solution of NaOH with concentrations, g/l: 1 - 10; 2 - 20; 3 - 50; 4 - 80; 5 - 110; 6 - 120;

With increasing processing time, the rate of degradation slows down. This indicates that during tanning, the main part of chromium compounds interacts with carboxyl groups in the surface layers of collagen fibrils and only a smaller part of them penetrates into the fibrils. In addition, as the destruction in the surface layers of crosslinked fibrils formed by chromium compounds, the ability of collagen to swell in alkaline solutions increases, which reduces the rate of diffusion of the degrading agent.

The increased effect of degradation occurs with an increase in the concentration of alkali in the solution. At the same time, in alkaline solutions, large mass (protein) losses are observed, which increase with increasing processing time and with increasing NaOH concentration in the solution (Pic. 2).

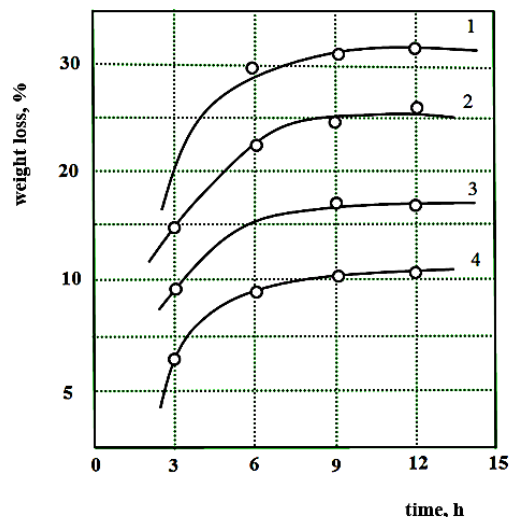
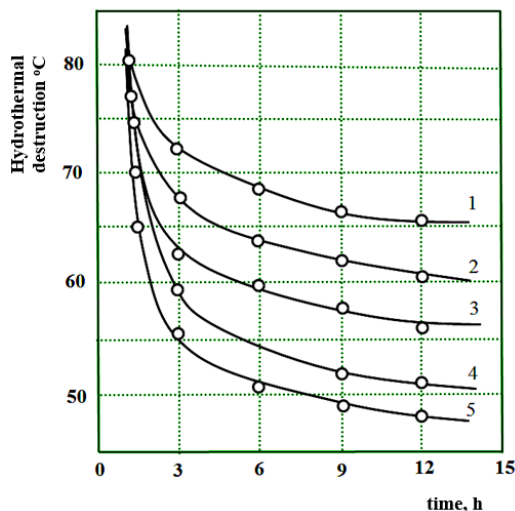


Pic. 2. The mass loss of chrome leather waste during degradation in NaOH solution with a concentration, g / l: 1 - 10; 2 - 20; 3 - 50; 4 - 80; 5 - 110

It is well known that not only alkali, neutralizing salts [10], but also some organic compounds [11] have a degrading effect. In this case, the displacement of protein carboxyls from the inner sphere of chromium complexes is promoted by both OH-ions, which are formed during the hydrolysis of the salt, and the anions of the reagents used. With the degradation of chrome waste of leather in ethylene glycol solution, the hydrothermal destruction in the first 3 hours decreased within 56-72.3 ° C, and the content of Cr2O3 after treatment was 0.8%. There is no loss of weight during processing, but the efficiency of degradation of ethylenediamine solution is less than in alkaline.

The best results of degradation were obtained when treating chrome waste of leather in caustic soda solution (NaOH) and ethylenediamine (H2NC2H4NH2). With increasing concentration of NaOH in solution, the effect of degradation increases. The concentration of ethylenediamine ranged from 150-220 g / l.

The greatest degradation occurs during the processing of chrome skin waste in a solution containing 110 g / l NaOH and 150 g / l ethylenediamine. After treating the chrome wastes of the skin in such a solution for 15 hours, the hydrothermal destruction decreased from 82.4-47.6 ° C (Pic. 3), and the residual Cr2O3 content was 0.6%.



Pic. 3. Change in hydrothermal destruction during degradation in a solution of an alkaline composition with a concentration of components (NaOH: H₂NC₂H₄NH₂), g / l: 1-10: 220; 2-20: 200; 3-50: 190; 4-80: 170; 5-110: 150

Pic. 4. Protein loss during degradation in a solution of an alkaline composition with a concentration of components (NaOH: H₂NC₂H₄NH₂), g / l: 1-20: 200; 2-50: 190; 3-80: 170; 4-110: 150

Weight loss during treatment with an alkaline composition is insignificant, but with an increase in processing time and concentration of alkalis, they increase (Pic. 4).

It has been established that under these conditions the degradation of the chromium compound is not completely removed, however, the hydrothermic destruction of the collagen-containing matrix after treatment approaches the temperature of the hydrothermal destruction of the shank, which ranges from 50-60 ° C.

From research results for disposal, recovery of leather waste, as well as for obtaining valuable products, the following parameters of processes and degradation operations are recommended:

1. Degradation in a solution of an alkaline composition for 7.5 hours at a temperature of 20 ° C, with a liquid coefficient (LC) 3. The concentration of NaOH is 110 g / l, ethylenediamine 150 g / l.
2. 2 Washing in a solution of Na₂CO₃ (25 g / l) for 10 hours at a temperature of 20 ° C, LC = 3.
3. Rinse in running water for 3 hours.

The main effect of degradation is achieved in a solution of the alkaline composition (Cr₂O₃ content 0.6%; 65% Cdst; protein loss 10.0%). Soda wash is used to reduce the alkali content of the material. At the same time, with soda rinsing, a further decrease in the chromium content and a decrease in the welding temperature occur (Cr₂O₃ 0.52%, tdst 48.3 ° C).

After washing, the synthesized collagen-containing matrix was dissolved in acid-alcohol (acetic acid: ethyl alcohol 90:10) medium, with LC = 0.4 for 4 h. After time, melting was carried out at 80 ° C and the viscosity was determined.

Physico-chemical indicators of collagen obtained from chrome skin waste are given in Table 2.

Table 2
Physico-chemical indicators of collagen obtained from chrome leather waste.

| № | Indicators | Unit of measurement | Meanings |
|---|---|---------------------|----------|
| 1 | Protein yield | % | 69,3 |
| 2 | Viscosity of the standard solution at 40% | °Э | 7,1 |
| 3 | Temperature | °C | 80 |
| 4 | Hydrogen indicator | pH | 3,2 |
| 5 | Duration | H | 4 |

V. CONCLUSION

Thus, it can be concluded that according to the above method of preparing tanned material for dissolution, protein solutions were obtained in both acidic and alkaline conditions. For degradation, it is possible to use leather waste with and without coating, chrome flap, cutting, trimming, chrome chips, etc. Protein solutions derived from chromium production wastes can be used in various sectors of the economy and in particular for filling chrome leathers.

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