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POTENTIAL USE OF COLLAGEN HYDROLYSATES FROM CHAMOIS LEATHER WASTE AS INGREDIENT IN LEATHER FINISHING FORMULATIONS

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Abstract: *The aim of this paper is the obtaining of value-added products from the dust resulted from chamois leather buffering, a solid waste that raises serious disposal problems, due to its physical state and complex chemical composition. Starting from leather waste, an alkaline hydrolysis was performed followed by the chemical modification of the polypeptyde hydrolysate by polycondensation with dispersions of copolymers of vinyl acetate with acrylic esters and reticulation with glutaraldehyde in order to improve its hydrophobicity. The resulted product can be used/was tested as an ingredient in leather finishing formulations, as binder or carrier agent. In this paper, new finishing mixtures were prepared using pigments and obtained polypeptide hydrolysates as a substitute for casein in pigment pastes. By this method, there were obtained two experimental variants of brown and black pigment pastes which were compared to the pigment pastes with casein binder. Natural grain Box bovine leather samples coated with such admixtures were subjected to physico-mechanical resistance tests, in accordance with the standardized methods. Specific tests carried on finished leather – tensile strength, tear resistance, resistance to grain cracking, dry and wet rubbing fastness, flexural fatigue strength test, etc – showed values of this characteristics comparable to those obtained with casein conventional finishing.*

Key words: *alkaline hydrolysis, polypeptide product, crosslinking, binder agent, coatings.*

1. INTRODUCTON

Collagen-based wastes coming from tanneries/leather processing are the subject of numerous research works, due to the different recovery posssibilities, by processing into useful products, with applications in: production of chemical auxiliaries for leather processing [1-3], cosmetics industry [4], health care [5], pharmaceutics [6], electronics [7], building materials [8,9], agriculture [10], bioplastics [11]. In leather industry for example, simple and modified collagen hydrolysates from leather waste, act as filler in re-tanning operations of leather processing [12] or can be a very good finishing agent for leather finishing [13,14].

It is the aim of this paper to obtain an alkaline hydrolysate starting from leather waste resulted from the buffing of chamois leather, in the following conditions: autoclaving with ammonium hydroxyde (NH_4OH) solution with pH 11, at 3 atm pressure, for 6 h. Heating the reactants dramatically accelerates hydrolysis. The same way as proteins, lipids were depolymerized or unbound by hydrolysis.

Alkali treatment, in the form of hydroxide solution, is used for rapid dissolution and then for hydrolysis of the proteins into small peptides and amino acids in the form of their ammonium salts. These salts can be removed by using membranes that retain the amino acids and peptides, by a dialysis process. Alkaline hydrolysis leads to the random breaking of nearly 40% of all peptide bonds in proteins. The vast majority of the products of the hydrolysis are single amino acids or small peptides in the 2-5 residue range (nearly 98% of the hydrolyzate). The hydrolysis process results in reducing the collagen proteins of about 30 KDa into small peptides having an average molecular weight between 2 and 5 kDa. [15].

The polypeptyde hydrolysate was isolated/separated from the reaction mass and chemically modified by polycondensation with dispersions of copolymers of vinyl acetate with acrylic esters followed by reticulation with glutaraldehyde to improve its hydrophobicity [16,17,18].

The operation of leather finishing also implies conferring an adequate ergonomic aspect with the help of certain film coatings with characteristic hygienic and physico-mechanical properties. The main substance in coating varnish and paints from the pigment paste is casein, a micellar phosphoproteide, extracted from cow milk, which tends to be replaced by other chemically modified compounds [19].

In this paper, new finishing mixtures were prepared by using pigments and afore mentioned hydrolysates as a substitute for casein in pigment pastes. Films and leather samples coated with such admixtures were subjected to physico-mechanical resistance tests, in accordance with the standardized methods.

2. MATERIALS AND EQUIPMENTS

a) Chamois powder wastes from/provided by S.C MESSY DANNY DAY tannery, with the following composition: total ash: 11,8 %; extractable fats (in trichloroethylene): 9,8 % [UNI EN ISO 4048 2000]; water soluble matter: 4,8 %; and pH: 10,5.

b) Chemical reagents and chemical auxiliaries: trichloroethylene, NH_4OH, NaOH, sulfated castor oil, glutaraldehyde, vinyl acetate, acrylic resin, nonionic surfactants (Boron), Casicolor Brown R Casicolor Black.

c) Equipment: Velp Sctientifica Vortex Mixer, AT 510 Kyoto Electronics for unionized α-amino groups determination, VESLIC - C4500 and IUP 450 for color resistance to friction, Bally Flexometer for flexing resistance, VELP Scientifica UDK 132 with semiautomatic Distillation unit for total nitrogen determination, Dialysis membrane cut off 800-100 Da, Krebs Viscometer.

3. EXPERIMENTAL

In a first stage leather waste was subjected to alkaline hydrolysis; the chemical process was carried out in a batch reactor provided with a pressure manometer and automatic temperature control. Thus 250 g chamois waste powder was treated for wetting/ swelling and partial degreasing process with a mixture of ammonium hydroxide and emulsion of nonionic tenside/trichloroethylene (1p/5p) at 20^0C, for 24 h. Then the mixture was placed in a stirrer-equipped autoclave at 250% fleet ratio, and heated at 130°C, 3 atm pressure, for 6 h. The resulted mixture was then cooled down to 20°C and the undissolved residue was separated by decantation-centrifugation at 6000 rpm, for 30 min, followed by filtration.

The operations for obtaining polypeptide alcalin hydrolysates are shown in Figure 1.

In order to extract fats from the liquid phase, a mixture of polypeptide filtrate and trichlorethylene was placed in extraction vials and continuously stirred at room temperature in a Velp Sctientifica Vortex Mixer shaker, vibration type, for 4 hours. The resulting fats were then removed by separation in a separating cone.

The characterization of the alcalin hydrolysate was performed by classical analyses (total solids, total solubles, ash, total nitrogen contents by Total Kjeldahl Nitrogen method, fat acids, soaps, pH and hydrolysis yield). The following results were obtained:

- total solids: 9,78%;
- total solubles: 25,12 g/l;
- ash: 7,9%;
- total nitrogen: 18%;
- fat acids: 2,94 g/l;
- soaps: 14,21 g/l: pH 8;

- hydrolysis yield: 67,65%.

The soluble molecular weight by dialysis process was: 800 -1000 Da. This value shows a strong fragmentation of the protein and formation of amino acid fragments.

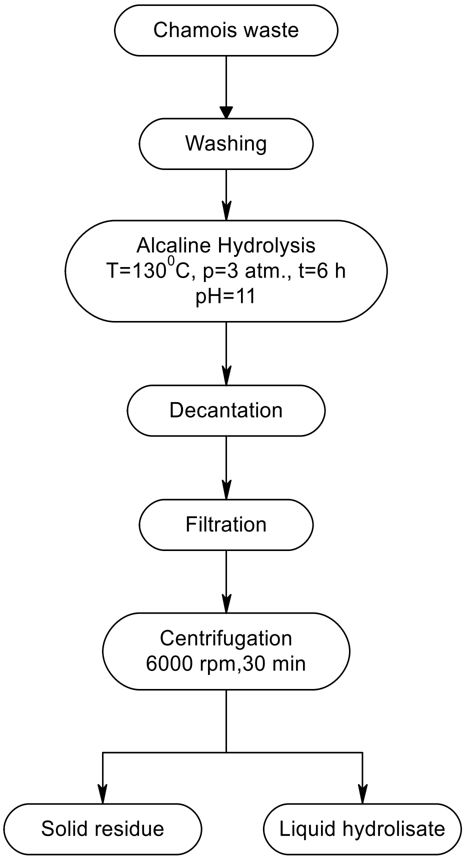

Fig. 1: *The operations for obtaining polypeptide alcalin hydrolysates*

In a second stage, the alcalin hydrolysate was chemically modified by polycondensation with dispersions of copolymers of vinyl acetate with acrylic esters at pH 8.5-9.0.

The resulted hydrogels were then brought to a final pH of 7-7.5 having the following characteristics:

- appearance: brown transparent solution;
- pH: 7 – 7,5;
- ash: 0,7%;
- dry matter: 17-25 %;
- total nitrogen: 16,5-17,8 %;
- proteic content: 85-97%;
- viscosity at 25°C: 50-100 CP.

In order to obtain the carrier agent, the afore mentioned hydrolysates were treated with glutaraldehyde as crosslinking agent which consumes the free unionised α-amino groups, at a pH of about 9 -10 (adjusted with 10% NaOH solution).

Starting for these chemically modified polypeptydes, new coatings based on inorganic pigments were obtained.

3.1. The obtaining of pigment pastes

In order to obtain pigment pastes with new chemically modified carrier, powder pigment was mixed with polypeptide product, wax emulsion and nonionic emulsifier followed by dispersing composition into acrylic binder, oil, antibacterial agent and water. The resulting dispersion system was subjected to mechanical stirring (50-80 rpm/min) at 25-30°C for 2-4 hours.

By this method, there were obtained two experimental variants of brown and black pigment pastes (Table 1) which were compared to the pigment pastes with casein binder (control sample).

Table 1: *Experimental variants of pigment pastes compared to the pigment pastes with casein binder*

Variant / **Composition (%)**	**Casicolor Brown R (control sample)**	**Variant 1 (Brown R)**	**Casicolor Black (control sample)**	**Variant 2 (Black)**
Pigment	10	10	10	10
Acrylic binder (resin)	35	35	40	40
Casein	5	-	5	-
Chemically modified polypeptyde product	-	5	-	5
Wax emulsion	2	2	2	2
Oils	10	10	10	10
Nonionic emulsifier	0,5	0,5	0,5	0,5
Antibacterial agent	1	1	1	1
Water	36,5	36,5	31,5	31,5

The new pigment paste had the following physico-chemical characteristics:

- dry matter: 40-45%;
- pH (1:10 solution): 6.5-8.0;
- stability over time without deposits or phase separation;
- uniform film deposition on the surface (glass plate).

These results are comparable to conventional pigment pastes based on casein (control samples: Casicolor Brown R, Casicolor Black- TFL Elvetia, pH: 7,5-8,5).

3.2. Finishing natural grain Box bovine leather using the new pigment pasta

The finishing technology with brown and black coatings of natural grain Box bovine leather is shown in Table 2.

Table 2: *Finishing technology with coatings* of *natural grain Box bovine leather (brown and black)*

Operations	**Recipe**
Application of the first coat (disperse solution)	- Solution preparation according to the recipe: 100 g/l pigment paste(brown, black) 30 g/l wax emulsion 300-400 g/l acrylic binder 470-570 g/l water - Spraying solution 1, 2 coats.
Intermediate ironing	- Performed on hydraulic press with mirror plate: temperature: 50-60°C; pressure: 50 atm.
Application of first coat (disperse solution)	- Spraying solution 2 coats.
Application of second coat (starch finish)	- Solution preparation according to the recipe: 700 g/L acrylic water emulsion 20 g/L wax emulsion for touch 280 g/L water - Spraying solution 2 coats.
Final ironing	- Performed on hydraulic press with mirror plate: temperature: 60-70°C; pressure: 50 atm.

The leather samples coated with the new finishings were subjected to physico-mechanical resistance tests, in accordance with the standardized methods (table 3).

4. RESULTS AND DISCUSSIONS

Table 3 presents the results obtained for physico-mechanical characteristics of natural grain Box bovine leather finished with the new coating pastes compared to the casein pigment pastes.

Table 3: *Physico-mechanical characteristics of natural grain Box bovine leather*

<table>
<tr><th rowspan="2">Physico-mechanical characteristics</th><th colspan="4">Brown natural grain Box [1-1,2 mm]</th><th colspan="4">Black natural grain Box [1-1,2 mm]</th><th rowspan="2">According to standard</th></tr>
<tr><td colspan="2">Casicolor Brown R (control sample)</td><td colspan="2">Sample 1</td><td colspan="2">Casicolor Black (control sample)</td><td colspan="2">Sample 2</td></tr>
<tr><td>Tensile strength [N/mm²]</td><td colspan="2">18</td><td colspan="2">16</td><td colspan="2">23</td><td colspan="2">22,7</td><td>SR EN ISO 3376: 2003</td></tr>
<tr><td>Tear resistance [N/mm]</td><td colspan="2">43,8</td><td colspan="2">43,2</td><td colspan="2">46,8</td><td colspan="2">45,7</td><td>SR 5045 : 1999</td></tr>
<tr><td>Resistance to grain cracking [N/mm²]</td><td colspan="2">12,8</td><td colspan="2">12,6</td><td colspan="2">12,9</td><td colspan="2">12,7</td><td>SR ISO 3378:2003</td></tr>
<tr><td>Elongation at 10 N/mm² stress [%]</td><td colspan="2">27</td><td colspan="2">26</td><td colspan="2">28</td><td colspan="2">27</td><td>SR EN ISO 3376 : 2003</td></tr>
<tr><td rowspan="2">Dry and wet rubbing fastness [Note: 1-5]</td><td>wet</td><td>dry</td><td>wet</td><td>dry</td><td>wet</td><td>dry</td><td>wet</td><td>dry</td><td rowspan="2">SR EN ISO 11643:2002</td></tr>
<tr><td>4/3</td><td>5/4</td><td>4/3</td><td>5/4</td><td>4/3</td><td>5/4</td><td>4/3</td><td>5/4</td></tr>
<tr><td>Flexural fatigue strength test (Bally) [no.]</td><td colspan="2">200 000</td><td colspan="2">180 000</td><td colspan="2">200 000</td><td colspan="2">190 000</td><td>SR EN ISO 5402: 2003</td></tr>
</table>

These results show characteristics of the new finishing pastes comparable to those obtained by casein based conventional finishes.

5. CONCLUSIONS

1. The polypeptide product obtained by alkaline hydrolysis/chemical modification allowed its use as a carrier to obtain pigment pastes.
2. This new hydrolysis product has been used as a substitute for casein in pigment pastes with characteristics comparable to conventional pigment pastes based on casein.
3. The new coatings for leather finishing show physico/mechanical resistance values in the limits imposed by current standards.
4. The applied method allows the obtaining of value-added products from the dust resulted from chamois leather buffering,

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