De-Chroming of Chromium Shavings without Oxidation to Hazardous Cr^{6+}*

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Abstract

After the process of hide tanning to leather, almost 25 % weight of input raw material proceeds to chromium tanned waste. The occurrence of such a large amount of waste presents economic and mainly ecologic problem for this branch; heavy effort in the world is given to development of technologies of processing eventually disposal of chromium tanned waste. The results of this effort are technologies based on different principles, where is possible to separate chromium from collagen. Application of these procedures in industry and also the proportion of valuation of chromium waste depend on effective application of obtained products. The aim of our work was development of ecological de-chroming technology of chromium shavings without oxidation of Cr^{3+} to Cr^{6+} with kept fibril structure. The pH value, temperature and number of dechroming bath have an influence on amount of removed extracted chromium. The influence of these parameters on losses of collagen after hydrolysis was determined. The degree of hydrolytic collagen decay was evaluated by determination of iso-electric point and determination of collagen increased solubility in dependence on de-chroming temperature. The results are: the optimized technology, determined influence of temperature, pH, and number of de-chroming bath on amount of released Cr^{3+}, and determined qualitative collagen parameters.

Resumen

Luego del proceso de curtido de la piel a cuero, casi el 25% del peso de las pieles ingresadas termina como residuos curtidos al cromo. La aparición de esta gran cantidad de residuos presenta un problema económico y principalmente ecológico para esta industria, por lo que un sustancial esfuerzo global es dado al desarrollo de tecnologías mejoradas para la disposición de residuos curtidos al cromo. Los resultados de este esfuerzo son diferentes tecnologías dónde es posible separar el cromo del colágeno. La aplicación de estos procedimientos en la industria y también el porcentaje de valorización de residuos de cromo depende de la aplicación efectiva de los materiales obtenidos. El objetivo de nuestro trabajo fue el desarrollo de una tecnología ecológica de des-cromado de virutas de cromo evitanto la oxidación de Cr^{3+} a Cr^{6+} y manteniendo una estructura fibrilar aceptable. Los valores de pH, temperatura y el número de baños de descromado tienen una influencia sobre la cantidad del cromo extraído. La influencia de estos parámetros sobre la pérdida de colágeno después de la hidrólisis fue determinada. El grado de descomposición del colágeno hidrolízado se evaluó mediante la determinación del punto isoeléctrico y la determinación de la mayor solubilidad del colágeno dependiendo de la tempertaura de descromado. Los resultados incluyen la optimización de la tecnología, la determinación de la influencia de la temperatura, el pH, la cuantificación del Cr^{3+} liberado en el descromado y la determinación de los parámetros cualitativos de colágeno.

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Introduction

Leather tanneries may be considered as typically waste productions with regard to the technology and character of processed raw material. However, solid leather tanning waste containing chromium (leather tanning sludge, chromium shavings and wet-blue trims) is a specific problem because it presents a very high load for the environment and its disposal can be very expensive. The interest of producers is therefore to minimize the occurrence of solid waste and to use know-how in the full scale from the area of processing of leather waste first of all tanned—(collagen cross-linked with basified Cr^{3+}). Regarding to chemical composition, chromium shavings are possible to be considered as a complex of collagen proteins and Cr^{3+} salts. In spite of the fact, that this is the raw material from renewable sources, the significant problems of its wider exploitation are: insufficient separation of Cr^{3+} from proteins, economic consumptive technology, and problematic processing of chromium sludge with the share of collagen. Leather tanning waste cannot be classified as inert, because during determined period of dump monitoring it will be liable to degradation in higher or lower rate. At present in Slovakia, this waste is disposed above all by dumping and burning. A part of chromium shavings is hydrolyzed by unsuitable dumping; there is a risk of chromium release to ground water and a possibility of its oxidation to carcinogenic Cr^{6+} at its contact e.g. with chlorine oxidation matters. The content of chromic oxide in shavings and trims is in the weight range 3–4% of the dry content matter.

Processing of leather tanning waste by action of enzymes and by acid hydrolysis was solved in the project Copernicus in co-operation with BLC (Leather Technology Centre), Northampton, England, Tomas Bata University in Zlin (Czech rep.), VIPO a.s. Partizánske (Slovak rep.) and leather tannery—Kegar from Poland. Laboratory research in VIPO was aimed at preparation of collagen hydrolysate from Cr-shavings by acid hydrolysis. Technology was patented No. AO-247036 "The process of hydrolysate preparation"[1] with the accent on application of hydrolysis as a fertilizer and Cr-sediment as tanning agent. Optimal sedimentation of chromium sludge and very low concentration of Cr^{3+} in collagen hydrolysis was obtained by the procedure according to the mentioned patent. Hydrolysis prepared by mentioned procedure was microbiologically harmless, chromium content was less than 4.5 mg Cr/liter, and there was a possibility to apply it as a fertilizer or as an additive for cosmetic industry. At the same time, with the production of hydrolysis, there was necessary to solve also processing of Cr-sludge. Obtained Cr-sediments were dissolved in concentrated H_2SO_4 in the ratio of 1:1, filtered, and applied as 50% substitution of pickle solutions. Chrome tanned leather satisfied the boiling test, but surface equality and shade do not meet the required standard.

The procedure of solid Cr- waste processing is according to Slovak Patent No. 277999. The process of preparation of reduced tanning tan-liquor[2] ensured required qualitative parameters of tanning Cr salts: concentration of Cr^{3+}, density, pH, basicity, degree of masking, and absence of Cr^{6+}. Obtained results on processing of chromium shavings, according to proposed technology, enable to use basic components of shavings by almost waste-less technology:

- collagen for reduction of sodium dichromate,
- chromic sulphate as a part of recycled tanning solutions.

The environmental processing of leather tanning waste and cleaning of waste water were solved in the project of 5th Frame program of European Union titled "Radical Environmentally Sustainable Tannery Operation by Resource Management" (RESTORM).[3,4] In this project, VIPO a.s. in co-operation with CSIC Barcelona (Spain) and Tomas Bata University in Zlin (Czech rep.), solved the processing of Cr shavings with application at surface finishing of leather and at development of ecologic polycondensation adhesive mixtures. Processing of Cr shavings by enzymatic hydrolysis in alkali medium and following applications is described in papers.[5-10] The processing of chromium shavings is solved in such a way that after milling or grinding removes Cr^{3+} by oxidation to Cr^{6+} in alkali medium. After filtration, washing and dehydration Cr^{6+} is reduced to Cr^{3+} in acid medium. Repeating this cycle, residual chromium is almost completely eliminated. There is used dosing up to 10% of hydrogen peroxide during 20 min. and 2.5% of formaldehyde; changing alkali and acid medium reaches complete elimination of chromium after 8 cycles.[11,12]

Research of laboratory preparation of collagen from chromium waste and interruption of Cr—collagen bond

Systematic structure of three-helixes adds to collagen fibers strength and formability, while their further mechanic and chemical stability results from intra and intermolecular bounds. Creation of network bounds **in vivo** is interposed by hydroxylase enzyme during the lifetime. Degree of cross-linking in vivo grows with increasing age. Technically significant modification reactions of collagen **in vitro** have practical application in the technology of leather, in production of furs, synthetic bowels, semi-synthetic leather and also at improvement of gelatins and glutinous adhesives. At these modifications, there are irreversible cross-bounding interactions in collagen by action of bi-functional and poly-functional agents; collagen is consequently physically as well as chemically changed. Tanning matters could be divided into two base groups:

1. inorganic compounds—coordinative compounds of Cr, Al, Zr, Fe, salts of rare soils, izopolyacids and heteropolyacids of Si, P, W, Mo,

2. organic compounds—vegetal tannins, syntanes, aldehydes, chinones, fats, sulphochlorides, some synthetic polymers.

Collagen cross-linking by chromium

Blazej and Svancer measured donor power of individual ligands in regard to chromic cation and assembled this line with increasing donor power:

$SCN^- < NO_2^- < M_2O < J^- < ClO_4^- < NO_3^- < Br^- < Cl^- < SO_4^{2-} < CO_3^{2-} < B_4O_7^{2-}$

$< HCOO^- < <$ gelatin $<$ tartrate $<$ acetate $<$ EDTA $<$ oxalate $< PO_4^{3-} < SO_3^{2-} <$ citrate

In this line, ligands appearing behind gelatin have much bigger donor power than collagen blue sheetings. Chromic salts, which are coordinated by them, have not tanning properties. Relatively high temperature of shrinkage of chromic leather shows to relatively high content of cross bounds in comparison with other methods of tanning. In the molecule of tropo-collagen, there are about 30 binding sites able to react with chromic complex at creation of cross bound.[13,14] Unattached ligands exist in a form of molecules or ions and they can capture the definite number of slots in the internal sphere of the complex. There can be created a common formula for a single core complex:

$(Cr^{A}_{6-x}M_x)^{3-x}$ A—anion ligand
M—cation ligand

Anions of various acids and salts, and the hydroxyl group belong to the anionic ligands. Water, amines, and various alcohols belong to the molecule ligands. Chromium complex salts, containing bisulphate ions next-to hydroxyl groups in their internal sphere, have tanning efficiency. Hydroxyl groups in single-core complexes are able to react with two chromium atoms; so multi-nuclear complexes, where atoms forming the complex are linked by one, two, or three bridges, are formed. The process is called olification.

In technical tanning chromium solutions, the main component is cationic olificated double-nuclear alkaline chromium disulphate. Chromium salts (aluminum salts in smaller scale) are used in leather tanning industry mostly at leather tanning. The important criterion of tanning efficiency is a possibility to create permanent linkages with collagen, which are not hydrolyzed by water. The main principle is the creation of ionic linkages. At the pH value of 3-4, chromium is forming stable basic oligomer complexes with acid residues in the collagen molecule.[13,14] Chromium waste from industrial leather tanning production was used for research in laboratory preparation of dechromed collagen.

The following procedures of dechroming of chromium waste were compared under laboratory conditions:

1. influence of EDTA—di-sodium salt of ethylendiamintetraacetic acid (Chelaton III.) on degree of dechroming in acid medium,

2. influence of inorganic acids on degree of dechroming,

3. influence of organic acids on degree of dechroming,

4. influence of reductive reagent HSO_3^- in alkali medium, with following cross-linking with formaldehyde and elutriation of $Cr_2(SO_4)_3$ in acid medium,

5. influence of changing of alkali and acid medium on degree of dechroming.

The laboratory results of this de-chroming confirmed the assumption that it is possible to reduce the content of chromium in chrome tanned waste by mentioned procedures and chemicals.

- De-chroming under effect of Chelaton III was carried out at high temperature in acid medium, at creation of violet colored complex, while the Cr-collagen bond is weakened by the effect of EDTA. The reached degree of dechroming was approx. 85% while losses of collagen were within the range 20–25%.

- De-chroming under effect of inorganic and organic acids. The best results were obtained by vitriol acid. Maximal efficiency is approx. 70%, while losses of collagen were proportionally increased with the temperature and concentration of the acid. The advantage of this procedure is possible regeneration of chromium de-chroming bath in leather tannery. The disadvantages are high losses of collagen by hydrolysis and low efficiency of de-chroming.

- De-chroming under effect of reduction reagents as they are: sulphites, hydrosulphites, dithionites etc. with current cross-linking of collagen by aldehyde and elutriation Cr in acid medium. The efficiency of de-chroming is approx. 90%; losses of collagen are lower than 10% in consequence of collagen cross-linking. The disadvantage of the procedure is that collagen cross-linked by aldehyde losses its previous properties (the ability of swelling in dependence on pH value).

- De-chroming under change of pH value (changing of alkali and acid pH value). The advantages of the procedure are: high approx. 99% efficiency of de-chroming of chromium waste, low losses of collagen by hydrolysis, high cleanness of extracted $Cr_2(SO_4)_3$, fibril structure of collagen substrate (what enables its better applications), separation and processing of de-chroming baths in conjunct with waste water from tanning.

EXPERIMENTAL

The research of de-chroming technology of solid chromium waste without oxidation of Cr^{3+} to Cr^{6+}, continued by the proposal of the technologic procedure, its verification and optimization. Cr-shavings from industrial production were used for the development of technology. In laboratory conditions, the work continued by optimization of dechroming technology of chromium waste. De-chroming technology of extraction of solved chromic sulphate after previous treatment in alkali medium $Ca(OH)_2$ was proposed for interruption Cr^{3+}–OOC—collagen bond. In alkali medium pH >11, some aminoacids are decomposed and amide nitrogen is decreasing, what results in the movement of iso-electric point of collagen to acid pH range. The decrease is expressed by weakening of Cr–collagen bond and easier extraction of Cr from collagen structure. In the experimental part of work, the influence of concentration of alkali and acid, temperature and number of de-chroming baths on de-chroming degree and a loss of collagen were observed. Collagen substrate of fibril structure with dry content matter 20% after pressing was prepared from chromium waste by the technology of changing alkali and acid pH.

The originality of the aims consists in environmentally friendly processing of solid chromium waste generated in the technology of leather production.

- dechroming technology of chromium shavings will be possible to realize in usual technologic equipment,
- the risk of oxidation of Cr^{3+} to carcinogenic Cr^{6+} is minimal,
- primary structure of collagen is kept,
- standard leather tanning chemicals are used, temperatures are below the temperature of collagen denaturation,
- high cleanness of extracted Cr^{3+} is ensured contrary from all other types of collagen hydrolysis, what enables to recycle chromic sulphate from dechroming bath,
- dechroming bath will be possible to separate and recycle together with operational water with the content of $Cr_2(SO_4)_3$ with concentration 1 to 4 g of Cr_2O_3 per liter at the producer of waste,
- collagen is natural non-toxic easy biodegradable biopolymer, it improves technical parameters of polycondensation adhesive mixtures e.g. viscosity, pot-life, gel time, physical and mechanical parameters of glued products, and environmental parameters by lowering of formaldehyde emissions.

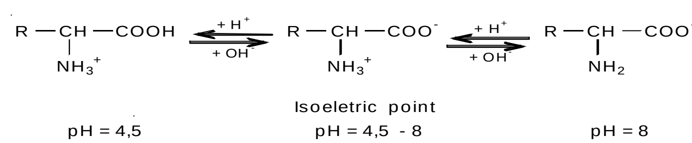
Qualitative evaluation of parameters of collagen substrate after de-chroming

Three types of collagen substrates from chromium waste were prepared at three different temperatures. Qualitative parameters of collagen were evaluated by following characteristics:

- iso-electric point,
- degradation—hydrolysis of native structure of collagen was evaluated as its increased solubility at the temperature of 38 °C and at two pH values (6.8 a 1.5) during 12 hours,
- amount of residual Cr in the collagen substrate after de-chroming in $mg.kg^{-1}$,
- pH value of de-chromed collagen,
- dry content matter of recycled collagen in [%],
- content of ash in collagen in [%],
- total nitrogen in [%].

Collagen, similarly as well as other proteins, is an amphoteric polyelectrolyte, what causes that its ion reactions run in dependence on pH value of medium. It means that one part of groups of side chains is ionized in alkali and another part in acid pH range. Collagen in the iso-electric point can react as ligand by two donor atoms of oxygen on carboxyl group and nitrogen atom of aminogroup:

R- collagen



Iso-electric point [IP] represents the pH value where acid COOH and alkali NH_2 groups in collagen are in a balance. Iso-electric point of native collagen is at the pH value of 7.5; the pH value can be changed and moved by technologic treatments in the range of pH value 4.5–8.0, while some properties are changed:

- stability,
- reactivity,
- ability of hydration—swelling. . .

The decrease of IP is connected with the decrease of amide nitrogen, as a consequence of hydrolysis of amide bounds of some aminoacids. Iso-electric point movement from neutral to acid range indicates some changes of native collagen.

At the determination of IP, there is necessary:

1. to prepare a sample of collagen with removed extraneous substances—contaminators, residual technologic chemicals—lime, salts, Cr^{3+}, acids...

2. to prepare a puffer, with pH value covering supposed value of iso-electric point.

RESULTS AND DISCUSSION

Determination of iso-electric point of collagen after de-chroming

Three types of collagen substrates from chromium waste were prepared at temperatures of 20, 30, and 40°C. Basic parameters of collagen substrates after extraction of extraneous substances are:

- dry content matter 20 ± 0.1%,
- pH value of collagen in the range of 6.5 ± 0.1.

The amount of 2.0 g of cleaned collagen was researched in the citrate puffer according to the scheme described in tables 1 to 3. Iso-electric point was determined by intersection of both lines in Fig.1 to 3.

Optimizing of technology, determination of the influence of temperature, pH, and number of dechroming baths on amount of released Cr^{3+} and qualitative parameters of collagen

For optimization of technology of de-chromed collagen preparation, chromium waste from industrial production was used with following parameters:

- dry content matter 48–50%,
- content of Cr …………….3.6–3.8%,
- ash ……………………..... 9.8–10.2%,
- total N.............................16.8%.

TABLE I

Values of measurement for determination of iso-electric point of collagen jelly No. 1 prepared from chromium waste at the temperature of 20°C

Sample No.	pH buffer	pH sample	change of pH
1	3.19	3.53	+ 0.34
2	4.37	4.66	+ 0.29
3	5.62	5.52	+ 0.10
4	6.45	6.37	– 0.08
5	7.35	7.19	– 0.16
6	8.38	8.12	– 0.26

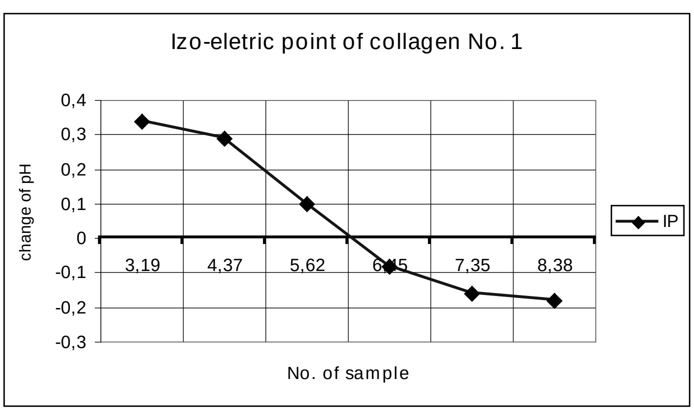


Figure 1. Iso-electric point of collagen No. 1 determined in citrate puffer is at the pH value 6.0.

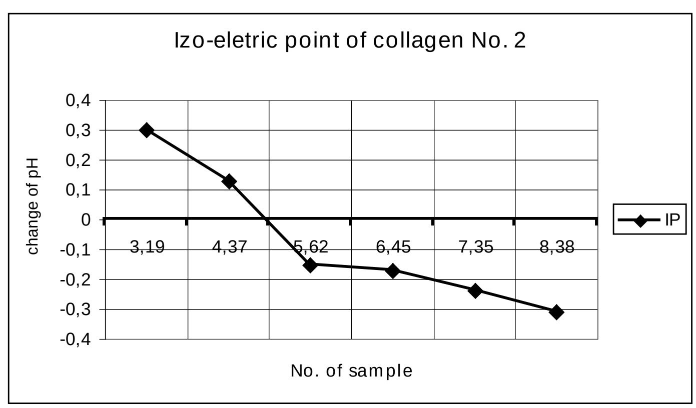


Figure 2. Iso-electric point of collagen No. 2 determined in citrate puffer is at the pH value 5.0.

TABLE II

Values of measurement for determination of iso-electric point of collagen jelly No. 2 prepared from chromium waste at the temperature of 30°C

Sample No.	pH buffer	pH sample	change of pH
1	3.19	3.49	+ 0.30
2	4.37	4.5	+ 0.13
3	5.62	5.47	– 0.15
4	6.45	6.28	– 0.17
5	7.35	7.11	– 0.24
6	8.38	8.07	– 0.31

TABLE III

Values of measurement for determination of iso-electric point of collagen jelly No. 3 prepared from chromium waste at the temperature of 40°C

Sample No.	pH buffer	pH sample	change of pH
1	3.19	3.44	+ 0.25
2	4.37	4.39	+ 0.02
3	5.62	5.50	– 0.12
4	6.45	6.26	– 0.19
5	7.35	7.14	– 0.21
6	8.38	8.15	– 0.23

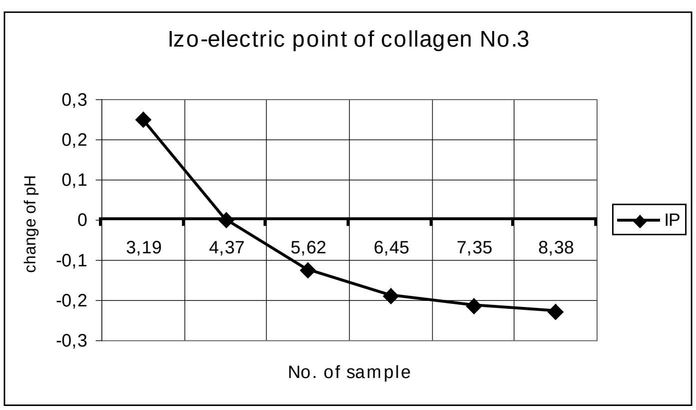


Figure 3. Iso-electric point of collagen No. 3 determined in citrate puffer is at the pH value 4.37.

At this pH value, collagen changes own reactivity, degree of swelling, etc. Chemical analysis of dechromed substrate and dried collagen hydrolysis is in the table 4.

Research on optimizing of chromium leather waste de-chroming technology continued as follows:

- it was observed the influence of temperature of 20°C, 30°C, 40°C and three dechroming baths—extractions on the concentration of Cr and losses of collagen in dechroming baths, (samples for testing were taken every 30 minutes),

- concentrations of released chromium and hydrolyzed collagen in [%] are presented in tables 5 to 7.

Determination of the de-chroming efficiency

The amount of Cr^{3+} in de-chroming bath was determined by spectrophotometric measurements of extinction at wavelength $\lambda = 578$ nm. The principle of the method is the fact that Cr^{3+} creates a violet colored complex at boiling with EDTA. Biuret agent was used for determination of the amount of hydrolyzed collagen as verification and

TABLE IV

Chemical analysis of dechromed substrate and dried collagen hydrolysis

Parameter	Collagen No.1	Collagen No.2	Collagen No.3
Dry content matter	20%	20%	20%
pH after treatment	4.0	4.0	4.0
Ash	6.7%	4.4%	3.4%
Hydroxyproline	10.1%	9.7%	9.1%
Total N	16.0%	15.3%	14.1%
Chromium - Cr^3+[mg Cr^3+/kg dry]	152.3	56.6	15.1
Extractable matter	not determined	not determined	not determined

TABLE V

Concentration of Cr and collagen in the 1st, 2nd, and 3rd de-chromation bath at the temperature of 20°C and pH value of 1.5

Time [min]	Amount of released Cr [%]	Losses of collagen [%]
1st dechromation bath		
0	0	--
30	26.8	--
60	54.2	--
90	67.3	0.09
120	75.6	0.15
150	80.5	0.37
180	84.4	0.51
2nd dechromation bath		
0	0	--
30	3.7	--
60	7.0	0.09
90	9.6	0.12
120	10.3	0.47
150	11.1	0.98
180	11.6	1.35
3rd dechromation bath		
0	0	–
30	0.5	0.35
60	1.1	0.87
90	1.4	0.87
120	1.4	1.24
150	1.5	1.62
180	1.6	2.43

TABLE VI

Concentration of Cr and collagen in the 1st, 2nd, and 3rd de-chroming bath at the temperature of 30°C and pH value of 1.5

Time [min]	Amount of released Cr [%]	Losses of collagen [%]
1st dechromation bath		
0	0	–
30	27.2	–
60	51.2	–
90	68.6	0.14
120	76.1	0.38
150	81.8	0.62
180	85.5	0.98
2nd dechromation bath		
0	0	–
30	3.9	–
60	7.2	0.14
90	10.1	0.36
120	10.8	0.96
150	11.6	1.35
180	11.9	2.00
3rd dechromation bath		
0	0	–
30	0.6	0.08
60	1.0	0.32
90	1.3	1.23
120	1.6	1.98
150	1.7	3.10
180	1.8	4.92

TABLE VII

Concentration of Cr and collagen in the 1st, 2nd, and 3rd de-chroming bath at the temperature of 40°C and pH value of 1.5

Time [min]	Amount of released Cr [%]	Losses of collagen [%]
1st dechromation bath		
0	0	0
30	27.3	0.04
60	53.3	0.16
90	66.1	0.32
120	76.3	1.00
150	84.1	1.65
180	85.8	2.52
2nd dechromation bath		
0	0	0
30	3.8	0.07
60	7.9	0.22
90	10.2	0.55
120	10.9	1.10
150	11.7	2.36
180	12.0	4.17
3rd dechromation bath		
0	0	0
30	0.6	0.12
60	1.4	0.47
90	1.6	0.88
120	1.7	2.05
150	1.8	4.04
180	1.9	7.15

quantitative method for determination of proteins in water solutions. From experimental measurements follow, that de-chroming temperature has the significant influence on efficiency of de-chroming but currently it increased losses of collagen by its hydrolytic decomposition. The rate of releasing—extraction of Cr from chromic waste and amount of technologic losses of collagen by hydrolysis significantly depend also on size of particles, specific surface, time, pH, movement of iso-electric point, amount of inorganic salts etc.

Influence of dechromed tanning solutions on qualitative parameters of tanned leather

Chromium waste from leather tanning production was the input raw material for dechroming technology. In this stage of work, the research was aimed at determination of the influence of temperature and pH in three de-chroming baths on amount and cleanness of extracted chromium salts. Results of obtained amount and cleanness of extracted chromium salts are described in the tables 8 and 9.

TABLE VIII

Experimental dependence of influence of temperature and three de-chroming baths on efficiency of de-chroming

Released Cr	20°C [%]	30°C [%]	40°C [%]
1. dechroming bath	84.4	85.5	85.8
2. dechroming bath	96.0	**97.4**	97.8
3. dechroming bath	**97.6**	99.2	99.7

TABLE IX

Experimental dependence of influence of temperature and three de-chroming baths on losses of collagen – quality of chromium salts

Released Cr	20°C [%]	30°C [%]	40°C [%]
1. dechroming bath	0.51	0.98	2.52
2. dechroming bath	1.86	**2.98**	6.69
3. dechroming bath	**4.29**	7.92	13.84

From experimental results and measurements follow, that mainly first de-chroming bath and temperature have the significant influence on the efficiency of de-chroming and on losses of collagen by its hydrolytic decomposition. From obtained results follow, that efficiency of de-chroming in the second de-chroming bath at 30°C was comparable with de-chroming in the third de-chroming bath at 20°C. Collagen losses decreased from 4.29% in the third bath to 2.98% in the second bath. Optimization of temperature and addition of inorganic salts enable speeding up the technology, lowering of collagen losses by hydrolysis, saving a part of technologic water at keeping of qualitative parameters of collagen. Obtained dechroming baths containing Cr^{3+} were coagulated and dehydrated by adjustment of pH value. Prepared chromic hydroxide was acidified by vitriol acid and after dissolving analyzed. Parameters of chromic tanning salts prepared from extracted dechroming baths after their concentration were:

- pH value of 10% solution 3.3,
- content of Cr_2O_3.....................120g/liter,
- basicity ....33.5°Sch—expressed in Shörlemer degrees,
- density ....1.168g/cm^3,
- content of Cr^{6+} ....not determined—test on 1,5-diphenylcarbonohydrazide

Also repeated application of chromic tanning salts in the technology of tanning without their concentration was laboratory tested. Samples of extracted Cr^{3+} de-chroming baths with concentration of extracted chromic sulphate in the range of 1.5–3.8 g Cr_2O_3/1liter, pH value in the interval 1.3 to 1.5 and amount of inorganic salts approx. 5%, after separation and filtration, were repeatedly applied in the technology of leather tanning as 100% substitution of pickle and partial substitution of tanning solution.

Quality of tanned leather was evaluated:

- subjectively: color shade, equality, tanning through the whole cross-section of blue sheetings,
- objectively: temperature of retraction, degree of exhaustion of tanning salts.

All investigated parameters of vet-blue meet the usual standard. Further testing and optimizing technology as a unit will continue the research of this part of the project.

CONCLUSION

Technologies for de-chroming of chromium waste, without oxidation to carcinogenic Cr^{6+}, were proposed and experimentally verified under laboratory conditions. De-chroming of chromium waste by the proposed technology has following advantages: high approx. 99% efficiency of de-chroming of chromium waste, low losses of collagen by hydrolysis and high cleanness of extracted $Cr_2(SO_4)_3$. Collagen substrate has fibril structure, which improves its applications, i.e. de-chroming baths are possible to separate and to process commonly with wastewater from tanning. Qualitative parameters of collagen substrate were evaluated after de-chroming at three different temperatures. Parameters of collagen were evaluated by determination of: iso-electric point, amount of residual Cr in collagen substrate after de-chroming in $mg.kg^{-1}$, pH of de-chromed collagen, dry matter content of collagen in [%], content of ash in collagen in [%], and total nitrogen in [%]. The method of determination of collagen IP was proposed and experimentally verified.

The research of optimal technology of de-chroming of chromium leather tanning waste continued by investigation of the influence of temperature of 20°C, 30°C, 40°C and three de-chroming baths—extractions on concentration of Cr and losses of collagen in de-chroming baths, (samples were taken for testing every 30 minutes). Concentration of released Cr and hydrolyzed collagen in [%] were determined by calibration curves. From obtained results it follows; that optimization of the technology enables to speed up the technology, and to save a part of technologic water at keeping of qualitative parameters of collagen. For example, de-chroming in the second bath at increased temperature to 30°C has comparable efficiency as in the third de-chroming bath at the temperature of 20°C with current decrease of collagen losses from 4.29 to 2.98%.

The effect of temperature and pH value on amount and cleanness of extracted chromium salts was proposed and experimentally verified in three de-chroming baths in laboratory conditions. From obtained results follow, that optimization of temperature enables to speed up the technology and to low losses of collagen by hydrolysis. Parameters of chromium tanning salts prepared from extracted de-chroming baths after their concentrating meet the standard. The advantage of proposed technology is that the de-chroming technology produces considerably cleaner chromium salts when compared to hydrolytic technologies of waste processing. De-chroming chromium water is possible to separate with water from technology of tanning and commonly concentrate in usual technologic equipment.

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REFERENCES

1. Matyašovský, J. et al.: The process of hydrolysis preparation. Slovak Patent No.: AO—247036, 1990.
2. Matyašovský, J. The process of preparation of reduced tanning tan-liquor. Slovak Patent No. 277999, 1994.
3. Matyašovský, J. et al. Ecoadhesives with biopolymers. In: RESTORM Report—WP1, 12 month Progress Meeting. Intermediate report of 5th frame program EU. Prague, 24 p., 2003.
4. Matyašovský, J. et al. Ecoadhesives with biopolymers. In: Report- RESTORM—WP1, WP6, 36 month Progress Meeting. Final report of 5th frame program EU. Netherlands, 2003–2005, 15 p.

5. Langmaier, F., Kolomaznik, K., Sukop, S., Mladek, M.; Products of Enzymatic Decomposition for Chrome-Tanned Leather Waste. *J. So. Leather Technol. Chem.* **83**, 187–195, 1999.
6. Langmaier, F., Kolomaznik, K., Mladek, M.; Modifying Products of Enzymatic Breakdown of Chrome-Tanned Leather Wastes with Glutaraldehyde. *J. Soc. Leather Technol. Chem.* **87**, 55–61, 2003.
7. Kolomaznik, K., Shanelova, K., Dvorackova, M.; Modified aminoplasts by protein hydrolysates for gluing ofwood. In: Adhesives in woodworking industry. TU Zvolen, 1999.
8. Kolomaznik, K., Mladek, M. Langmaier, F., Janacova D., Taylor, M., M.; Experience in Industrial Practice of Enzymatic Dechromation of Chrome Shavings, *JALCA* **95,** 55–63, 2000.
9. Kolomaznik, K., Mladek, M. Langmaier, F., Shelly, D. C., Taylor, M. M.; Closed Loop for Chromium in Tannery Operations, *JALCA* **98**, 487–490, 2003.
10. Kolomaznik, K., Vasek, V. Zelinka, I., Mladek, M. Langmaier, F.; Automatic Control of Recycling Technology for Chromium from Liquid and Solid Tannery Waste, *JALCA* **100**, 119–123, 2005.
11. Cabeza, F. L.; Isolation of protein products from chrome leather waste. *J. Soc. Leather Technol. Chem.* **83**, 14–19, 1997.
12. Cabeza, F. L., Taylor, M. M.; Processing of leather waste: Pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chrome. Waste Management **18**, 211–218, 1998.
13. Blazej, A. et al.; Structure and properties of fiber proteins. Bratislava: VEDA, 1978.
14. Blazej, A., et al. ; Technology of leather and fur. Praha: SNTL, Bratislava: ALFA, p. 20–85, 208–215, 1984.