EXPERIMENTS TO OBTAIN NEW BIOPRODUCTS BASED ON PROTEIN EXTRACTS FROM WET-WHITE LEATHER WASTE INTENDED FOR THE TOTAL OR PARTIAL REPLACEMENT OF PHENOL FORMALDEHYDE RESINS IN WET FINISHING OF LEATHER

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ABSTRACT. Leather retanning is a key operation in the wet finishing stage, playing a very important role in diversification of assortments, but at the same time using complex chemicals can induce important eco-toxic effects especially in the liquid effluents (residual float). This paper presents some of the achievements related to the expansion of eco-friendly auxiliary product range for wet finishing of leather (filling-retanning) with predominantly natural (protein) components, combined with metal oxides other than Cr2O3 and without phenolic compounds, concomitantly with the leather industry's advance towards circular economy and increasing eco-efficiency. An experimental model was developed for functionalization of collagenic materials obtained by acid hydrolysis of pre-tanned wet-white bovine hide waste in order to obtain new bioproducts intended for the replacement of phenolic compounds for wet finishing of leather (filling-retanning).

KEY WORDS: leather waste, circular economy, retanning products

EXPERIMENTĂRI DE OBŢINERE DE NOI BIOPRODUSE PE BAZĂ DE EXTRACTE PROTEICE DIN DEŞEURI DE PIELE TĂBĂCITĂ ÎN SISTEM WET-WHITE DESTINATE ÎNLOCUIRII TOTALE SAU PARŢIALE A RĂŞINILOR FENOLFORMALDEHIDICE LA FINISAREA UMEDĂ A PIEILOR

REZUMAT. Retăbăcirea pielii este o operaţie cheie în etapa de finisare umedă, jucând un rol foarte important în diversificarea sortimentelor, dar în acelaşi timp utilizarea substanţelor chimice complexe poate induce efecte eco-toxice semnificative, mai ales în efluenţii lichizi (flota reziduală). Această lucrare prezintă unele realizări legate de lărgirea gamei de produse auxiliare eco-prietenoase pentru finisarea umedă a pieilor (umplere-retanare) cu componente preponderent naturale (proteice) în combinaţie cu oxizi metalici alţii decât Cr2O3 şi fără compuşi fenolici, concomitent cu apropierea industriei de pielărie de economia circulară şi creşterea eco-eficienţei. S-a dezvoltat un model experimental pentru funcţionalizarea materialelor colagenice obţinute prin hidroliză acidă a deşeurilor de piele bovină wet-white pretăbăcită pentru a obţine noi bioproduse destinate înlocuirii compuşilor fenolici la finisarea umedă a pielii (umplere-retanare).

CUVINTE CHEIE: deşeuri piele, economie circulară, produse retanare

EXPÉRIENCES POUR OBTENIR DE NOUVEAUX BIOPRODUITS À PARTIR D'EXTRAITS PROTEIQUES DE DÉCHETS DE CUIR WET WHITE POUR LE REMPLACEMENT TOTAL OU PARTIEL DES RÉSINES PHÉNOL-FORMALDÉHYDE DANS LA FINITION DU CUIR

RÉSUMÉ. Le retannage du cuir est une opération clé dans l'étape de finition humide, jouant un rôle très important dans la diversification des assortiments, mais en même temps, l'utilisation de produits chimiques complexes peut induire des effets écotoxiques importants, en particulier dans les effluents liquides (bain résiduel). Cet article présente quelques réalisations relatives à l'élargissement de la gamme de produits auxiliaires écologiques pour le finissage humide du cuir (remplissage-retannage) avec des composants principalement naturels (protéines), en combinaison avec des oxydes métalliques autres que Cr2O3 et sans composés phénoliques, concomitamment avec le progrès de l'industrie du cuir vers l'économie circulaire et l'amélioration de l'efficacité écologique. Un modèle expérimental pour la fonctionnalisation de matériaux collagéniques obtenus par hydrolyse acide de déchets de cuir de bovins wet white a été développé afin d›obtenir de nouveaux bioproduits pour le remplacement des composés phénoliques dans l'étape de finition humide (remplissage-retannage).

MOTS-CLÉS : déchets de cuir, économie circulaire, produits pour le retannage

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INTRODUCTION

Leather tanned up to the wet-blue/wet-white phase is processed according to typical technologies, diversification of assortments being carried out subsequently through wet finishing operations [1, 2].

If we study individually the factors that determine the diversification of assortments starting from the same type of substrate, we first find the existence of factors related to a series of constructive and functional characteristics of the machines used for wet and surface finishing.

Although the worldwide production of semi-finished leather is dependent both on the fluctuations of fashion (which from one season to another may evolve in the most unexpected directions) and on the ecological requirements of the consumers (for example, "free of chrome"/FOC leather), the selected technologies must invariably take into account the favourable influences of each technological operation on:

- surface yield (economic aspect);
- improvement of the aesthetic characteristics, resistance, special characteristics etc. (qualitative aspect);
- environmental protection and safety of individuals, from tannery workers to users of leather products (ecological aspect).

Leather retanning is a key operation in the wet finishing stage, playing a very important role in diversification of assortments, but at the same time using complex chemicals can induce important eco-toxic effects especially in the liquid effluents (residual float).

Generally, for the correct management of the retanning operation, the properties and effects of auxiliary materials used must be taken into account, depending on the desired characteristics to be obtained for each assortment of semi-processed leather:

- the actual tanning effect;
- the filling effect;
- the influence of softness;
- the dispersion effect of natural tannins;
- the effect on the colour (dark/light);
- natural colour;
- the influence of the dyeing capacity;
- the influence of mechanical resistance;
- ecological implications.

This paper presents some of the achievements related to the expansion of eco-friendly auxiliary product range for wet finishing of leather (filling-retanning) with predominantly natural (protein) components, combined with metal oxides other than Cr_2O_3 and without phenolic compounds, concomitantly with the leather industry's advance towards circular economy and increasing eco-efficiency.

MATERIALS AND METHODS

Materials

The following materials were used in experiments:

- bovine leather tanned in wet-white system (INCDTP - Division ICPI), split and shaved;

- commercial auxiliary products for wet finishing of leather (neutralizing, fixing, acidifying, fatliquoring, washing, degreasing agents);

- pre-tanned bovine leather waste with titanium-zirconium based tanning agents (shavings) (INCDTP - Division ICPI);

- industrial water;

- acids for technical use (formic, lactic);

- commercial acrylic resin;

- aluminium triacetate (commercial product).

Machines/Devices Used

- CALORIS reactor (Romania) for hydrolysis of wet-white leather waste;

- VALLERO rotating drum (Italy) for wet finishing of bovine leather;
- GIULLIANI device (Italy) for the determination of hydrothermal resistance (shrinkage temperature).

Methods Used

- laboratory analytical determinations for physical-chemical characterization of waste, collagen materials, new bioproducts, retanned leather in accordance with the regulations (standards) in force;
- physical-mechanical tests for the characterization of crust semi-finished leather obtained in accordance with the regulations in force.

EXPERIMENTAL

Experimental Model for Obtaining Collagen Hydrolysates Extracted from Tanned Wet-white Leather Waste

The use of protein materials (collagen) to obtain new auxiliaries for leather processing is an important component of research in the field [3-13]. Figure 1 schematically shows the experimental model for obtaining collagen hydrolysates from chrome-free tanned (wet-white) leather waste.

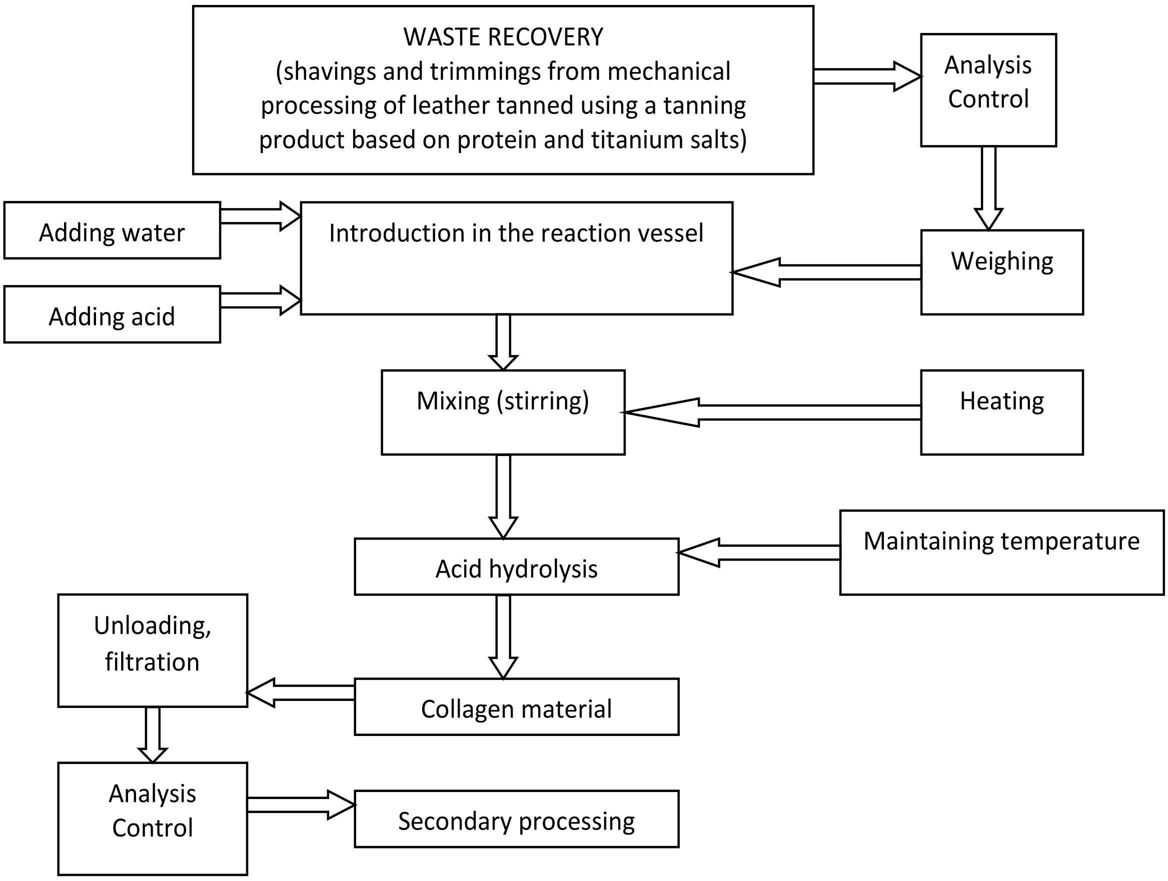

Figure 1. Diagram of the experimental model for obtaining collagen hydrolysates from chrome-free tanned (wet-white) leather waste

Table 1 presents the technological algorithm (according to the proposed experimental model) for obtaining (hydrolysed) collagen intended for the formulation of new filling-retanning agents.

Table 1: The technological algorithm for obtaining (hydrolysed) collagen for the formulation of new filling-retanning agents

No.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Waste recovery		Shavings as well as trimmings are collected as a result of the shaving and trimming operation performed on wet-white leather pretanned with the HCT product (based on titanium oxides and proteins, both recovered from unrecyclable untanned hide waste)	
2.	Analysis/control		Physical-chemical characterisation (see Table 4)	
3.	Grinding		Only large pieces of trimming are ground	
4.	Weighing		Waste is weighed to determine the net weight considered as reference for dosing the other materials	
5.	Filling the reaction vessel	30-35% waste 60-70% water 2-5% formic acid	The reactor is filled in the specified order, under continuous stirring	
6.	Hydrolysis		Stirring is continued at the temperature of 85-95°C for 12-24 h	Control pH=4-5 hydrolysate homogeneity
7.	Filtration (release from the reactor)		Once released from the reactor, the obtained hydrolysate is filtered (Nuce filter, porous/textile material)	
8.	Analysis/control		Physical-chemical characteristics of the collagen material (hydrolysate containing metal oxides) are determined (see Table 2)	
9.	Weighing		Collagen material is weighed to determine net weight	

The physical-chemical characteristics of the obtained collagen material (marked R_0) are presented in Table 2.

Table 2: Physical-chemical characteristics of the collagen material obtained (R_0)

No.	Characteristic	UM	Resulting values	Standard
1.	Dry substance	%	30-35	SR EN ISO 4684-2006
2.	Ash	%	25-30	SR EN ISO 4047-2002
3.	Total nitrogen	%	10.5-11.5	SR ISO 5397-96
4.	Protein substance	%	60-65	SR ISO 5397-96
5.	pH 10% solution	%	4-5	STAS 8619/3-1990
6.	Metal oxides	%	20-22	

Experimental Model of Formulation/ Functionalization of Protein Materials

Figure 2 schematically presents the experimental model of formulation/ functionalization of protein materials in order to obtain new bioproducts for leather retanning.

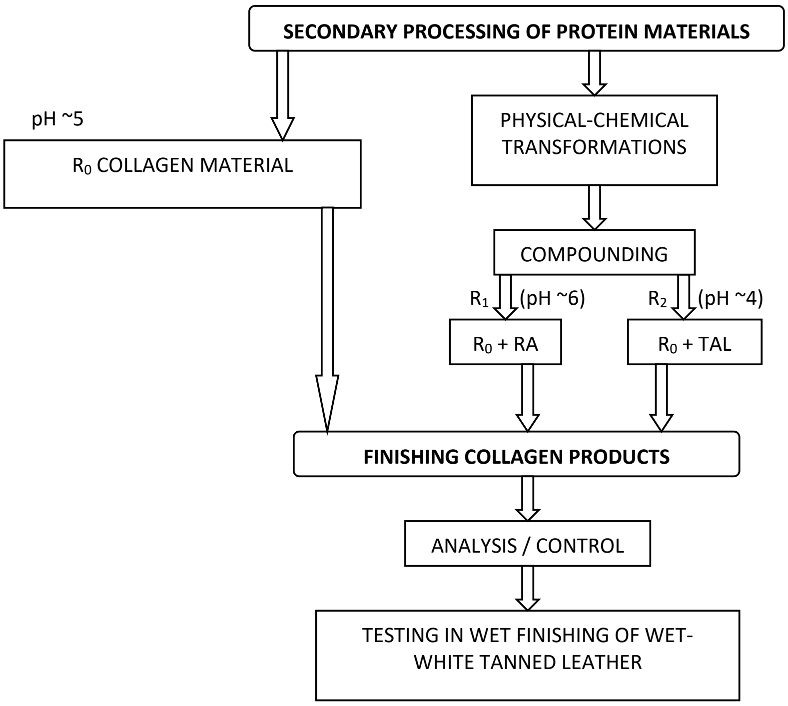

Figure 2. The experimental model of formulation/functionalization of protein materials in order to obtain new bioproducts for leather retanning (R_0: - collagen hydrolysate obtained by acid hydrolysis of leather waste tanned with titanium-zirconium-based products, R_1: R_0 + acrylic resin, R_2: R_0 + alumnium triacetate)

Experimental Model for Obtaining New Bioproducts for Leather Retanning

Table 3 presents the experimental model for obtaining new bioproducts for leather retanning.

Table 3: Experimental model for obtaining new bioproducts for leather retanning

No.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Physical-chemical transformation by compounding	**R1** 75-80% R0 20-25 acrylic resin **R2** 70-80% R0 20-30 Al triacetate	After adding acrylic resin and the aluminium triacetate compound, the mixture is stirred for 15-20' in a mixer-type reaction vessel, the compounding components being solid and/or paste, without exceeding the temperature of 30-35°C	Control: Homogeneity of resulting pastes is controlled
2.	Finishing collagen products			
3.	Analysis/control		Physical-chemical characteristics of the new retanning bioproducts are determined (see Table 4)	
4.	Unloading device			

Characterisation of New Bioproducts for Wet Finishing of Leather

Table 4 presents the physical-chemical characteristics of the new bioproducts intended for leather retanning.

Table 4: Physical-chemical characteristics of new bioproducts intended for leather retanning

No.	Characteristic	UM	Resulting values		Standard
			R_1	R_2	
1.	Dry substance	%	33-36	40-45	SRENISO 4684-2006
2.	Ash	%	25-30	28-31	SRENISO 4047-2002
3.	Total nitrogen	%	9-10	7.0-7.5	SRISO 5397-96
4.	Protein substance	%	50-55	36-41	SRISO 5397-96
5.	pH 10% solution	%	5.0-6.5	4.0-4.5	STAS 8619/3-1990
6.	Metal oxides	%	9-11	25-27	SRENISO 4684-2006

Figure 3 shows the new biomaterials for wet finishing (retanning) of leather.

Figure 3. New biomaterials for wet finishing (retanning) of leather

Testing New Bioproducts for Retanning Wet-white Bovine Leather

Obtaining wet-white leather that will be used to test the new wet finishing materials

Table 5 presents the framework technology for obtaining wet-white leather.

Table 5: The framework technology for obtaining wet-white leather

No.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Pre/tanning	-30-70% pickling float 20-25°C -3-5% tanning agent based on polyaldehyde and/or glutaraldehyde -2-3% pre-fatliquoring agent resistant to electrolytes	After adding the pre/tanning agent the drum rotates for 30' then the pre-fatliquoring agent is added and stirring is continued for another 80-90'	Control: pH=2,8-2,9
2.	Basification	+0,5-1,5% self-basification agent	After adding the self-basification agent, the drum rotates for 240-360'	Control: pH=3,9-4,2 T_s = 70-75°C
3.	Unloading drum			
4.	Rest		Leather left on the pallet for 24-48 h	
5.	Sammying	Sammying machine with cylinders and felt		
6.	Splitting	Splitting machine with belt tape knife	Leather is split at a thickness as close to that of shaving (+0,1-0,2 mm)	
7.	Shaving	Shaving machine with sharp knives	Shaving at the required thickness for the desired assortment	
8.	Trimming	Manually, using a knife/special scissors	Adhesions, areas with varying thickness or unusable areas are removed	
9.	Weighing	Calibrated industrial scales	The net weight of shaved leather is determined, as reference for dosing floats and wet finishing materials	

Wet Finishing of Wet-white Bovine Leather Using the New Bioproducts

Table 6 presents the technological algorithm for wet finishing of wet-white leather using the new bioproducts.

Table 6: Technological algorithm for wet finishing of wet-white leather using the new bioproducts

NO.	Operation	Method		Remarks
		Formulation	Procedure	
1.	Washing, degreasing	200% float at 30°C 0,5% surfactant	Leather is drummed for 10-15'	
2.	Draining			
3.	Neutralization	150% float at 30°C 2-3% neutraliztion agent	Leather is completely deacidified in cross section. The drum rotates for 60'. If the section is not fully neutralized, neutralisation is continued until reaching the desired effect (even over night with intermittent stirring)	Control: pH=4,2-5,8 Ø=100%VBC

4.	Draining			
5.	Washing	200% float at 20-25°C	Leather is washed for 20-30’	
6.	Draining			
7.	Fatliquoring	100% float at 50-55°C 6-10% oil mixture	Drum rotates for 40-60’	Organoleptic control
8.	Fixing (acidification)	+0,5% formic acid (diluted 1:10)	Leather is drummed for 15-20’	White base leather (**NR**)
9.	Draining			
10.	Retanning	100% float at 30-35°C 3-8% $\mathbf{R_0}$ / $\mathbf{R_1}$ / $\mathbf{R_2}$		Leather and float control
11.	Fixing (acidification)	+0,5% formic acid	Drum rotates for 15-20’	pH=4-4,5
12.	Draining			
13.	Rinsing	200% float at 20°C		
14.	Unloading drum			
15.	Rest	Minimum 12h		

Figure 4 shows the crust leather obtained using the new materials (after drying and staking).

Figure 4. Crust leather obtained using the new materials (after drying and staking)

RESULTS AND DISCUSSION

The crust leather obtained using the new materials have organoleptic, physical-chemical and mechanical characteristics at least comparable to those of leather processed using classical technology.

Characterization of Crust Wet-white Leather Using the New Bioproducts

Visual and Organoleptic Characterization

Table 7 presents the visual-organoleptic characteristics of the crust leather wet finished using the new bioproducts.

Table 7: The visual-organoleptic characteristics of the crust leather wet finished using the new bioproducts

No.	Characteristics	Nr	R_0	R_1	R_2
1.	Thickness (mm)	0,8-0,9	1,0-1,1	1,1-1,2	1,2-1,3
2.	Colour (visual)	white-slightly yellow	white-cream	white-cream	white-cream
3.	Fullness (organoleptic, marks 1-5)	1 (poor)	2-3 (moderate)	4-5 (good, very good)	5 (very good)
4.	Softness (organoleptic, marks 1-5)	2-3 (moderate)	3-4 (good)	2-3 (moderate)	5 (very good)
5.	Grain appearance (visual, organoleptic)	smooth, slight loosening	smooth, fine	smooth, full, firm	smooth, full, firm

Figure 5 shows the increase in thickness (volume) of the leather retanned with (R_0, R_1, R_2) compared to non-retanned leather (only fatliquored / white base).

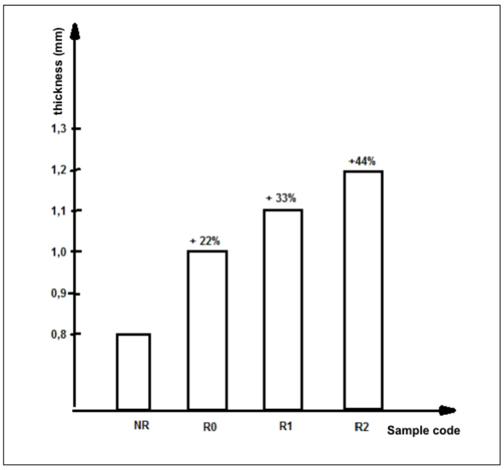

Figure 5. Thickness (volume) of the leather retanned with (R_0, R_1, R_2) compared to non-retanned leather (only fatliquored / white base)

As seen from Table 7 and Figure 5, all the new bioproducts have very good filling ability, highlighted by the obvious increase in volume (thickness).

Characterization of crust (wet-white) leather retanned using the new bioproducts in terms of hydrothermal resistance

Table 8 shows the shrinkage temperature values of the crust leather retanned using the new bioproducts in terms of hydrothermal resistance.

Table 8: Shrinkage temperature values of crust leather retanned using the new bioproducts

No.	Characteristic	UM	Sample code					Standard
			WW	NR	R_0	R_1	R_2	
1.	Shrinkage temperature	°C	70-72	75-76	76-78	78-80	81-82	SR EN ISO 3380:2003

Figure 6 shows an increase in hydrothermal resistance (shrinkage temperature) of the retanned leather (with R_0, R_1, R_2) compared to the non-retanned leather (only neutralized and fatliquored / white base) and the pre-tanned (wet-white) leather.

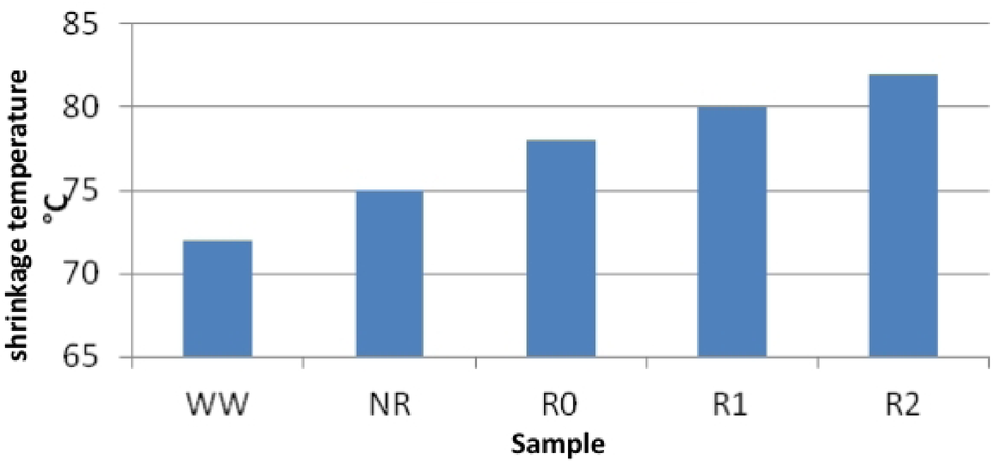

Figure 6. Shrinkage temperature of retanned leather (with R_0, R_1, R_2) compared to non-retanned leather (NR) (only neutralized and fatliquored / white base) and pre-tanned (wet-white) leather (WW)

The new bioproducts for filling-retanning also have tanning ability, increasing hydrothermal resistance of leather (shrinkage temperature) by 4-12°C.

Physical-chemical Characteristics of Crust (Wet-white) Leather Wet Finished (Retanned) Using the New Bioproducts

Table 9 presents the physical-chemical characteristics of the crust (wet-white) leather wet finished (retanned) using the new bioproducts.

Table 9: Physical-chemical characteristics of crust (wet-white) leather wet finished (retanned) using the new bioproducts

No.	Characteristics	UM	Sample code								Standard
			NR		R_0		R_1		R_2		
1.	Tensile strength and percent elongation										SR EN ISO 3376-2012
	Elongation:										
	-at 10N/mm	%	45	66	32	54	32	85	52	82	
	-at break	%	75	104	68	54	74	128	91	120	
	-tensile strength	N/MM	9.6	20	10.3	10.0	27	17	21	16	
2.	Tear strength	N/MM	67	78	32	28	59	55	52	49	

Physical-mechanical characteristics of crust leather obtained from wet white retanned with the new bioproducts are comparable to those of similar assortments obtained internationally, and even with those of leather tanned using Cr salts and retanned with commercial products commonly used in the industry.

Characterization of the Residual Float

Table 10 shows the residual residual float in terms of phenol content when using the new retanning bioproducts (R_0, R_1, R_2) compared to those used industrially (M).

Table 10: Characterization of residual float in terms of phenol content when using new retanning bioproducts (R_0, R_1, R_2), compared with those used industrially (M)

No.	Characteristic	UM	Sample code / resulting values				Standard
			M	R_0	R_1	R_2	
1.	Phenol content	mg/l	20-80	0.4-0.5	0.5-0.6	0,5-0.7	SRISO 6439:2001

CONCLUSIONS

An experimental model was developed for functionalization of collagenic materials obtained by acid hydrolysis of pre-tanned wet-white bovine hide waste in order to obtain new bioproducts intended for the replacement of phenolic compounds for wet finishing of leather (filling-retanning).

The use of new bioproducts in the wet finishing of bovine leather (retanning-filling) has led to:

- semi-processed wet-white crust bovine leather with physical-mechanical and aesthetic characteristics at least comparable to those produced internationally but also to those produced industrially with classical recipes (tanned with chrome salts and using phenolic compounds for retanning-filling);
- non-modification of existing industrial technologies;

- an obvious retanning effect characterized by an increase in shrinkage temperature by 8-12°C, a 10-30% increase in volume, which gives leather fullness and superior strength.

In addition to technical advantages presented above, production and use of new bioproducts based on collagen hydrolysate extracted from waste resulting from leather processing intended to replace the materials currently used for filling-retanning of leather (phenolic compounds) also induce multiple advantages, such as:

- environmental:
  - reduction/elimination of phenolic compounds from liquid effluents from wet finishing (from 20-80mg/l to 0.5-0.7mg/l phenol);
- social:
  - protection of tannery workers by eliminating some compounds with eco-toxic potential (phenolic compounds);
  - the possibility of creating new jobs through the creation of chemization stations in the tanneries;
- economic:
  - the reduction of depollution, storage and/or waste elimination expenses;
  - obtaining high value products relatively simply;
  - reduction of expenses for the purchase of auxiliary materials.

In conclusion, it can be stated that this work contributes to the expansion of the range of eco-friendly auxiliary products for wet finishing of leather (filling-retanning) with predominantly natural (protein) components concomitant with the leather industry's advance towards circular economy and increasing eco-efficiency.

Acknowledgements

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