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MALCOLM K. LEAFE, B.Sc.
Honorary Editor J.S.L.T.C.
49 NORTH PARK STREET
DEWSBURY
WEST YORKS. WF13 4LZ
Tel: 01924-460084

HYDROLYSIS OF CHROME SHAVINGS: APPLICATION OF COLLAGEN HYDROLYSATE AND "ACRYLIC-PROTEIN" IN POST TANNING OPERATIONS

C.S. CANTERA,[1] M. DE GIUSTI [2] AND A. SOFIA[1]

[1]*Leather Research Centre (CITEC), C.C. nº. 6 (1897) M.B. Gonnet, Argentina*
[2]*National University of La Plata—Engineering Faculty, 1 y 47, (1900) La Plata, Argentina*

Summary

The tanning industry is a generator of liquid wastes as well as tanned and non-tanned solid wastes plus those derived from the waste water treatment plant. This situation requires the introduction of "cleaner leather technologies" and of treatment systems for both effluents and solid wastes, so that pollutant discharge standards can be reached.

Particularly, solid wastes from chrome tanned leather require special attention because of their volume and of the requirements by authorities for their direct disposal in landfill sites. A technological alternative for upgrading these wastes is the detanning of chrome shavings (and wet-blue trimmings) through alkaline hydrolysis assisted by the action of proteolytic enzymes at a moderate temperature (55°C), so as to obtain a collagen hydrolysate and a "chrome cake", both with potential applications in the tanning industry.

This paper describes experiments performed in the application of collagen hydrolysates and of "acrylic-protein" polymers (acrylic acid / hydrolysed collagen polymers) in post-tanning processes for the manufacture of bovine leather for "softy" uppers. The retanning capacity of synthesized polymers and the positive effects attained from hydrolysates in the fatliquoring process ("nutrient and cosmetic effects") were assessed by means of a subjective evaluation and through a statistical analysis of the physico-mechanical strengths of the leathers.

Results are also shown from a laboratory test with chrome tanned hide powder aimed at assessing the "retanning degree" of these products. The test was developed to allow the comparison of the retanning agents under analysis and to complement the retanning test.

Introduction

The tanning process with chrome (III) salts is still the one most used worldwide. However, attempts continue to be made to develop technologies that may replace, either fully or partially, Cr (III) in the liquid or solid wastes produced. These attempts towards a reduction in the release of Cr (III) or to its recycling in leather making, coincide with the wishes of health authorities which, with slight national differences, apply severe limits to the discharge of Cr (III). The toxicity of Cr (III)—as opposed to that of Cr (VI)—is presently under consideration by health authorities in various countries, as well as by representatives from the tanning industry and from research institutes. Although arguments are proposed indicating that no scientifically demonstrable reasons exist for the establishment of such strict limitations to the discharge of Cr (III), the health authorities in many countries, applying a conservative policy, are maintaining such limits. On the other hand, around the world, the tanning sector is claiming for lower limits in the discharge of Cr (III) and, in some cases, their complete elimination. Also, several research institutions are carrying out studies and gathering scientific results on the toxicity of Cr (III–VI), aimed at consolidating these industrial demands and recommending that the established limits should be based on the risk involved against the natural environment (documents prepared by the IUE Commission of the IULTCS).

In the US, the Environmental Protection Agency (EPA) has excluded from its regulations all the chrome tanned solid wastes as hazardous materials (Federal Regulation 40, parts 260 to 299, July 1, 1990). However, these solid wastes could be upgraded, with respect to their volume thus "free space" would be left for the disposal of other wastes that are not amenable to upgrading.

Enhancing solid wastes means changing the modality used for "throwing away" the proteins contained therein and considering their re-utilization, for instance, in agricultural application as well as to manufacture industrial products to be used in the tannery itself. Particularly, wet-blue solid wastes require special attention due to the amounts produced (60 kg of wet-blue trimmings and 125 kg of shavings for every ton of salted bovine hides processed), and because of the health authorities' requirements for their direct disposal.

A technological alternative for the upgrading of these wastes is the de-tanning of chrome shavings by means of alkaline hydrolysis aided by the action of stable proteolytic enzymes at a high pH (between 10 and 11), so as to generate two products: collagen hydrolysate (CH) and chrome hydroxide precipitate (PCr), both with potential applications in the tanning industry. As examples of this alternative see references 1,2,3,4,5,6, as well as reference 7 which describes an industrial facility to process daily 4000 kg of chrome shavings. The collagen hydrolysate obtained is used mainly for landfill stabilization and as fertiliser (Pfister and Vogel Leather Company in USA).

CITEC's publication,[5] introduced a study of the relevant variables in the hydrolysis process which were used as the bases for the development of the de-chroming technology applied in the fabrication of the collagen hydrolysate analysed in this report. The features of this hydrolysate are described in Appendix 1. Fig. 1 shows an outline of the shavings de-chroming procedure and in Appendix 2, details of the method of preparation are given.

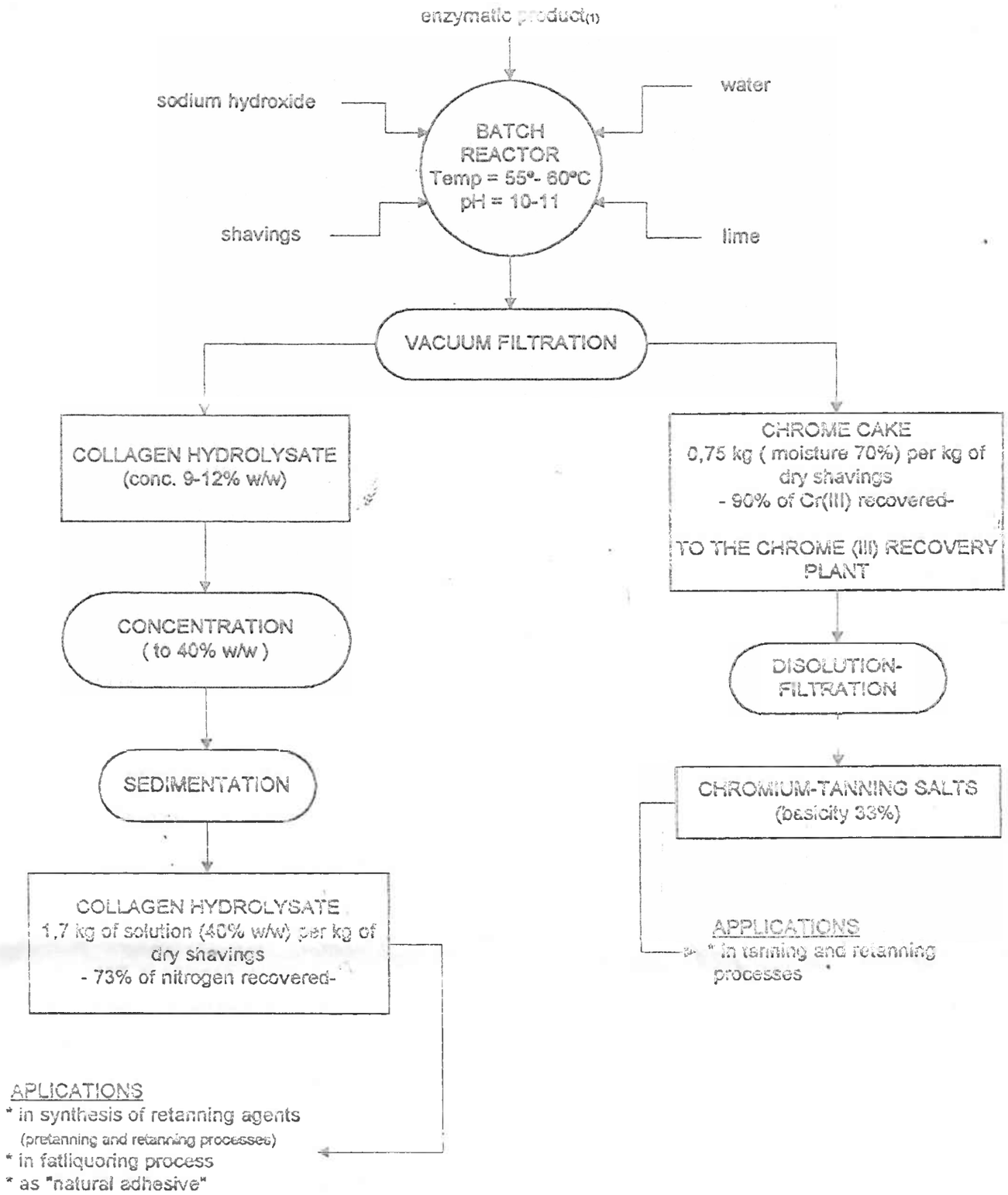


Figure 1. Procedure for the detanning of chrome shavings.

[1] Commercial enzymatic product "Alcamax" (Cergen s.a.), proteolytic activity 1800 LV (units Löhlein Volard). References to brand or firm name does not constitute endorsement by CITEC over others of a similar nature not mentioned.

The following can be produced from every kg of dry shavings:

- 1.7 kg of hydrolysate at 40% w/w (mixture of polypeptides + inorganic salts, 73% of the "proteins" in the shavings is recovered).
- 750 g of PCr, moisture 70% (highly-basified chrome (III) salts + inorganic salts), from which 85–95% of chrome may be recovered, depending on the filtration system employed.

Objectives

In addition to those mentioned in the Introduction, one driving force in a project aimed at upgrading wastes is the existence of appropriate markets for the by-products. The following goals have been fixed for this project:

- to evaluate the behavior of acrylic/acrylamide based retanning agents (modified collagen hydrolysates or MCH) obtained by using—*as a component of polymerization*—the collagen hydrolysate recovered during the dechroming of chrome shavings *via* alkaline hydrolysis;
- to evaluate the behavior of non-modified collagen hydrolysate (CH), through its application in fatliquoring.

Experimental Development

a) Experimental design

For the leather making processes performed at the CITEC's tannery plant, a factorial experiment design was introduced in which the variables are the *retanning agent* and the *hydrolysate*. Each one of the variables is taken as a factor; the retanning factor was set at five levels corresponding to retanning agents called MCH-105, MCH-106, MCH-87 and DM-692, and to a retanning agent free process (see section b). The CH factor appears at two levels: i.e. when it is absent and when it is incorporated in the fatliquoring formulation (see section c). The data on the properties being tested were submitted to variance analysis and the most appropriate linear polynomial model was established for each property on the basis of the significant factors and interactions.

The experiments were performed using 8 sides of split and shaved wet-blue bovine leather, with a good classification, selected at random from a production batch in a local tannery (4 left sides and 4 right sides). One left side and one right one were taken at random in order to make up one leather. All the leathers were then cut into butts and divided into eight pieces of about 30–40 cm each.

Each experimental group (8 as a whole) comprised 4 pieces and included a piece from each one of the leathers. The experimental units were numbered from 1 through 32, starting with the lowest right piece, as indicated in Fig. 2, and continuing in the same way with the rest of the leathers. The procedure described is aimed at attaining a homogeneous "population of experimental units" with replication, so as to allow adequate statistical analysis of the results.

b) Retanning agent variable

Using CH as one of the components, a local company manufacturing acrylic- and acrylamide-based retanning agents synthesized three of them for evaluation studies: two acrylic/collagen hydrolysate agents: MCH–105 and MCH–106, and an acrylic–acrylamide / collagen hydrolysate one: MCH–87. In addition a commercial acrylic retanning agent DM–692 manufactured by the same company was evaluated. Each one of the products was used as the only retanning offer, as 10% of the shaved weight (net offer: 3.5%). Appendix 3 gives brief manufacturing details of the products.

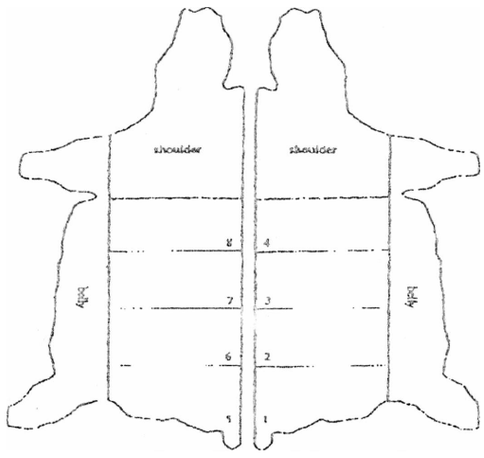


Figure 2. Selection of leather pieces.

In order to provide a control sample, (without any retanning agent) after neutralization and before the application of each product, a piece of leather was separated from each group and returned to the drum before fatliquoring.

c) Collagen hydrolysate variable

Preliminary experiments involving the application of CH in the retanning process, using chrome-tanned leathers and hide powder, have shown that non-modified CH has no retanning properties. However, tests involving application during fatliquoring showed that when leather properties were judged subjectively, the hydrolysate was of use.

On the basis of these experiments, 7% CH (in a 40% solution) was added to the fatliquor in a mixture with other components, before forming the emulsion.

Each group was assigned a single retanning agent selected at random. Four of the groups were treated with CH in the fatliquoring formulation, so that the variables with and without CH in fatliquoring could be available for each retanning agent.

d) Post-tanning procedure—manufacture of softy upper leather—(1.2–1.4 mm)

All the wet blue leathers were neutralized in the same experimental drum with sodium formate (1.2%) and sodium bicarbonate (0.5%) until a 4.4 final float pH was reached in a 100% float with water at 40°C and in a 1h run. Then the groups were assembled, while withdrawing the pieces of the "control group without retanning agent", and distributed in four identical experimental drums to start the retanning process (offer 10%, float 200% at 40°C, 1/run). Next, after adding the control pieces, fatliquoring was performed: 3% sulfated neatsfoot oil + 1% synthetic oil + 7% CH—net offer 2.8%—(only in those groups in which the CH variable was applied), float 200% at 50°C, 45 min run and later fixation at pH 3.9–4.1 with formic acid. All the pieces were removed

TABLE I
Tests with chrome-tanned hide powder(chp) and results of the chromatograms

	MCH-87	MCH-105	MCH-106	692
MCH uptaken (%) by the chp*	29.1±9.6 vc 33.0%	32.6±6.6 vc 20.2%	34.6±7.7 vc 27.2%	27.5±9.3 vc 33.8%
Retanning value (%) (see appendix 2)	4.6±4.8 vc 32.9%	16.1±3.3 vc 20.5%	17.3±3.8 vc 22.0%	13.7±4.6 vc 33.6%
Area reduction (%)**	20	37	40	39.2

* in practical terms, the collagen hydrolysate was not taken up by the chrome-tanned hide powder.
** gel filtration test before and after the application of MCH to leathers (see Fig. 3).
vc = coefficient of variation.

from the drums and were placed on horses, where they were left until the next day. Drying was performed in a Secotherm + vacuum + toggling; after 20–22% moisture content was attained; all the pieces were staked.

Tests Applied

a) Retanning power of MCHs

In order to assess the usefulness for retanning of the synthesized products, a chrome-tanned hide powder* was used, applying a procedure developed at CITEC that follows the basic methods for the assessment of the tanning degree for vegetable tannage[8] and the guide provided in reference 9 on procedures for the analysis of vegetable and synthetic tannins but incorporates temperature and pH variables (see Appendix 4).

This type of analysis complements the retanning tests on leathers and provides data on what we could define as "retanning value", which is useful for product comparison. Additionally, attempts were made to determine whether there is a correlation between these results and those obtained in the application of retanning agents to leathers.

b) MCH gel filtration chromatography before and after their application

For each of the retanning agents used in these experiments with wet-blue leathers and in the chrome-tanned hide powder test, a chromatogram was obtained before and after each application, using a column 36 cm high × 1.6 cm in diameter filled with Sephadex G 50, eluting with 0.05 M sodium chloride solution + 0.005 M borax. The tanning agent's degree of absorption was assessed by evaluating the decrease in the typical peak area.

c) Leather evaluation

Subjective properties: CITEC's technicians and those from the tannery evaluated the leather for fullness, tightness and mellowness of the grain, the visual appearance of the grain surface and the colour of the semi-finished leather (without dyeing). We also used the device developed by the British Leather Confederation for assessing the "softness"[10] (the property "softness" includes the properties of the fibrous structure, such as fullness, firmness, flexibility, elasticity and density).

*Chromiertes Hautpulver für die gerbstoffanalyse, Darmstadt.

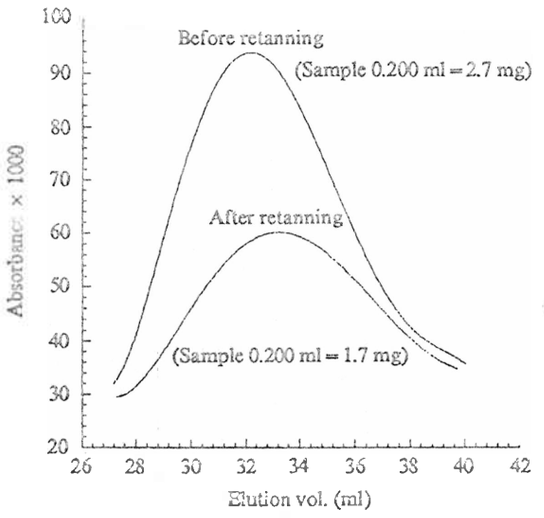


Figure 3. Gel filtration chromatography (MCH-105).

Physico-mechanical properties: The tensile (IUP 6) and tear (IUP 8) strengths (both parallel and perpendicular to the backbone) were evaluated, as well as to load and distension at grain crack and at burst (Lastometer–IUP 9). Data are available on each retanning agent (with and without the addition of CH in fatliquoring) for the statistical evaluation of each one of the physico-mechanical properties under examination.

UV radiation fastness: samples from all the leathers were exposed to UV radiation for 4 and 24 h. After exposure, the samples were submitted to heat treatment at 80°C for 1 h (thermal development)[11] and evaluated by means of a grey scale.

Suitability of the grain surface for dyeing: Dyeing was not included in the post-tanning processes in order to allow for a better appreciation of the above mentioned subjective properties and of the fibrous structure. For obtaining data on the behavior of the grain surface when dyed, a 15 × 15 cm sample from each one of the leathers was spray-dyed with a metallic-complex black dye in aqueous solution including a penetrator. The leathers were evaluated and sorted by colour and intensity.

Results and Discussion

1) Retanning power of MCHs and gel filtration chromatography

Taking into consideration the variability that is inherent in this material and the analytical procedure, 11 determinations for each retanning agent were performed with chrome-tanned hide powder (chp). Table I shows the average value and dispersion parameter of each MCH for the measurements of the retanning agent uptake and of the "retanning value".

Table I includes the reduction in the area of the peak for each MCH assessed by chromatography corresponding to the experiments performed with leathers.

Fig. 3 shows the type of diagram obtained during the chromatographic runs, the data relate to MCH 105

One interesting point in Table I is that the MCH values taken up by the chp show a correlation to be considered with the MCH absorption in the experiment with leathers. It must be stressed that the addition of the temperature and pH variables to the procedure developed

with chrome-tanned hide powder (see Appendix 2) allowed us to attain higher "tanning agent uptake" values, approximately doubling those obtained when the method described in reference 9 is applied, the latter being a modification of the official method.[8] These results show the importance of giving consideration to the above mentioned variables (pH, temperature) in the procedure used for retanning chrome-tanned hide powder to attain behaviour approaching that experienced with retanning agents in practical leather manufacture.

2) Physico-mechanical properties

In the presentation of the statistical analysis of results, aimed at facilitating the reading of this section, average values will be shown graphically instead of individual data and dispersion parameters. Also, only the conclusions considered as relevant will be shown with reference to the variables under analysis, and a description will be made of the final models that best reflect experimental data, without showing the results of the statistical analysis supporting the conclusions.

However, mention must be made of the fact that the statistical analysis involved the assessment of the homogeneity of the variance; the performance of variance analyses; the assessment of the linear polynomial model and its validity through the residual analysis.

a) Tensile strength

Specific load parallel to the backbone

Fig. 4a shows the average values for each retanning agent in the presence or absence of hydrolysate. A statistical analysis of the data showed, with a 5% probability, that the value of this property is a function of the MCH, of CH and of interaction between these two factors. It must be noted that the presence of CH increases the value of the specific parallel load and that, in the peculiar case of MCH–105, this situation is reversed. This led to the performance of an analysis of the variance without the MCH–105 data.† In this case, it was shown that the appropriate model is of the type:

$$estimated\ value = constant + CH$$

That is, the improvement in the value of the analysed property is a direct function of the presence of the collagen hydrolysate.

The peculiar behavior of MCH–105 (see also tear strength) invites further investigation comparing it with MCH–106, both with a similar chemical composition (presently, application experiments are being performed in tanneries with both retanning agents and a pilot development scale, as well as in production drum batches).

Specific load perpendicular to the backbone

This property showed a variable variance, thus hindering the statistical analysis of the data. However, a transformation of the data allowed an appropriate analysis of the results.[14] (Fig. 4b shows the average values of this property for each retanning agent with and without CH.

As occurred with the parallel specific load, in those leathers that received CH in fatliquoring, the figures

† Sometimes, when the mean values in one or two processes are far higher than other (or show particular features) and have a more significant variation, these processes may be withdrawn from the analysis. See references 12, 13 and 14.

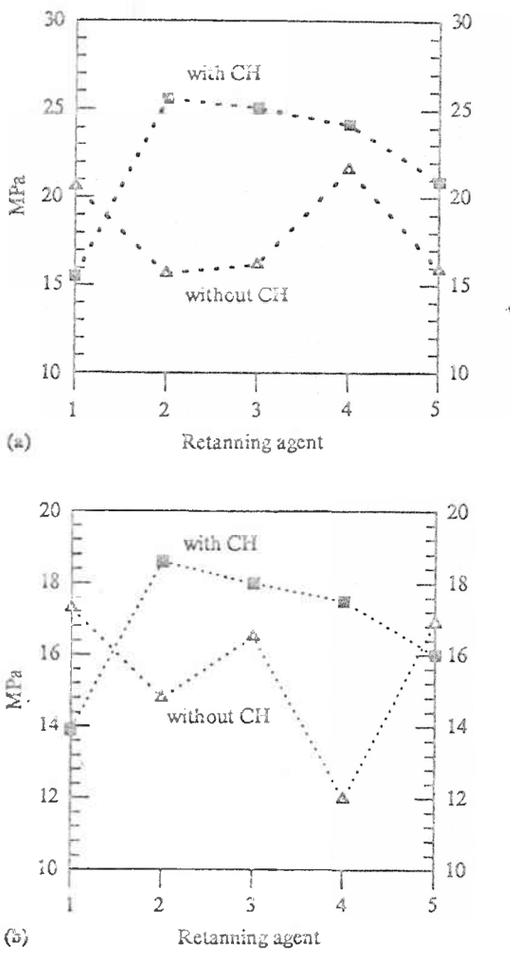


Figure 4. a) Tensile strength (IUP/6); parallel specific load (MPa).
b) Tensile strength (IUP/6); perpendicular specific load (MPa).

1 = MCH–105; 2 = MCH–106; 3 = MCH–87; 4 = 692; 5 = without retanning.
'with CH' means: application of collagen hydrolysate (net offer 2.8%) in fatliquoring (see item 3d).

showed a tendency to improve. A peculiar behavior was also shown by MCH–105. A statistical analysis without the presence of the data from MCH–105 reduces the model to the:

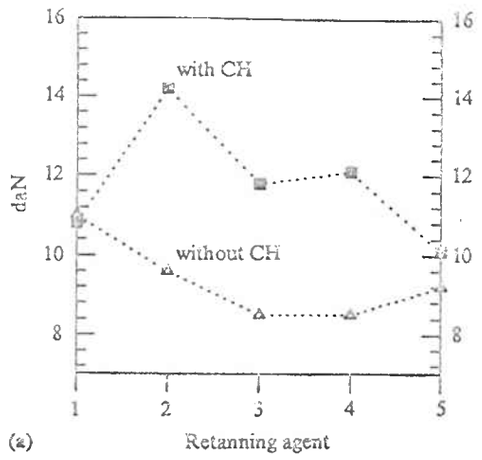
$$estimated\ value = constant + CH\ type$$

b) Tear strength

Tear parallel and perpendicular to the backbone

The average values for each retanning agent, with and without the CH factor, during fatliquoring are shown in Fig. 5a for the parallel direction and in Fig. 5b for the perpendicular one. Concerning this property, as for tensile strength, there is a significant influence of the presence of CH, as well as a peculiar behavior by MCH–105, both in the presence and in the absence of CH. An analysis of the variance for 5% probability showed that the only significant factor is CH. The resistance of the fibrous structure in the non-retanned leathers, when submitted to tear strength, in both directions, was also increased in the presence of CH.

When only the CH factor is considered (32 values with CH and 32 without CH), the following averages and standard deviations are obtained:



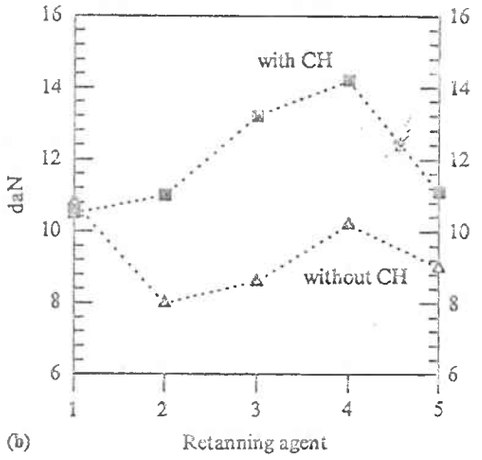
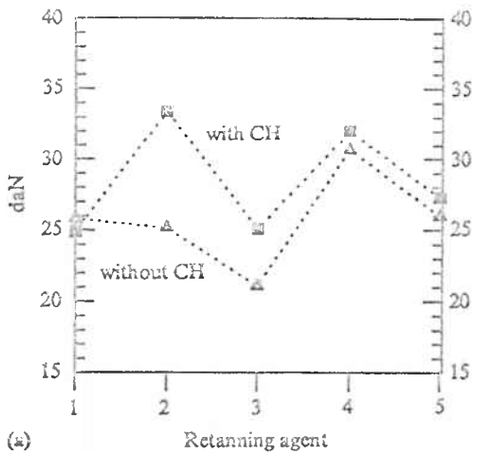


Figure 5. a) Tensile strength (IUP/6); parallel load (daN).
b) Tensile strength (IUP/6); perpendicular load (daN).

1 = MCH–105; 2 = MCH–106; 3 = MCH–87; 4 = 692; 5 = without retanning.
'with CH' means: application of collagen hydrolysate (net offer 2.8%) in fatliquoring (see item 3d).

Average thickness (mm) of the tear strength specimens.

	Parallel	Perpendicular
MCH–105		
with CH	1.43	1.44
without CH	1.43	1.40
MCH–106		
with CH	1.29	1.28
without CH	1.37	1.34
MCH–87		
with CH	1.40	1.34
without CH	1.31	1.30
692		
with CH	1.39	1.39
without CH	1.36	1.34
without retanning		
with CH	1.27	1.24
without CH	1.21	1.18



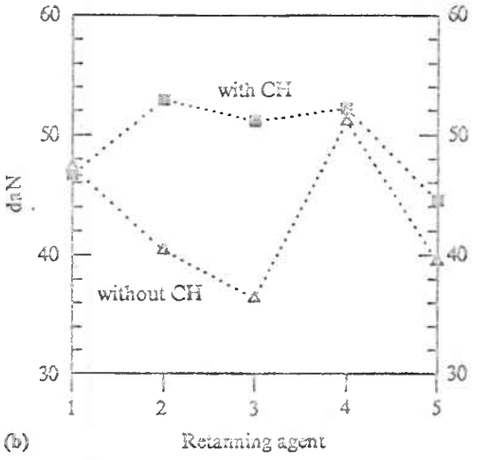


Figure 6. a) Lastometer (IUP/6); strength at grain crack (daN).
b) Lastometer (IUP/6); strength at leather burst (daN).

1 = MCH–105; 2 = MCH–106; 3 = MCH–87; 4 = 692; 5 = without retanning.
'with CH' means: application of collagen hydrolysate (net offer 2.8%) in fatliquoring (see item 3d).

Retanning	Distension at grain crack (mm)	Distension at leather burst (mm)
MCH–105		
with CH	9.9 ± 0.5	13.0 ± 0.7
without CH	9.9 ± 0.9	13.4 ± 1.2
MCH–106		
with CH	9.4 ± 0.4	12.4 ± 1.0
without CH	9.9 ± 1.4	12.9 ± 0.8
MCH–87		
with CH	9.2 ± 0.5	13.2 ± 0.8
without CH	9.0 ± 1.0	11.7 ± 0.6
692		
with CH	10.0 ± 1.2	12.8 ± 1.5
without CH	10.3 ± 0.9	12.7 ± 0.8
without retanning		
with CH	9.5 ± 0.8	12.7 ± 1.2
without CH	9.6 ± 0.6	12.4 ± 0.9

	with CH	*without CH*
Parallel tear	11.7 ± 2.8	9.4 ± 2.4
Perpendicular tear	11.9 ± 2.9	9.3 ± 2.8

A similar behavior to that described for tensile and tear strength in the collagen hydrolysate under analysis (mixture of polypeptides) is shown in reference 15 dealing with the synergistic effect of modified proteins (obtained from the detanning of wet-white shavings) applied along with appropriate acrylic retanning agents and catalysts. On the basis of the results we have obtained, it may be said that there is no need for using special tanned solid wastes (such as wet-white shavings or other chrome-free products) as described in reference 15, when the goal is the fabrication of "protein acrylic retanning agents" and collagen hydrolysates.

The "lubricating effect" of CH upon the fibrous structure, as well as the softness provided by the hydrophilic property of protein hydrolysates serves as an explanation of the resistance against mechanical stress. It must be noted that CH reverses the general trend shown by polymeric syntans in decreasing tear strength when used to increase the filling effect in chrome-tanned leather. As was shown in Table I, CH does not have any retanning properties.

c) Lastometer test

Load and distension at grain crack and burst

Figs. 6a and 6b show the average values of the load at grain crack and burst, respectively, for each one of the retanning agents, with and without CH. On the attached table the distension data corresponding to both loads are included, where non-significant difference were found. An increase in resistance by the fibrous structure is also observed in this property when the collagen hydrolysate is present, as well as special behavior by the MCH-105, as described previously for other physico-mechanical properties. All of the results for the physico-mechanical properties complied with the requirements of the tanner for this particular leather.

3) Subjective properties

When an evaluation was made of the grain tightness, fullness and softness of the leathers, the visual appearance and the colour of the semi-finished leather (undyed), 50% of the 32 pieces were classified as within the tannery's standards (high quality upper with regard to firmness and appearance of the grain). Among the pieces below standard, we found those that were not retanned, 4 pieces of MCH-87, 4 of DM-692, 3 of MCH-106 and, the least excluded, MCH-105 with one piece. Development experiments performed in the same tannery with sides, applying MCH-105 as a single offer, confirmed the subjective results of this experiment, as well as those obtained regarding mechanical properties. The tannery supplying the wet-blue uses a mixed Cr/synthetic/vegetable tanning system.

As a general rule, among the evaluated subjective properties, there was no evidence of a significant influence of the collagen hydrolysate (CH) variable, as it was observed for the mechanical strength of the leather; however, the latter produced a better grain softness ("cosmetic effect"). All the results obtained for the physico-mechanical and subjective properties complied with the requirements of the leather manufactured by the tanner (softy upper leather).

4) UV radiation fastness

An evaluation, after 4 h of UV radiation plus thermal development for 1 h at 80°C of the leather samples corresponding to each one of the retanning agents, (with and without CH) showed a value of 4 on the grey scale for the valuation of colour change, while the same process after 24 h irradiation resulted in value 3. It must be taken into account that the grey scale classes fastness 5 as representing no colour contrast and 1 as maximum contrast. Tests performed by submitting the leather samples to heat for 24 and 48 h at 90°C showed similar results as those mentioned above for UV radiation. The results described as obtained for "accelerated ageing" are acceptable.

5) Suitability of the grain surface for dyeing

A visual comparison of dye intensity in the application test described under 4c above allowed us to rank the retanning agents in the following decreasing order of intensity:

leather without retanning > [*MCH-105 and 692*] > *MCH-106* > *MCH-87*

Development experiments carried out at tanneries with retanning agent MCH-105 have confirmed an increase in colour intensity when the "protein retanning agent" is used, as compared with the usual retanning system. Similar results are described in reference 15 regarding the application of acrylic retanning agents and modified proteins, as well as in reference 16, describing the application of a hydrolysate obtained from wet-white shavings in the retanning process by replacing part of the total amount of retanning agents.

Summarising the analysis of the experimental results, it may be said that:

- On the basis of the subjective and physico-mechanical properties evaluated, acrylic retanning agents MCH-105 and MCH-106, obtained from the use of collagen hydrolysate by synthesis, have shown that they have appropriate retanning uses for the type of leather manufactured softy upper.
- "Acrylic-protein" retanning agents MCH-105 and MCH-106—used as the only offer in retanning—allowed for the production of a semi-finished leather with the same qualities as that obtained in the tannery using a mixed retanning system (chrome/synthetic/vegetable).
- The collagen hydrolysate used in the fatliquoring process increased the resistance of the fibrous structure to tensile and tear strength, as well as in the Lastometer test.
- The features of the collagen hydrolysate and the results obtained indicate that this product deserves further study in post-tanning processes for different types of leather, in which their hygroscopicity, when adequately controlled (appropriate amount of the product added or its reduction by chemical reaction) might be beneficial, as well as its "cosmetic" action (grain tightness).

Conclusions

The applications of the "collagen hydrolysate" in the retanning process (use of synthesized acrylic-based hydrolysate retanning agents) and in the fatliquoring process (use of unmodified hydrolysate) are two relevant

alternatives in the search for ways of absorbing the considerable amount of hydrolysates generated during the upgrading of the shavings: 1.7 kg of CH—40% solution—per kg of dry chrome shavings.

Alkaline–enzymatic hydrolysis at a moderate temperature (50–55°C) is a useful process that can be easily applied to give a collagen hydrolysate with useful properties for use in leather manufacture or for use in the synthesis of acrylic–protein retanning agents.

An additional conclusion is related to the test performed with chrome–tanned hide powder (chp). In order to evaluate the behavior of retanning agents (determination of what we have defined as "retanning value") it would be advisable to give further consideration to the official method of analysis for the evaluation of vegetable and syntan tanning agents, including the temperature and pH variables, while adjusting the retan–chp ratio and the reaction time giving consideration to industrial application conditions. The aforementioned suggestion should be discussed within the IULTCS–IUC commission.[17]

Trials carried out in tanneries using acrylic–protein retanning agent and collagen hydrolysate in processing upholstery, grain upper leather and split upper leather will be reported shortly.

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Appendix 1

Features of the "collagen hydrolysate" (CH) (moisture free basis)

total ash (550°C)	– range 13.5%–16.0%
TKN	– range 14.0%–16.0%
fats (extractable in petroleum ether)	– range 0.2%–0.7%
chrome(III)	– range 50–150 ppm
pH (15% solution)	– range 9.5–10.5
proteinous matter	– mixture of polypeptides (MW range 7000–10000) (capilliary chromatography assessment)

Product storage (biological degradation)

The 40% CH solution obtained by concentrating (vacuum at 85–90°C) the hydrolysis product (10% CH solution), did not degrade when maintained in the laboratory under normal temperature conditions for a period of about 4 months. Bacterial degradation, after that period, was confirmed. It is advisable to protect the product with an appropriate biocide if proposing to store it in a tannery. Biodegradation assays are under way to select the most suitable biocide which will not interfere in the synthesis of the MCH's.

Appendix 2.

Collagen hydrolysate: method of preparation
(All percentages mentioned are referred to dried shavings weight)

700% of water (55°C) is added to the reactor together with 2.0% calcium hydroxide (lime is dispersed in part of the water 30 min before addition). Chrome shavings are added and the mix is stirred for 30 min. Afterwards, the shavings are treated with 8.0% sodium hydroxide for 3 h (alkaline hydrolysis step), and then 1.5% of a commercial enzyme product—proteolytic activity stable in alkaline medium—is added (enzymatic hydrolysis step), the mixture is further agitated continuously for 3 h.

The reaction was carried out at temperatures between 55 and 57°C, while the final pH value was within the range 10.0–11.0.

The conditioned alkali–enzyme chrome shavings are then submitted to an "extraction" or "cook" time at 90°C for 30 minutes. The reaction products are then left to stand, without heating, for 16 hours. The dispersion is then vacuum filtered, and the hydrolysate (10–13% w/w) is concentrated to 40% w/w—CH—ready for use.

Appendix 3

Some characteristics of the retanning agents used

In the development of the "acrylic–protein" retanning agents—with the incorporation of collagen hydrolysate as one of the polymerisation components—a local company, Cahesa s.a., synthesized three products following a classic catalysed redox acrylic/acrylamide polymerisation. These experimental products (approx. 35% w/w) have been named "Modified Collagen Hydrolysate (MCH)"

MCH–105 and MCH–106 are polyacrylic acid partly neutralized and "modified" with collagen hydrolysate (polypeptide chains). The collagen hydrolysate replaces the 30% of the total amount of acrylic acid normally used by the company for the manufacturing of its retanning agent commercialised under the trade mark DM–692). According with manufacturer's information, and taking into consideration conditions of production, retanning agent MCH–106 has a higher molecular weight than MCH–105.

Retanning agent MCH–87 was obtained in a similar way to MCH–105 and 106, but used a mixture of acrylic acid and acrylamide instead of acrylic acid.

The products are not a simple mixture of polyacrylic acid + collagen hydrolysate; these 'experimental products' are at present being assessed by molecular weight and further characterisation. Gel filtration chromatography has shown that they are not physical mixtures. In comparison, when a mixture has been deliberately made, two phases have separated after a couple of weeks showing component separation.

Appendix 4

Determination of "retanning value" using chrome–tanned hide powder

The retanning value is determined by applying a given amount of the retanning agent to chromed hide powder (chp), so as to maintain a

total solids / g chp ratio of 0.5±0.02. An approximately 13% (p/v) solution of the retanning agent is prepared (and filtered, if suspended components exist) and the total solids are determined by drying 10 ml of the solution by evaporation in a vacuum at 98°C–100°C.

A given amount of chromed hide powder (with known moisture content) is weighed so as to contain 3.0 g of dry substrate. The latter is placed in a 50 ml covered Erlenmeyer flask.

100 ml of a solution is prepared with the necessary amount of the retanning agent to be tested, maintaining the aforementioned 0.5 ratio, plus distilled water as required. This solution is poured into the Erlenmeyer flask, which is agitated manually for a few seconds and then placed into a thermostatic bath at 40°C±2°C equipped with a reciprocating platform. The system is left to react for 2 hours under continuous agitation.

After 2 hours, the Erlenmeyer flask is removed and the pH is measured and adjusted to the value at which the retanning agent will be used in production. Then, the flask is placed into the thermostatic bath and agitated for 1 hour. After removal, its contents are filtered through a No. 43 Whatman filter. If the resulting liquid is not clear it must be filtered through a 0.45 microns membrane. 25 ml of the filtered liquid is pipetted into a crystalliser or into a capped capsule and dried by evaporation in a vacuum oven at 98°C–100°C to constant weight (two weighings at an interval of one hour do not differ by more than 2 mg).

A blank is run, without adding the retanning agent solution and a double determination is performed, using two different samples. Then, the following calculations are made:

(1) weight of offered solids

% of total solids of the original solution × pipetted vol. (ml) / 100

(2) weight of residue after treatment

[weight of residues in 25 ml (g)
– weight of the blank residue in 25 ml (g)]
× 100 ml / 25 ml

(3) weight of solids taken up by the chp

uptake weight = (1) – (2)

(4) weight of the solids taken up as a percentage of the offered weight

(3)/(1) × 100

The "*retanning value*" is assessed by means of the following ratio:

retanning value = [*weight of the solids taken up / 3.0 g chp*] × 100.