Application of Gelatin Extracted from Chrome Shavings for the Glazed Finishing of Leather

by

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Abstract

The objective of this work was to ascertain the performance of extracted gelatin from dechromed leather shavings as a coating in the finishing of leather. Gelatin is a protein-based material isolated from chrome-tanned collagenic wastes. A comparison between a commercial protein-based product, extracted gelatin and a mixture of extracted gelatin/glycerol was carried out. Based on the results obtained in previous studies, two fixing agents were used to fix the finishing: 5-ethyl-1-aza-3,7-dioxabicyclo[3,3,0]octane (oxazolidine II) and ethylene glycol diglycidyl ether (EGDE). The mixture gelatin/glycerol (using glycerol as a plasticiser) presented satisfactory results, compared with the commercial product, for the abrasion, gloss and flex resistance, although a poor performance under wet rub fastness (assessment of 1 on the grey scale (ISO 105-A02, A03) and adhesion tests were found due to the hygroscopic nature of glycerol. The formulation for potential further studies was the extracted gelatin fixed with EGDE, which showed the best performance on dry rub fastness (4-5 on the grey scale) and finish adhesion, and a good performance on resistance to abrasion and to flex (low loss of finishing and no cracking observed). The results confirmed the potential for gelatin, obtained from chrome shavings, to be used as a leather finishing agent.

Resumen

El objetivo de este trabajo es determinar el comportamiento de gelatina extraída de virutas de cuero descromado como un acabado en la terminación del cuero. Gelatina es un material proteínico procedente de desperdicios colagénicos curtidos al cromo. Una comparación entre un producto comercial basado en proteína, gelatina extraída y una mezcla de gelatina extraída/glicerina fue efectuada. Basado en resultados obtenidos en estudios previos, dos agentes fijadores se utilizaron en el acabado: 5-etil-1-aza-3,7-dioxa biciclo [3,3,0] octano (oxazolidina II) y etilen glicol-diglicidil éter (EDGE). La mezcla gelatina/glicerina (usando glicerina como plastificante) presentó resultados satisfactorios, en comparación con el producto comercial, en cuanto a abrasión, brillo, y resistencia a las flexiones, pero se encontraron rendimientos bajos de solidez al frote en húmedo (evaluado en 1 en la escala gris ISO 105-A02, A03) y en las pruebas de adhesión debido a la naturaleza higroscópica de la glicerina. La formulación potencialmente apta para futuros ensayos fue la de gelatina extraída estabilizada con EDGE, que demostró el mejor rendimiento en cuanto a solidez al frote en seco (4-5 en la escala gris) así como en adhesión del acabado, y buen rendimiento en cuanto resistencia a la abrasión y a las flexiones (baja pérdida del acabado y ningunas hendiduras fueron observables). Los resultados confirmaron el potencial empleo de gelatina, obtenible de virutas al cromo, para usarse como un agente de acabado para cuero.

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INTRODUCTION

Collagenic chrome-tanned waste produced during tanning operations may generate an environmental impact due to the large volume of waste generated and its chromium content, although chrome-tanning is based on the use of chromium(III) which is not toxic.[1-4] This situation requires the introduction of "cleaner leather technologies" and treatment systems for tannery effluents and solid wastes.[5-8]

To date, the current mode of disposing chrome-tanned waste is by land-filling,[9] which is expensive and environmentally inappropriate. Although there is no evidence of leaching of chromium in any form from sludge under normal conditions,[10-12] the possibility of Cr(III) being converted to Cr(VI) by oxidation under specific conditions such as alkalinity (pH > 9), temperature and aeration of the soils, exists[10, 11, 13, 14] and therefore needs to be considered when disposing the said waste.

There is a necessity to process this waste (which has the potential for re-utilisation) or to dispose of it in an environmentally acceptable manner.[15] The research into feasible treatments for chromium-containing solid waste has been undertaken during recent years.[16-29] The methods are mainly based on chemical and/or enzymatic hydrolysis,[19, 30, 31] with or without a previous dechroming of the material. The objective is to remove as much chromium from the chrome shavings as possible, enhancing the re-usability of chrome and collagenic waste.

Dechromed shavings can be treated in order to obtain gelatin, a natural polymer with multi-functional properties. Thermal denaturation, physical and chemical degradation of collagen involves the breaking of the triple-helix structure into random coils to produce gelatin. The functional properties of gelatin, as a film-forming polymer, make it a suitable component in finishing leather formulations. Film-forming polymers play an important role in the physical performance of finished leather.[32] However, the practical use of gelatin as a polymeric binder may be limited by its relatively poor mechanical properties. Fixing agents are employed frequently in finishing in order to improve the properties (such as stability, water resistance, molecular weight) of the polymeric binders used in coatings, and such an approach may be valuable for the extracted gelatin.

For the spraying application, it is necessary for the finishing polymers to have a low molecular weight. A liquid with low viscosity will promote flow and fusion into a coherent film.[33] Once the low molecular weight polymer film is formed, a crosslinking reaction can be induced which increases the molecular weight and improves the physical properties (rub fastness, abrasion resistance) of the finishing film. Fixing also removes hydrophilic groups (thus improving water resistance) and improves the inter-coat adhesion.[34, 35]

An old finishing technique that achieves natural, transparent and aesthetically pleasing leather is glazing or polishing. Glazing consists of applying a polishable sealer coat, usually a protein, followed by mechanical treatment (using a glass cylinder) on the dried leather. The leather is held against the roller and the action of the machine is to flatten the grain and produce a "soft handle."[36] The friction across the finish produces an elevated temperature which promotes hardening of the protein and a quick smoothing action at the same time. This result is a smooth, well sealed, high gloss surface.[37] Casein, a milk protein, is currently utilised in glazing finishes.

Traditionally, for protein-based finishes such as casein, formaldehyde was used as a fixing agent, but its use has now been restricted due to the considerable problems it causes on toxicological and environmental grounds, therefore a more recently identified, less toxic fixing agents, such as ethylene glycol diglycidyl ether (EDGE) and 5-ethyl-1-aza-3,7-dioxabicyclo[3,3,0]octane (oxazolidine II), will be evaluated for this type of finishing.

The leather finish process requires efficiency and safety in the application of the finish, and also to be an economically viable process.[38] The objective of this work was to investigate the substitution of commercial protein-based products, used in the finishing of glazed leather, with protein products obtained from the solid waste of the same tannery. If this can be achieved it will promote a more efficient, economically viable and environmentally acceptable option.

MATERIALS

Leather for finishing was obtained by tanning 10 calf skins. The hides and all the chemicals used during tanning were supplied by the tannery of the British School of Leather Technology, The University of Northampton, Northampton, UK.

The extracted gelatin from dechromed shavings was evaluated in comparison with a commercial binder (BI-01, Stahl, UK). This gelatin was obtained by thermal hydrolysis of dechromed shavings for 5 hours at 80ºC. The plasticiser (glycerol) and the fixing agents: 5-ethyl-1-aza-3,7-dioxabicyclo[3,3,0] octane (oxazolidine II) and ethylene glycol diglycidyl ether (EGDE), were supplied by Sigma-Aldrich, UK.

METHODS

Finishing of leather

A modified formulation for glazed finishing (Table I), supplied by finishing technicians from the British School of Leather Technology and Stahl, was used. The recipe was based on the use of a commercial protein-based binder (BI-01) as a control for the formulation of a glazed finish. Trials include the use of the commercial, substitution of the commercial binder with the extracted gelatin, and a mixture of gelatin and glycerol (2% (v/v)). The percentage of glycerol used is based on the results obtained from previous work (data not shown). A concentration of fixing solution of 3 M (based on the equivalent formaldehyde concentration traditionally used), of oxazolidine or EGDE, was used for all experiments.

TABLE I

Recipe for protein-based glazed finishing (applied by spraying)

	Amount (parts)	
	A	B
Water	500	500
Selladerm® brown (TFL)	50	—
Control (BI-01) or gelatin or gelatin-glycerol	200	200
BI-596 (Stahl)	200	300
FI-242 (Stahl)	50	—

After the application of the finishing formulation (by spraying 2 thin coats of formulation A and 2 thin coats of formulation B (Table I)), fixation was carried out (spraying 2 thin coats of the required fixing agent). The samples were dried in a drying tunnel for 24 hours at room temperature after which the samples were glazed by a finishing technician using a glazing machine from the tannery of the British School of Leather Technology, The University of Northampton, Northampton, UK.

Physical testing of the leather

Sampling of the hides was carried out according to ISO 2418. The different samples of leather, including a sample of crust, or non-finished leather, were conditioned for a minimum of 48 hours at a constant temperature of 20ºC and relative humidity of 65%.

Colour fastness to wet and dry rubbing was measured according to the ISO 11640 (IUF-450) method. The grey scales were used to assess changes of the leather colour as well as the colour transfer to felt pad according to ISO 105-A01, A02 and A03 (IUF 120, 131 and 132). Grey scales range from 1 (complete change in colour) to 5 (no change).

The level of adhesion of the finish to the leather was measured by the force required to pull the finish away from the underlying leather, according to the ISO 11644 (IUF 470) method.

The Martindale abrasion test was carried out according to the SATRA TM31 method, for 100 abrasion cycles (i.e. 1600 revolutions). Loss of finishing and colour change of the leather due to abrasion, were assessed subjectively and using grey scales. Loss of finishing may be visible on the whole surface of the sample or by forming a halo or ring. The subjective assessment refers to severe, medium, low or very low loss of finishing.

Measurement of finish flex endurance by the Bally flexometer method was carried out according to ISO 5402 (IUP 20).

The gloss was measured using a glossmeter, model 101N, supplied by Sheen, UK. The glossmeter measured the ratio of the intensity of an incident and reflected beam of light at 60º angle; the result were expressed as gloss units. A perfect reflecting surface, such as a mirror, will have a 100 gloss units.

Images of the leather surface were obtained using a scanning electron microscope (SEM) which allows the presence of cracks on the surface of the film, as well as salts, stain or defects on the leather to be observed. A Hitachi S-3000N Scanning Electron Microscope was used to analyse the surface characteristics of the finished leather.

RESULTS AND DISCUSSION

Rub fastness

The results of the rub fastness tests (ISO 11640) are given in Table II. As might be expected, wet rub fastness test showed a higher colour change or colour transfer than the dry test. In general, protein-based glazed finishes do not have good wet-rub properties[36]. The performance for finishes based on gelatin or gelatin/glycerol for dry and wet rub fastness, was comparable with the performance of the control (commercial protein-based product). After 1024 cycles, an average value of 3 in the grey scale assessment for the dry samples and 1-2 for wet rubs were obtained. However, even the sample of crust leather (non-finished leather), showed high colour transfer (2 in the grey scale).The best performance observed corresponded to the control fixed with EGDE, and gelatin-based formulations fixed with oxazolidine or EGDE.

Comparing the dry and wet rub fastness results, the performance of the finishes decreased during wet rub fastness. However, with the extracted gelatin the performance obtained was comparable to the control. The poor performance of the biopolymer films during wet rub fastness may be related to swelling, which tends to open up and weaken the structure of

TABLE II

Grey scale results after dry and wet rub fastness testing (ISO 11640) for non-finished and glazed-finished leather samples; 1024 cycles

(5 = very good; 1 = very poor)

Binder	Fixing agent	Dry rub fastness		Wet rub fastness	
		Leather	Pad	Leather	Pad
(Crust leather)		3	4	4	2
Control (BI-01)	None	4-5	3-4	1	1-2
	Oxazolidine	4	3-4	1-2	2
	EGDE	4	4-5	1-2	1-2
Gelatin	None	3-4	3-4	1	1
	Oxazolidine	4-5	4	1	1-2
	EGDE	4-5	4-5	1	1-2
Gelatin-glycerol	None	3-4	3	1	1
	Oxazolidine	4-5	3-4	1	1
	EGDE	4	3-4	1	1-2

the polymer allowing the pigment to diffuse out. Swelling should decrease with the addition of fixing agents and this behaviour was confirmed by an improvement in the performance of wet rub fastness with the samples fixed with EGDE and oxazolidine. However, the improvement after fixing was more evident for the dry rub fastness. The EGDE fixing agent showed the best performance with an assessment of 4-5 for the gelatin finish. This may be due to the properties that EGDE-fixing conferred to gelatin films, such as improved toughness, as well as reduced breakdown of the film which would allow the loss of pigment. In general, formulations based on the mixture gelatin/glycerol showed a poor performance as compared with the gelatin-based formulations. This behaviour could be explained by the hygroscopic nature of glycerol, which tends to weaken the polymer structure.

Finish adhesion

The results of the adhesion test showed a poor adhesion of the finish to the leather for all the samples tested. Values were found to be below 2 N for all cases. These results could be due to the poor penetration of the finish into the leather causing the finish not to adhere properly. Figure 1 shows the average of the results obtained for samples parallel and perpendicular to the backbone of the hide.

The sample with the highest value for adhesion was the sample finished with the formulation based on extracted gelatin as a protein substitute and fixed with EGDE. It should be noted that this formulation also showed the best performance for rub fastness (assessment of 4-5 on the grey scale for dry rub fastness).

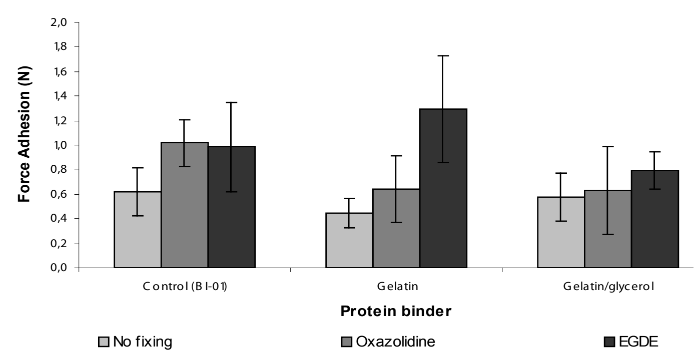

Figure 1: Results for the finish adhesion test (ISO 11644) for glazed-finished leather samples (using different protein binders and fixing agents).

A clear influence of the fixing for samples with extracted gelatin as a protein binder, can be observed (Figure 1), whereas no change was observed after fixing for the samples based on the mixture gelatin/glycerol. Comparing the extracted gelatin with the control, it can be seen that there is an improvement in the adhesion of the finish obtained with gelatin-EDGE. However, gelatin containing glycerol showed poor results for adhesion, which may be related to the introduction of weak bonds into the gelatin matrix, which affect the adhesion of the film to the grain.

TABLE III

Grey scale and subjective results for the Martindale abrasion test for the non-finished and glazed-finished leather samples

(5= good resistance to abrasion; 1= poor resistance to abrasion)

Binder	Fixing agent	Abrasion (grey scale)	Subjective assessment (Loss of finishing)
(Crust leather)		4	Polished
Control (BI-01)	None	3	Severe
	Oxazolidine	3	Very low
	EGDE	2-3	Low
Gelatin	None	3-4	Medium-severe
	Oxazolidine	4-5	Very low
	EGDE	2-3	Low
Gelatin-glycerol	None	2-3	Low
	Oxazolidine	3-4	Low
	EGDE	3	Low

Abrasion

Table III shows the results for the Martindale abrasion resistance test (SATRA, TM31). In almost all cases, a slight improvement could be observed after fixing, demonstrating that fixing has beneficial properties. However, in almost all the samples a loss of finish was visible, although not over the whole surface. A halo or ring was found on the surface of the samples, which may be due to the circular clamping mechanism that holds the sample.

The control (protein-based commercial product) without fixing, showed a severe loss of finishing occurring over the whole test area. The results obtained with samples fixed with oxazolidine showed the highest value (4-5) on the grey scale assessment. Again formulations based on gelatin showed an overall superior performance by having a grey scale value of 3-5.

Gloss

Table IV shows the results of the gloss measurement for all the samples. As expected, a large difference was found between the crust and glazed leather. The crust, or non-finished leather, showed a very low gloss index of 1.40 gloss units, whereas after finishing and glazing the samples showed, in general, values ranging from 15-30 gloss units.

The samples showed a decrease in gloss after fixing for all the protein binders studied. Average gloss values of approximately 28 gloss units for non-fixed samples, and 24 and 14 gloss units for oxazolidine and EGDE fixing were found, respectively. The sample finished with the mixture gelatin/glycerol in general showed a slight improvement on the gloss value (Table IV); however, using EGDE as a fixing agent, a "duller" effect on the leather was produced.

TABLE IV

Results obtained for gloss measurements for non-finished and glazed-finished leather

Binder	Fixing agent	Gloss (gloss units)
(Crust leather)	1.38 ± 0.04	
Control (BI-01)	None	28.25 ± 1.70
	Oxazolidine	25.23 ± 12.13
	EGDE	18.35 ± 2.12
Gelatin	None	27.23 ± 0.32
	Oxazolidine	22.25 ± 1.34
	EGDE	13.50 ± 0.92
Gelatin glycerol	None	28.28 ± 2.72
	Oxazolidine	22.93 ± 1.94
	EGDE	9.93 ± 1.24

Resistance to flex

Assessment

Similar results of flex resistance were obtained for all the samples tested. Samples under 10x magnification showed no cracking after 10 minutes, 30 minutes, 1 hour, 2 hours, 4 hours, 8 hours and 24 hours flexing. Initial studies of the isolated films (protein-based commercial binder, extracted gelatin and mixture gelatin/glycerol) showed some brittleness, however, this effect was not observed after the flexometer test, indicating all the films had flexibility for the application as a finishing/coating agent.

Scanning Electronic Microscope (SEM)

The surface of all the samples were observed under Scanning Electron Microscopy (50x magnification) in order to confirm the absence of cracking (Figure 2). No cracking was observed under the microscope, the change in the "smoothness" of the surface before and after flexing was due to the flexing of the leather rather than cracks in the finish.

CONCLUSIONS

The satisfactory result obtained from the flexometer test, as well as the promising results found from the physical tests confirmed the potential of extracted gelatin, obtained from dechromed shavings, to be used as a component in the finishing formulation of leather. The formulation of gelatin fixed with EGDE, showed a potential for further research. This particular formulation showed a superior performance for dry rub fastness, finish adhesion, resistance to abrasion and flex endurance.

The production of a bioproduct (gelatin) from tannery solid waste (chrome shavings) and its use as a finishing agent in the same leather-making process, promotes an environmentally friendly industry and leads to important environmental and economical benefits.

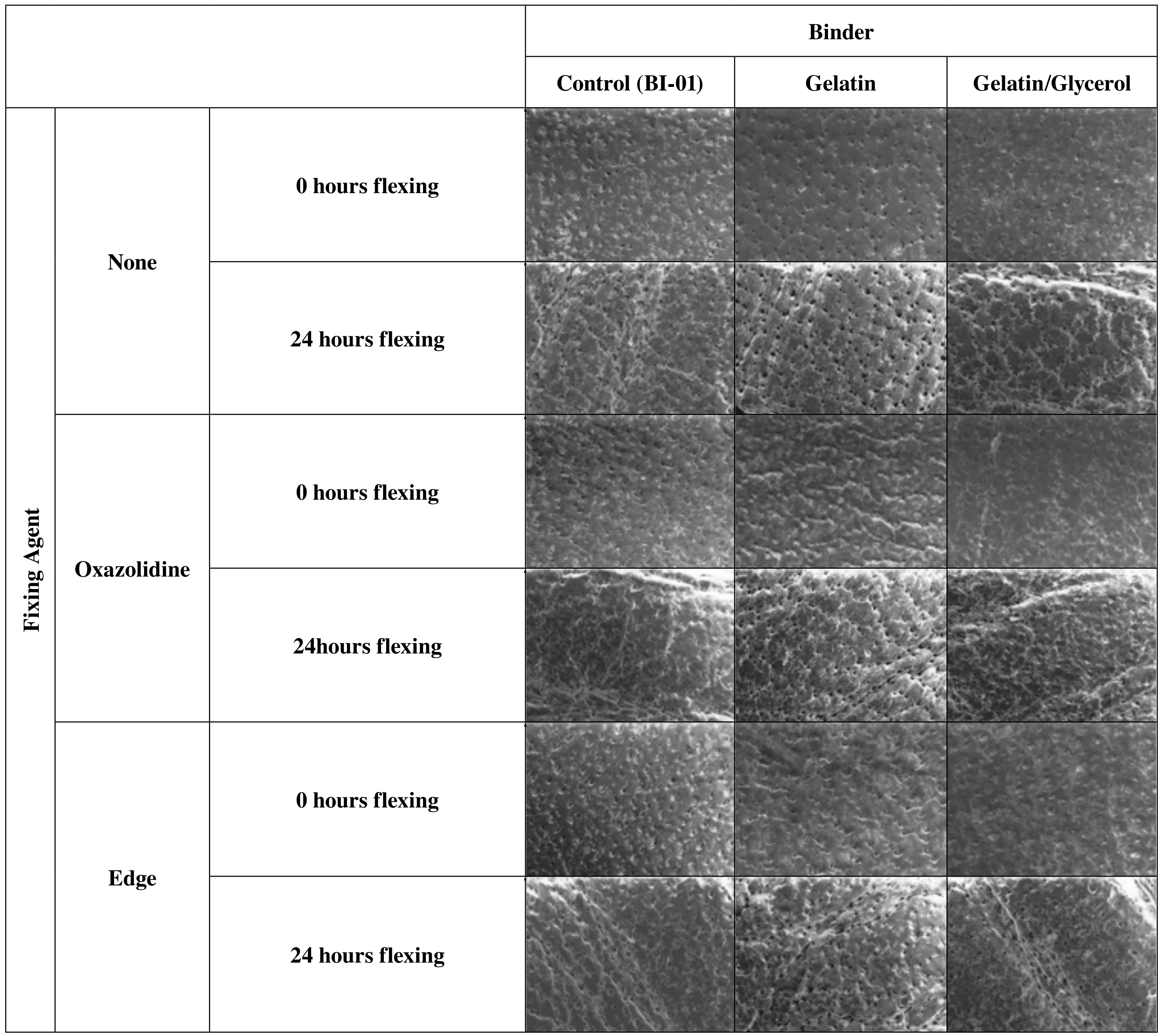

Figure 2: Scanning Electroinc Mocroscope images of the surface of finished-glazed leather (using different protein binders and fixing agents), after 0 and 24 hours flexing (10kV, 50x magnification)

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