Oil Extracted from Seal Hides: Characterization and Use as Leather Fat Liquor

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ABSTRACT: Extracting natural grease from leathers and skins is a necessary process designed to avoid the appearance of undesirable blemishes in finished articles. Also, degreasing of pickled skins is an important preliminary step in which excess fats are removed. Fat content of some skins is high. In this paper, we study the characteristics of the extracted fatty substances from seal skins. Extracted fats, which were considered waste, can be used as fat liquors in leather manufacture. The primary function of leather lubricant is to prevent adhesion of the leather fibers and to influence the degree of fiber cohesion that takes place during drying of wet leathers. In mineral tannage or semi-mineral tannage (e.g., semi-chrome), this is achieved by the fat-liquoring of leather, for which purpose mostly anionic emulsifiable oil products are used. Seal oil is made into an emulsifiable anionic product by sulfation or by addition of anionic emulsifiers. We tested these products in lambskin fat-liquoring and we studied the physical properties of leather and fatty spue (white efflorescences that appear sometimes on the surface of leather) formation after aging for 3 mon. The oil extracted from seal skins has good characteristics as fat liquor, and the quality of the resulting leather is comparable to leathers fat-liquored with a commercial reference material.
JAOCS 75, 1015–1019 (1998).

KEY WORDS: Anionic surfactant, chrome tanning, degreasing, extraction, fat-liquoring, leather, lipids, oil characterization, seal oil, sulfation.

During the preliminary stages of the leather manufacture, dehairing, liming, bating and degreasing, most of the natural oils from the skins are removed, and at the time of completion of tanning, the leather does not contain sufficient amounts of lubricants to prevent it from drying into a hard material. Proper lubrication or fat-liquoring is necessary to obtain leathers with requisite characteristics. The term fat-liquoring is used for the incorporation of oils and fats into leather in the form of an emulsion. It safeguards the leather against cracking because adhesion of the fibers is prevented during drying by this operation. The main characteristics of fat-liquored leathers are softness, feel, and a certain degree of water repellency. The physical characteristics such as break, stitch tear resistance and tensile strength, as well as comfort properties (particularly for clothing) of leathers, depend on fat-liquoring (1).

The fat-liquoring operation is designed to introduce oils and fats into the leather matrix in finely dispersed form in a water medium. This is usually achieved by emulsification processes through the introduction of sulfate, sulfonate, and sulfite groups into the structure of oils and fats (2) or by addition of surfactants to the composition of fat liquors. The ability of emulsifiable products to impart different characteristics to leather is governed by various factors, such as fatty acid composition of the fat products and the extent of unsaturation in the emulsifiable oil. The softness of fat-liquored leather increases with unsaturation of the oil, but the increase in softness is at the cost of fullness (firmness).

A great quantity of oil is recovered when degreasing pickled seal skins (skins are acidified to make their preservation possible for storage and transport and to make degreasing easier through decomposition of the protoplasmic membranes of cellular fats) in the presence of solvents before the tanning operation. The use of these lipids in leather processing itself is interesting. After characterization of these fats, we studied the more appropriate formulation of fat liquors and assessed their fat-liquoring ability by practical tests.

MATERIALS AND METHODS

Skin degreasing process. Seal skins from Canada were placed into a drum (cylindrical vat used in leather manufacture, generally made of wood, and turning around a revolution axis) with sodium acetate (4% by weight) and white spirit (14% by weight) and stirred at 30°C for 2 h. The solvent medium was filtered to separate pieces of hides from the liquid phase. Fats were recovered from the liquid phase by evaporation under reduced pressure, and they were analyzed. Then the hides were washed twice in water with 1% (by weight) of anionic surfactant Biotergol-PB (L. Lamberti, Albizzate, Italy) for 15 min.

Tanning process. Lamb skins from France were chrome-tanned (i) by a traditional process or (ii) by a new non-polluting TEMA (Tannage Ecologique en Milieu Aqueux) process (3):

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(i) Pickled lamb skins were tanned in an aqueous medium (200%) that contained 8% NaCl (by weight/pickled weight) and a commercial chrome powder Chromosal B (Bayer, Leverkusen, Germany) at 8% (trivalent chromium sulfate at 33% Schorlemmer basicity). Pickled hides were drummed (stirred in a drum) with chrome extract powder for 30 min and 1% sodium formate for 5 h and 30 min. After this period, the liquor was changed to pH 4 with sodium bicarbonate. The hides were drummed 12 h and aged for 48 h after taking them out of the tanning liquor. Then they were neutralized to pH 5.5–6 with a mixture of sodium acetate (2%) and sodium bicarbonate (2%) and kept for 1 h in aqueous medium (250% by weight/pickled weight) at 35°C. The leather was then washed in water.

(ii) Pickled lamb skins were tanned in aqueous medium with an autobasifying trivalent chromium sulfate salt (trivalent chromium sulfate powder with an autobasifying substance, such as sodium bicarbonate or calcium carbonate, which progressively increases the pH during the tanning process to avoid important changes in pH). We used Baychrom 2420 (Bayer) in the presence of masking agents (organic acids or their salts, which retard bonding of the chromium to the amino acids of the collagen by masking the reactive groups of this protein and thus improve the penetration of the tanning liquor into the fibrous structure) (Mesa QR, Gaches Chimie, Toulouse, France).

Fat-liquoring and dyeing processes. The tanned leathers were fat-liquored (appropriate amounts of oils or fat liquors were incorporated into the leather) with a commercial fat liquor KKP (anionic-cationic product from ICL, Milano, Italy) or our fat liquors (S_{15}, S_{17}, and HPS; LCCFP/Ecole Nationale Supérieure de Chimie de Toulouse, Toulouse, France) made with seal oil. The temperature of the fat-liquoring bath was 50°C, and the float during fat-liquoring was 200%. The fat liquor was finally fixed with 0.5% formic acid. After this pre-fat-liquoring, the leathers were neutralized completely to pH 7.5–8 by addition of 1% ammonia to an aqueous bath (300%) at 60°C. The neutralized leathers were dyed and fat-liquored simultaneously. The dye used was Brun Tiacuoio CGM (L. Lamberti), and the quantity of dye used was high (20% weight/pickled weight) to increase the fatty spue formation. Fat liquors used were 8% of the pickled weight. During dyeing and fat-liquoring, the temperature was maintained at 60°C. After 2 h of dyeing and fat-liquoring, the bath was slowly exhausted by addition of formic acid (2/3 of the quantity of dye used). The leathers thus dyed and fat-liquored were washed with cool water and dried.

Seal oil characterization. Viscosity of extracted fats was determined in a Brookfield viscometer (Rheoviscosimeter M; Viscometers UK Ltd., London, England) with a no. 2 spindle at 25°C and 100 rpm. Density, iodine number, unsaponifiable materials, phospholipids content, and acid, peroxide, and saponification values were determined according to experimental procedures described in AFNOR (Association Française de Normalisation) (4). The constituents of unsaponifiable material were identified by thin-layer chromatography with silica gel on aluminum support, the eluent was hexane/ether 70:30, and spots were visualized by means of H_2SO_4 (50%). Fatty acid composition was determined by gas chromatography (CG6000; Carlo Erba, Milano, Italy) under the following conditions: oil transesterification to methyl esters; carbowax capillary column 25 m × 0.35 mm i.d.; helium as carrier gas (40 kPa pressure); air pressure 100 kPa; hydrogen pressure 50 kPa; injection on column; flame-ionization detection at 220°C; and programmed oven temperature from 40 to 180°C at 10°C/min.

Preparation of emulsions. Addition of an anionic surface-active agent. Sodium dodecyl sulfate (SDS)was used (Prolabo, Fontenay s/bois, France). In a 500-mL reactor at 60°C, we introduced successively 60 g of oil (stirring for 15 min), Neutraktan D (ICI, Cleveland, England) at 2% by weight (stirring for 15 min), SDS at 2.5, 3.5, 4, 5, or 12% by weight/total emulsion weight (stirring for 20 min), bovine casein (Fluka, St. Quentin Fallavier, France) at 2% by weight/total weight of oil and SDS (stirring for 30 min), and water at a sufficient quantity to make 100 g solution (stirring for 20 min).

Sulfation (5) of the oil extracted from pickled seal skins. In a 1-L reactor, we introduced 200 g of seal oil. Sulfuric acid (92 to 98%) (Prolabo) was added at 15% based upon weight of the oil, and the mixture reacted for 4 h. The reaction is exothermic and had to be carefully controlled. Temperature may increase from 15°C at the start of the sulfation to 25°C when all sulfuric acid has been added. After reacting for 4 h, the acid oil was washed and neutralized to pH 4 with sodium hydroxide. After increasing the pH of the mixture with ammonia to pH 6.5–7 and checking for moisture, the oil was ready for use as leather fat liquor. Moisture was determined by entrainment distillation (6). Sulfur content was determined according to the experimental procedure described in AFNOR (4).

Stability tests of emulsions. Emulsion stability is tested at different temperatures, 4°C, 40°C, and ambient temperature. Ten mL of water was added to 1 g of emulsion; in acidic medium, 10 mL water and 1 mL formic acid were added to 1 g of emulsion; in basic medium, 10 mL water and 1 g Na_2CO_3 were added to 1 g of emulsion; in the presence of electrolytes, 10 mL water and 1 g NaCl were added to 1 g of emulsion.

Exhaustion of fat-liquoring bath. This test was carried out by the Rose-Gottlieb method, which is used in the determination of lipid content in milk: to 20 mL of fat-liquoring bath exhausted by formic acid, 10 drops of ammonia and 22 mL of ethyl ether/ethanol mixture (55:50) were added. The ether phase was recovered after two successive extractions of fat-liquoring fluid. Fats were recovered from the solvent phase by evaporation under reduced pressure and subsequent weighing. Fat content of final fat-liquoring bath = $100 \times (1 - MGf/MGi)$, where MGf = g fat in the fat-liquoring bath after extraction, and MGi = g fat in the initial fat-liquoring bath.

Extractable fats from fat-liquored leathers. Unfat-liquored samples were obtained by removing leather samples from the drum just before adding fat liquor. Fat-liquored samples were cut into pieces of approximately 1 × 1 cm and weighed;

aliquots were extracted in a Soxhlet apparatus for approximately 3 h (10 refluxes). The solvent (hexane, 200 mL) was then evaporated. Finally, extracts were weighed, and the fat liquor percentage was calculated for 100 g of dried leather.

Leather physical properties tests. The tongue-tear and stitch-tear strengths were determined by the CTC tests (Centre Technique du Cuir, Graulhet, France) according to AFNOR procedures (NF G 52-014 and NF G 52-005) (obtained from Association Française de Normalisation, Tour Europe, 92049 Paris La Défense Cedex-France).

RESULTS AND DISCUSSION

The extracted yield of seal oil by white spirit from pickled seal skins was high, 40–45% (by dried weight), compared to other skins, such as lamb skins (6–30%) (7), which are considered fat, cattle hides (1–12%), and goat skins (2–3%) (8).

The main characteristics of fats extracted from seal skins and the fatty acid composition of this orange-yellow oil are shown in Tables 1 and 2, respectively. The acid value was high and can be explained by hydrolysis and fat degradation during the storage of pickled skins. The iodine value of 58.6 was low compared to freshly extracted seal oil, which is typically 160. The peroxide value was 48.2 meq O_2/kg against 1.5 for fresh oil. The peroxide value of up to 5 means a high degree of oxidation of the oil. Because of its high degree of unsaturation, which leads to significant oxidation, this oil cannot be used in fat-liquoring of pale dyed leathers. The seal oil contained a small quantity of unsaponifiable compounds (0.37%). These compounds are located in the lower epidermal layer, which is removed during the beamhouse process, which prepares the hide for tanning by several stages (complete rehydration of the skin, washing, dehairing, removal of the epiderm, pickling), but they can migrate to the derm. Because this unsaponifiable content was so low, we did not study the influence of these compounds in fat-liquoring of leathers (9–10). Phospholipids are, with cholesterol and glycolipids, the main lipids of the cell membranes. There was only a trace amount of phospholipids (0.02%). Oleic ester was the major fatty ester (27.34%), followed by palmitoleic (19.34%) and eicosaenoic esters (13.64%). The ratio of unsaturated fatty esters (87.58%, with 62.35% of monounsaturated and 25.23% of polyunsaturated) to saturated fatty esters (12.42%) is well above 1 (approximately 7). Moreover, because of the absence of stearic ester and the low amount of palmitic ester (7.44%), which are responsible for the fatty spue formation (11,12), this oil seems to be a good raw material for making leather fat liquors.

TABLE 1
Characteristics of Seal Oil Extracted from Pickled Seal Skins

Physicochemical characteristics	
Density 20°C	0.938
Viscosity 25°C (centipoises)	94
Iodine value (Wijs)	58.6
Acid value	8.6
Peroxide value (meq O_2/kg)	48.6
Saponification value	180
Unsaponifiable matter content (%)	0.37
Unsaponifiable composition	Cholesterol, tocopherol, and other nonidentified constituents
Phospholipid content (%)	0.02

TABLE 2
Fatty Acid Composition of Seal Oil (%)

Myristic (14:0)	4.98
Palmitic (16:0)	7.44
Palmitoleic (16:1)	19.34
Oleic (18:1)	27.34
Linoleic (18:2)	2.90
Linolenic (18:3)	1.30
Eicosanoic (20:1)	13.64
Eicosadienoic (20:2)	4.39
Eicosapentaenoic (20:5)	6.30
Erucic (22:1)	2.02
Docosapentaenoic (22:5)	3.29
Docosahexaenoic (22:6)	7.05

During the fat-liquoring operation, the fats are introduced into the leather matrix in finely dispersed form in a water medium. Fat molecules have to be emulsified, so that the fat liquor can transfer from the aqueous bath to the leather and penetrate it. Emulsifiers must therefore have both a strong hydrophilic and a strong hydrophobic group (13). This is necessary to emulsify fat liquors through the formation of micelles, with the hydrophilic component oriented toward the water phase, so that the emulsion can remain stable. In the aqueous bath, the fat molecule and fiber will undergo a physical bond, which is stronger than the bond between fat and emulsifier. Therefore, migration out of the leather is no longer easy after the emulsifier is removed by washing.

Leather oil products fall into four categories: anionics, cationics, nonionics, and raw oils. In chrome tanning, fixation of anionic fat liquors is generally easier than that of cationic fat liquors in all layers of the skin. The largest group of anionic compounds is the sulfated oils. These oils are produced by first oxidizing a highly unsaturated oil, such as cod, herring, menhaden, or almost any mixed fish oil (14). The usual sulfating agent reacts both with the double bonds and the hydroxyl groups. Not all oils or fat products are made emulsifiable under identical conditions, because of their varying nature; also, the nature of an oil has its own influence on the mode of addition of sulfuric acid for sulfation. Sulfated liquors are fairly stable at lower pH values. The degree of sulfation is an important factor for the stability of fat liquor and for the fixation of fatty matter while fat-liquoring. Sulfated oils are by far the largest category of fat-liquoring agents used by the tanning industry. These fat liquors are held in the leather by electrostatic forces between the protonated amino acids of the collagen molecules or the cationic groups of the chromium complexes and the negatively charged sulfate groups on the fat-liquor molecule. Seal oil can be made into an emulsifiable anionic product by sulfation and is called HPS. The sulfating agent has reacted mainly with the double bonds, which is shown by a decrease of the iodine value to

TABLE 3
Stability at Different Temperatures of the Prepared Emulsions

Emulsion	Time (d)	Temperature 4°C	Temperature Ambient	Temperature 40°C
S_{13} (SDS[a] 2.5%)	1	S[b]	S	S
S_{14} (SDS 3.5%)	1	S	S	S
S_{15} (SDS 5%)	1	H	H	H
	15	H	LRH	H
	30	H	LRH	H
S_{17} (SDS 4%)	1	H	H	LRH
	15	H	H	LRH
	30	H	H	LRH
S_{12} (SDS 12%)	1	S	S	S
HPS	1	H	H	H
	15	H	H	H
	30	H	H	H

[a]SDS, sodium dodecyl sulfate (sulfated fatty alcohol).
[b]H, homogeneous; S, separation; LRH, light oil rising.

39.4 after sulfation. A sulfated seal oil that contains 1.9% of combined SO_3 is a weakly sulfated oil (combined SO_3 from 0.8 to 2%). It is a brown red oil product. Its pH at 10% is 8. It is soluble in water, stable in neutral salts, acid, and alkali. Its water content is about 8% and can be adjusted to 18% for the commercial form. Seal oil can also be made into emulsifiable anionic products by addition of an anionic surfactant, such as SDS (sulfated fatty alcohol); S_{12}, S_{13}, S_{14}, S_{15}, and S_{17}. They form yellow emulsions. Their pH value at 10% is 7.5. The emulsions so prepared (by sulfation and addition of SDS) were tested for their stability after 1, 15, and 30 d at different temperatures and in different media. Results are reported in Tables 3 and 4. After 1 mon at room temperature, a few of the emulsions remained homogeneous (S_{15}, S_{17}, and HPS), whereas the others had undergone varying degrees of separation. So, for fat-liquoring tests, we retained S_{15}, S_{17}, and HPS, which showed good stability in different aqueous media.

For application to leather fat-liquoring, we used a commercial reference material, KKP. Among the concentrations of the tested fat liquors we have included the usual concentration for fat-liquoring with KKP: pre-fat-liquoring at 5% and fat-liquoring at 8% (weight/pickled weight), which gives the best results. Then, we determined the exhaustion rate of fat-liquoring baths; these rates are reported in Table 5. After formic acid addition, the bath became clear for all fat liquors, and we got good exhaustion rates.

TABLE 4
Stability Tests in Different Media (1 d)[a]

Emulsion	Medium: Aqueous	Acidic	Alkaline	Electrolytic
S_{15}	H	H	H	LRC
S_{17}	H	H	H	LRC
HPS	H	H	RH	LRC

[a]H, homogeneous; LRC, light cream rising; RH, oil rising.

TABLE 5
Exhaustion Rates of Fat-Liquoring Baths

Fat liquor	Exhaustion rate[a] (%)[b]
KKP	99.6
S_{15}	98.2
S_{17}	98.8
HPS	98.8

[a]Mean ± standard error (SE); $n = 6$, SE = 0.1.
[b]Exhaustion rate = 100 × (1 − MGf/MGi); KKP (ICL, Milano, Italy).

The leathers were subjected to aging for 3 mon, the duration between the production and utilization periods. All fat-liquored leathers were soft, with an agreeable touch, like KKP fat-liquored leathers, for all chrome tanning processes (traditional process and TEMA). Nevertheless, for S_{15} fat-liquored leathers, we have noted some dyeing blemishes. The tongue-tear and stitch-tear strength values were comparable to the reference (tongue-tear, 6.3 kg/mm; stitch-tear, 5.2 kg/mm) for HPS, but they were lower for the others (Table 6). The unstable character of S_{15} at ambient temperature and of S_{17} at 40°C is responsible for the emulsion's early breaking in the fat-liquoring bath. So, the fat liquors S_{15} and S_{17} are less effective, which is shown by lower tongue-tear and stitch-tear values, compared to KKP and HPS.

After fat-liquoring, a part of the fatty matter gets fixed to the leather, while the other part is simply distributed over the fiber texture (15). The extent of fixed fatty matter and free fatty matter, which can be easily extracted with solvents, differs with different fat liquors as well as with different tanning processes. Both the fixed fat and the free fatty matter are responsible for the final quality of the leather, *viz.*, feel, softness, and water repellency. The extractable fatty matter content is a quality criterion that is generally required. The lower the quantity of extractable fats, the better are the fat liquors and leather quality. Results are reported in Table 7. After a 3-mon aging period, the extent of extractable fats is less than that obtained just after fat-liquoring for all fat liquors tested. Furthermore, after 3 mon, the quantity of extractable fat is comparable for HPS and the commercial reference (KKP). For S_{15} and S_{17} fat liquors, the results are only acceptable.

The various oils differ considerably in their propensity to form fatty spue (white efflorescences that appear sometimes on the surface of the leather) due to stearic and palmitic acids. Fatty spue may be due, independently of the nature of the fats present in leather and skin, to the importance of moisture and

TABLE 6
Physical Characteristics of Fat-Liquored Leathers

Fat liquor	Tongue tear[a] (kg/mm)	Stitch tear[b] (kg/mm)
KKP	6.3	5.2
S_{15}	3.6	3.8
S_{17}	4.2	3.9
HPS	5.7	6.2

[a]Mean ± SE; $n = 3$, SE = 0.3.
[b]$n = 3$, SE = 0.3. See Tables 4 and 5 for company sources.

TABLE 7
Extractable Fatty Matter from Leathers

Fat liquor	Time	% Extractable fatty matter[a] (by weight of dried leather)
Unfat-liquored leather	1 wk	6.8
KKP	1 wk	15.63
	3 mon	11.50
S_{15}	1 wk	18.60
	3 mon	15.40
S_{17}	1 wk	17.30
	3 mon	13.10
HPS	1 wk	16
	3 mon	12

[a]Mean ± SE; $n = 6$, SE = 0.1. See Tables 4 and 5 for company sources.

temperature changes to which they are submitted during storage and utilization (16). It has been found that solid triglycerides and solid fatty acids can migrate from one surface of a piece of leather to another. The conditions under which this migration takes place depend on the nature of the fatty material: triglycerides spue when the temperature is relatively high (40°C for tristearin), especially in dry atmospheres; fatty acids, on the other hand, migrate and appear as spue at temperatures below 20°C, particularly at high relative humidities. As might be expected, the type of tanning is important; vegetable leather is far less likely to spue than chrome leather. The presence of dyes, mordants, and detergents has a strong influence on the formation of fatty spue. Detergents and fats compete for available sites on the grain fibers, and the detergent can displace fatty acids, which causes fat crystallization and spue formation. Spue increases when the quantity of detergent is increased because the detergents may themselves form spue. The effectiveness of the detergents in reducing spue is probably due to their ability to be more strongly adsorbed than fatty acids on the fiber surface. After 3 mon of storage at different temperatures and humidities, no fatty spue appeared on the leathers fat-liquored with S_{15}, S_{17}, and HPS, and the quality of the leathers fat-liquored with S_{17} and HPS was good.

Although anionic surfactants seem to destabilize the collagen fibers of chromium-tanned leather, lowering the shrinkage temperature (temperature at which the collagen is degraded, measured according to the AFNOR procedure) (17), this physical characteristic of the leather is the same (100°C) for HPS, S_{17}, and KKP, after the TEMA tanning process or a traditional tanning process with Chromosal B.

All results concerning the physicochemical properties of the seal oil, emulsion stabilities, fat-liquoring bath analyses, and quality of the leather have shown that the oil extracted from pickled seal skins during the degreasing stage is an interesting raw material for producing fat liquors in the leather industry.

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[Received October 1, 1997; accepted February 18, 1998]