

Hydrolysis of used leather and application of hydrolysates

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Abstract. The leather industry generates a significant amount of various wastes, and their utilisation is a serious task for researchers. Ways to reuse or decontaminate such waste are being developed intensively. Unfortunately, the reuse of finished leather, which eventually becomes waste, is almost unexplored. The present research is designed to evaluate the potential of finished leather hydrolysis to obtain protein hydrolysates suitable for reuse in leather processing and to establish factors that influence leather quality during such an application. Enzyme preparation Vilzim PRO Conc was characterised as a potential agent for such hydrolysis. The addition of 3–4% Vilzim PRO Conc is appropriate for the enzymatic stage of the hydrolysis process. It was established that after alkaline-enzymatic hydrolysis of used leather powder the obtained hydrolysates are complicated systems containing proteins, chromium compounds, dyes, fatliquoring materials, etc. Hydrolysates could be used for the dyeing of chromed leather. The method of preparation for dyeing and dyeing of wet-blue leather with the use of hydrolysate influences the depth of dye penetration and the quality of finished leather. It was established that the neutralisation process is not necessary before such dyeing. Also, an increased amount of formic acid is necessary to improve the bonding of fatliquors with dermal tissue after treatment with hydrolysate.

Keywords: exploited leather, hydrolysis, enzyme preparation, collagen, dyeing.

1. INTRODUCTION

The role of the leather industry in the world economy is indisputable: its global trade value is estimated to be approximately 100 billion US dollars a year [1]. In fact, leather manufacturing is one of the oldest and most widespread industrial activities in the world, in which a material (leather), mainly composed of a natural macromolecule (collagen), is chemically modified to obtain durable goods. The global leather industry produces about 1.7 billion m² of leather. Unfortunately, tanneries generate large amounts of solid and liquid wastes, which contain harmful chemical compounds affecting the environment, such as chromium, which is used in the tanning process. Until now, these compounds have been almost completely dumped in landfills [2].

Thus, of 1000 kg of raw hides, about 250 kg are found in finished products (including pelt splits), and the remaining 500 kg are hide wastes, containing gelatine, which can be exploited as biofertilisers and fertilisers for agriculture, and 250 kg are tanned and finished leather wastes for which organic valorisation solutions are sought [3].

Ozgunay et al. [4] divide all solid waste into three categories: untanned hides/skins waste (trimmings, fleshing wastes), tanned leather waste (shaving wastes, buffing dust), and wastes from dyed and finished leather (trimmings from leather).

The literature review allows the conclusion that wastes obtained before chrome tanning can be used in a relatively simple way [5,6].

The occurrence of chromium in wastes poses a major problem. Storage and incineration of tannery wastes does not eliminate the risk of secondary pollution of the en-

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vironment with chromium compounds [7]. The chromed leather waste can be recycled; as such, the waste consists of proteins and inorganic salts (chromium, etc.). The main problem in this case is the removal of chromium from collagen [8].

Literature analysis has shown that as wastes of finished leather, trimmings of leather [4] and leather polishing dust [3] were generally mentioned. On the other hand, no one should forget that since the world produces 1.7 billion m² of leather every year, a significant number of various products, containing possibly the same amount of leather, are discarded as garbage every year, as well.

Probably the most difficult part is namely the treatment of used finished leather because the material contains many chemicals: various inorganic and/or organic tanning substances, various dyes, fatliquors, synthetic polymers as fillers, etc. As a result, after finishing, the leather becomes chemically an extremely complex mixture, and the treatment of such waste should be more complex than that of the leather waste obtained after chrome tanning. In particular, the finished leather waste is considered a type of dangerous waste containing chromium since finished leathers are mostly processed from chrome-tanned leather, which means that this type of waste is strictly controlled in the process of disposal, storage, and transportation [9].

The literature presenting the possibilities to utilise the used leather is scarce. Probably the simplest method is to compost the leather waste. The composting process is an old and inexpensive method that converts organic waste into useful material (compost) that can be used as a soil conditioner and organic fertiliser. The authors state that the composting process represents a realistic way for the capitalisation of leather waste [9]. However, as composting is a lengthy process, there is a risk that chromium (Cr³⁺) compounds spread as leather waste is decomposed [10]. Furthermore, the use of compost containing relatively high levels of chromium compounds is also very limited.

The most often proposed technological solution to the problem of waste utilisation is the production of secondary or artificial leathers designed for footwear elements, fancy goods, or non-woven fabrics as substrates for leather-like materials [11]. There are suggestions to produce leather boards from buffing dust or blended fabrics [12,13].

Unfortunately, such propositions postpone the problem of end-product recovery and make it even more complicated as the composition of the product to be recovered becomes even more complex than that of the leather waste used to produce it.

More advanced solutions for the utilisation of finished leather should lead to a complete deconstruction of the leather down to the components and their applications to obtain added value products. The greatest benefits can be derived from leather wastes when they are converted into

proteins or their hydrolysates, which can be used for various purposes: cosmetic [14], medical [15], nutrition [16], fertilising [17], etc. Ding et al. [18] studied finished leather wastes as raw materials to obtain the collagen protein hydrolysate with high protein content, followed by the feasibility study of the hydrolysate on gypsum retardation. As the authors write, this study reveals a practical and sustainable route for the utilisation of finished leather waste. Voinichi et al. carried out a similar study [19], where the chemical, physical, and structural investigations of the properties of collagen hydrolysate showed that the chelating abilities due to carboxylic groups could be exploited for gypsum retardant additives. Collagen hydrolysate recovered from chrome-tanned leather through chemical treatments has also been used as a feed for anaerobic digestors to produce biogas [20].

Usually, the application of the hydrolysates of finished leather wastes is limited due to the presence of chromium and other materials used for leather finishing (dyes, fatliquors, fillers, etc.). While it is possible to separate collagen [21] from chromium by hydrolysis of the finished leather, the separation of collagen hydrolysate from the other aforementioned materials would be prohibitively cumbersome and not economically viable.

The simple hydrolysis of leather without the removal of chromium can be used to produce a solution that can be employed for the new tanning of leather, by mixing the untreated leather with the hydrolysate solution as it increases the overall chromium content. The industrial application of this process is straightforward from an industrial point of view since it requires low investment costs and can contribute to reducing the use of chromium salts and the costs of waste management [2]. Unfortunately, information in the scientific literature, which describes the possibility of using collagen hydrolysates for leather tanning, is related to the hydrolysis of leather shavings after chroming but not with the use of hydrolysis products from finished leather wastes [22].

The aim of the present research was to check the possibility of applying the existing methods of chromed leather wastes (shavings) hydrolysis to exploited leather hydrolysis by applying new enzyme preparations, to explore the composition of obtained hydrolysates, and to apply the obtained hydrolysate for leather processing.

2. MATERIALS AND METHODS

2.1. Materials

The leather for investigations was taken from a woman's leather jacket after it was disassembled, and the leather parts were separated from textile and other non-leather parts. It was pig leather red in colour. Ten small pieces

(5 × 5 cm) were cut from various places of this leather. The pieces were chopped and, afterwards, milled using homogeniser A 11 Basic (IKA, Germany) for obtaining leather powder.

The chromed semi-finished leather ('wet-blue') for investigation was purchased from the tannery 'Kėdainiū oda' (Lithuania). It was shaved to a thickness of 1–1.1 mm.

Proteolytic enzyme preparation (EP) Vilzim PRO Conc (Baltijos enzymai, Lithuania) with the proteolytic activity of 1400 units/g at pH 11 and the temperature 50 °C was used for hydrolysis.

Technical products used for the technological processes were: fatliquors Oleal 146, Oleal 1946; Fospholiker 661 and Fospholiker 6146, technical products by Codyeco S.p.a. (Vicolo del Grano, Italy); and Sellaset red H dye, produced by TFL Ledertechnik GmbH (Rheinfelden, Germany).

The chemicals used for the analysis were of analytical grade. Analytical and technical grade materials were used for the hydrolysis processes.

2.2. Procedures

Two methods of hydrolysis of the leather powder were employed for the experiments. The first was carried out according to the method described by Cantera et al. [21]:

- 10 g of powder; 2% (% based on mass of the powder) Ca(OH)₂; distilled water 1200%, mixed for 30 minutes in an incubated shaker KS 4000 model (IKA, Germany); NaOH 10%, mixed for 2 hours; addition of 4 or 6% EP Vilzim PRO Conc, mixed for 6 or 8 hours. Temperature of the treatment was 50 °C. After treatment, the liquid hydrolysate was separated from the solid product by centrifugation (20 minutes, 3000 rev/min), and both parts were analysed.

The second method of hydrolysis [8] was as follows:

- 10 g of powder; distilled water 1200% (% based on the mass of the powder) with 6% magnesium oxide, mixed for 48 hours at 50 °C. After treatment, the liquid hydrolysate was separated from the solid part by centrifugation (20 minutes, 3000 rev/min), and the liquid part (I) was analysed.
- Pouring of 200% distilled water on the solid part of the hydrolysate (% based on the mass of the solid part); addition of 1 or 3% EP Vilzim PRO Conc, mixing for 48 hours at 50 °C. Temperature of the treatment was 50 °C. After treatment, the liquid hydrolysate (II) was separated from the solid product by centrifugation (20 minutes, 3000 rev/min), and both products were analysed.

The control processes for the wet-blue leather were carried out as follows:

- Washing (here and for subsequent processes % based on chromed leather mass): water 100%, temperature 40–42 °C, 1 h, drain.

- Neutralisation: water 150%, temperature 35–40 °C, NaHCO₃ 1.5%, 0.5 h, NaHCOO 2.0%, 1.5 h, drain.
- Washing: water 100%, temperature 40–45 °C, 0.5 h, drain.
- Dyeing: water 200%, temperature 58–62 °C, dye Sellaset red H 1.5%, 2 h.
- Fatliquoring (in dyeing solution): water 200%, temperature 58–62 °C, Oleal 146 2%, Oleal 1946 4%, Fospholiker 661 3%, Fospholiker 6146 4%, 1 h, HCOOH 0.5%, 20 min, HCOOH 0.5%, 20 min, drain.
- Washing: water 100%, temperature 30 °C, 0.5 h, drain.
- Drying: the samples were placed on a table and dried in a free state for 48 h at 22–25 °C.

2.3. Analysis methods

The number of collagen proteins removed was estimated from the amount of hydroxyproline in the solid or liquid parts of the hydrolysate using a photo-colorimetric method [23]. Solid or liquid part samples were additionally hydrolysed using HCl at 120 °C for 10–12 h. The formation of a coloured soluble product was based on the reaction of hydroxyproline with p-dimethylaminobenzaldehyde. The absorption was measured with a GENESYS-8 spectrophotometer (Spectronic Instruments, United Kingdom) at a wavelength of 558 nm.

The total amount of protein was estimated using the Kjeldahl method [24]. The shrinkage temperature of the leather samples was determined as described in the literature using special equipment and replacing distilled water with glycerol [24].

The content of chromium compounds in the hydrolysate, dyeing solution and in the leather, and the content of extractable with dichloromethane matter in the leather were determined according to standard methods [25–26]. Physical and mechanical properties of the obtained leather were determined according to the standard [27].

The absolutely dry residue of the hydrolysate was determined gravimetrically by drying the sample at 105 °C. The amount of dye and other inorganic matter was calculated as the difference between the mass of dry residue and the sum of the masses of total proteins, chromium compounds, and the matter extractable with dichloromethane.

The pH of the hydrolysates was measured directly using a pH-meter (pH 526 WTW, Poland).

The penetration of dyes through the leather tissue was measured using a special scale optical microscope MPB-2 (Izyum Instrument Making Plant, Ukraine).

2.4. Statistical analysis

All data were expressed as the average value of measurements performed in triplicate. One sample was used for one measurement. Standard deviations did not exceed 5% for the values obtained.

3. RESULTS AND DISCUSSION

3.1. Hydrolysis of leather powder

During the investigation of leather powder hydrolysis using NaOH and EP Vilzim PRO Conc, two parameters were variable: the amount of EP was 4 or 6% and the duration of treatment after the addition of EP was 6 or 8 hours. The influence of the parameters on the properties of the obtained hydrolysis products (liquid part and solid part) was established, and the results are presented in Table 1.

The obtained results (Table 1) indicate that the amount of EP used and the duration of enzymatic treatment influence the yield of hydrolysed proteins. Also, the duration of the enzymatic treatment stage is more important than the amount of EP used. When this process is prolonged from 6 to 8 hours, the yield of protein materials (both collagenous and total) increases by about 10%. On the other hand, the same increase has a negative effect: the amount of chromium compounds in liquid hydrolysate also increases.

The organoleptic evaluation of the hydrolysates has shown that they were intensely red in colour. The assessment and comparison of figures, which define the amounts of chromium and protein materials with the amount of dry residue of hydrolysate, allows a proposition that probably the greater part of dyes, fillers, and materials extractable with dichloromethane, etc. was left in the hydrolysate.

The previous investigation allowed the conclusion that a much lower chromium content in hydrolysate, using the same method of hydrolysis, can be reached using chromed shavings – less than 10 mg/L [28]. Accordingly, the

method is suitable for finished leather powder hydrolysis only from a protein recovery point of view but is not appropriate due to the high content of chromium compounds in the liquid hydrolysate. Since the amount of chromium compounds was different depending on the hydrolysis conditions, a thorough analysis of any parameter of the process should be explored to achieve a higher dechroming level.

The second method of leather powder hydrolysis differed from the first one: it consisted of three stages. MgO was used instead of Ca(OH)₂ and NaOH for the first stage, obtaining liquid (I) and solid products. They were separated by centrifugation (liquid (I) product analysed) and, subsequently, the solid product was treated by adding 1 or 3% EP Vilzim PRO Conc. After enzymatic treatment, two products – liquid (II) and solid – were obtained, separated, and analysed. The results of the analysis are presented in Table 2.

The hydrolysis process using MgO in alkaline stage leads to a better recovery of chromium compounds – the yield reaches almost 95%, while the method with NaOH in the alkaline stage allows to achieve only 40–54% yield of chromium. It is observed that increasing the amount of EP for the enzymatic stage from 1 to 3% practically has no influence on the contents of both collagen and total protein in the hydrolysates. On the other hand, the amount of protein matter in liquid hydrolysates obtained after such hydrolysis is less than after the first hydrolysis method: 54–54.5% and 75.4–87.5% collagen protein and 66–67.8% and 78.1–85.3% total protein, respectively.

In summary, the hydrolysis of finished leather powder is significantly more complex than of chromed leather shavings, and obtained hydrolysates are complicated sys-

Table 1. Distribution of chromium compounds and protein matter in products of leather powder hydrolysis using NaOH and enzyme preparation (EP) Vilzim PRO Conc

Product of hydrolysis and index	EP Vilzim PRO Conc used for the enzymatic stage of hydrolysis, %*			
	4%		6%	
	Duration of EP treatment, hours			
	6	8	6	8
Liquid product:				
Amount of dry residue, %	9.18	9.08	9.72	10.28
Amount of Cr ₂ O ₃ , %	46.0	62.1	53.0	61.1
Total protein amount, %	74.8	85.3	78.1	84.0
Amount of collagenous protein, %	75.6	87.5	75.4	83.1
Solid product:				
Mass**, g	3.21	2.26	3.14	2.35
Amount of Cr ₂ O ₃ , %	54.0	37.9	47.0	38.9
Total protein amount, %	25.2	14.7	21.9	16.0
Amount of collagenous protein, %	24.4	12.5	24.6	16.9

* % based on the mass of the powder, ** absolute dry mass.

The collagen protein and chromium yields were based on the total mass of protein and chromium present in the leather powder used for hydrolysis.

Table 2. Distribution of chromium compounds and protein matter in products of leather fibre hydrolysis using MgO and EP Vilzim PRO Conc

Product of hydrolysis and index	EP Vilzim PRO Conc used for the enzymatic stage of hydrolysis, %*	
	1%	3%
Liquid product (I):		
Amount of Cr ₂ O ₃ , %	2.8	2.8
Total protein amount, %	14.1	14.1
Amount of collagenous protein, %	6.0	6.0
Liquid product (II):		
Amount of Cr ₂ O ₃ , %	3.1	2.4
Total protein amount, %	51.9	53.7
Amount of collagenous protein, %	58.0	58.5
Solid product:		
Mass**, g	3.71	3.73
Amount of Cr ₂ O ₃ , %	94.1	94.8
Total protein amount, %	34.0	32.2
Amount of collagenous protein, %	36.0	35.5

* % based on the mass of the powder, ** absolute dry mass.

The protein and chromium yields were based on the total mass of protein and chromium present in the leather powder used for hydrolysis.

tems containing proteins, chromium compounds, dyes, fatliquoring materials, etc.

3.2. Application of hydrolysate for leather processing

After the hydrolysis of leather powder, the obtained hydrolysate was assessed by evaluating its constitution. The dry residue of the hydrolysate was established to be 9.08%, the hydrolysate contained 0.33% chromium compounds (calculated as Cr₂O₃), 6.18% protein matter, 0.56% matter with dichloromethane, and 2.01% dye and inorganic matter with pH 10.5.

The next step was to investigate the dyeing process using hydrolysate. Because the hydrolysate is alkaline, two treatments were applied: dyeing after neutralisation and dyeing directly after washing, omitting neutralisation. 300% (% based on the mass of the sample) of hydrolysate was used for dyeing: temperature 58–62 °C, duration 8 hours, run continuously. The amount of chromium compounds and proteins in the treatment solutions and the physical-mechanical properties of the samples after

fatliquoring and drying were checked (Tables 3 and 4).

When hydrolysate was used for dyeing, the leather absorbed a significant amount of chromium compounds and proteins from the hydrolysate (Table 3). Moreover, most of them were absorbed during the first two hours of dyeing. Afterwards, absorption of proteins and chromium compounds markedly slowed.

The experiment was repeated using 300% hydrolysate for dyeing: other conditions as in the previous case except duration, which was 2 hours. After dyeing, the samples were fatliquored and dried. The chemical and physical-mechanical properties of the samples are presented in Table 4.

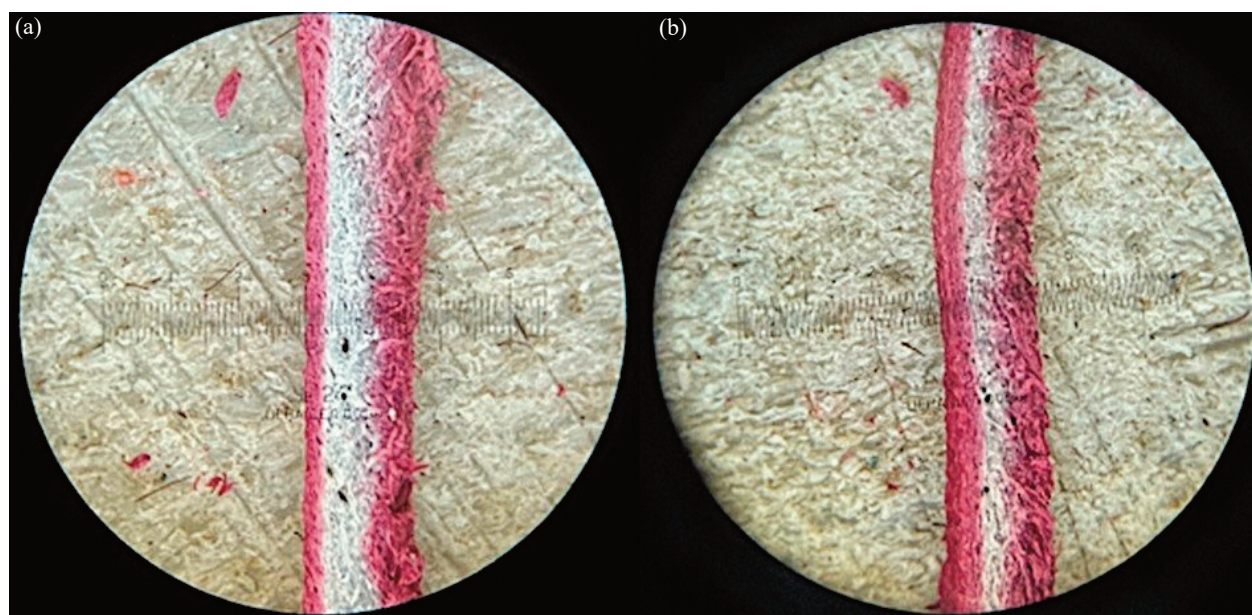
Unfortunately, the experimental dyeing had a negative influence on the strength of leather and the amount of matter extractable with dichloromethane. Both indexes were lower for leather dyed with hydrolysate in this case. The reason for this could be the excessively high pH of the solution at the end of fatliquoring. Due to acidification, a fatliquor emulsion degrades and the fatliquors bond to derma. The excessively high pH probably contributed to the low amount of matter extractable with dichlorome-

Table 3. Change of content of chromium compounds and protein matter in dyeing solution depending on duration of process

Dyeing duration, hours	Amount of Cr ₂ O ₃ in solution (%) when dyeing		Amount of proteins in solution (%) when dyeing	
	after neutralisation	without neutralisation	after neutralisation	without neutralisation
0	3.30	3.30	6.18	6.18
2	2.49	2.87	4.88	4.90
4	2.24	2.58	4.86	4.80
6	2.01	2.54	4.84	4.62
8	2.01	2.53	4.74	4.56

Table 4. Influence of dyeing on fatliquoring and properties of leather

Leather sample	Fatliquoring solution pH after process	Amount of matter extractable with dichloromethane, %	Tensile strength, N/mm ²	Relative elongation at the strain 10 N/mm ² , %
Dyed using hydrolysate without neutralisation	6.8	3.3	11.1	94.8
Dyed using hydrolysate after neutralisation	7.4	3.1	10.6	88.8
Dyed conventionally (control)	3.7	11.2	12.9	105.3

**Fig. 1.** Cross sections ($\times 15$) of dyed leather: (a) 150% hydrolysate and (b) 300% hydrolysate used for the process.**Table 5.** Influence of dyeing method on dye penetration

Dyeing method	Depth of dye penetration, %		
	Grain side	Flesh side	Total
Adding 300% hydrolysate	22.3	33.7	56.0
Adding 150% hydrolysate	17.3	20.8	38.1
Conventional dyeing (control)	7.3	7.4	14.7

thane and weaker tensile strength of the experimental samples.

In fact, for leather that does not need to be ‘dyed-through’, the dyeing time is usually 1–2 hours. Since the main purpose of dyeing is to provide colour to the leather, the dyeing experiment was repeated by adding 300 or 150% hydrolysate and dyeing for 2 hours. The samples were not neutralised. Cross-sections of the leather samples are shown in Fig. 1, and the data of dye penetration into derma are presented in Table 5.

The results of dye penetration measurement (Table 5) allow the conclusion that for qualitative ‘surface dyeing’, 150% hydrolysate is enough because dye penetrated deeper than in the control process.

Subsequently, the sample dyed with 150% hydrolysate was fatliquored by adding an increased amount of formic acid – 1.5% for acidification (experimental). After drying, chemical and physical-mechanical properties of the sample were determined and compared with the conventionally treated (control) sample (Table 6).

Table 6. Influence of dyeing and fatliquoring on chemical and physical-mechanical properties of leather

Leather sample	Amount of Cr ₂ O ₃ , %	Amount of matter extractable with dichloromethane, %	Tensile strength, N/mm ²	Relative elongation at the strain 10 N/mm ² , %
Experimental	4.81	6.3	10.6	49.9
Control	4.50	12.3	11.0	70.1

Therefore, using 150% hydrolysate for chromed leather dyeing allows to obtain well-dyed leather characterised by a high content of chromium compounds and good tensile strength. On the other hand, fatliquoring should be optimised to reach a better level of fatliquoring materials in leather.

4. CONCLUSIONS

The alkaline-enzymatic hydrolysis of finished leather is possible but more complicated compared to the similar hydrolysis of chromed shavings. The presence of dyes, matter extracted with dichloromethane, fillers, and various salts worsen the dechroming of finished leather during hydrolysis. The amounts of protein materials and chromium compounds in the hydrolysate depend on the method of hydrolysis. The use of NaOH for the alkaline stage leads to a higher content of protein matter in the hydrolysate compared with the use of MgO. On the other hand, the hydrolysates contain more chromium compounds in such a case.

Hydrolysate produced from exploited leather can be applied for leather processing, for example, dyeing. Neutralisation process can then be omitted. When dyed with hydrolysate, leather absorbs a significant amount of chromium compounds and proteins from the hydrolysate. The amount of hydrolysate used influences the depth of dye penetration and the quality of finished leather. 150% hydrolysate is enough to achieve qualitative ‘surface dyeing’. The increased amount of formic acid is necessary to improve bonding of fatliquors with dermal tissue and produce qualitative leather.

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