Sponsors, Exhibitors and Program Advertisers 111th ALCA Annual Convention Pinehurst Resort, Village of Pinehurst, NC June 10-13, 2015

Sponsors

Technical Session 2 - Automotive Leather
Eagle Ottawa LLC

Larry Shaver Golf Pro for Thursday Evening Golf Analyzer
Buckman North America

Gold
Buckman North America
Dow Coating Materials
D.R. Diedrich & Co., Ltd.
Eagle Ottawa LLC
Erretre SpA/Carlessi SRL
GST AutoLeather, Inc.
LANXESS Corporation
Stahl USA
TFL USA/Canada, Inc.
Union Specialties, Inc.

Bronze
Chemtan Company, Inc.
Hermann Oak Leather Co.
North American Minerals Corp.
Prime Leather Finishes Co.
Tannin Corp./BASF
Trumpler GmgH @ Co. KG
Wickett & Craig of America
Zschimmer & Schwarz

Silver
Atlas Refinery Inc.
Elementis LTP Inc.
Leather Miracles, LLC
National Beef Leathers
Quaker Color
SB Foot Co./Red Wing Shoe Co.
Tyson Foods, Inc.

Program Advertisers
Buckman North America
Dow Coating Materials
Elementis LTP Inc.
LANXESS Corporation
TFL USA/Canada, Inc.
Trumpler GmbH & Co. KG

Exhibitors
Dow Coating Materials
Erretre SpA/Carlessi SRL
KH Neochem Americas
World Leather Magazine

Note from the *Journal* Editor

Dear members, subscribers, authors, leather scientists and June 2015 Annual Convention guests,

The proceedings of our June Annual Meeting, including the Wilson Lecture, are published in this August issue. This 111th American Leather Chemists Annual Convention had one of the best programs in my recent memory, with an excellent diversity of presentations that included major issues affecting our global leather industries. The greater international attendance was very consistent with the more global reach of this *Journal*.

The Wilson Lecture by Dr. Dietrich Tegtmeyer set the stage for an invigorating conference that featured sustainability and automotive leather presentations. The lectures about advances in basic leather research were interspersed with stimulating international perspectives on hide trade and regulatory issues.

The *Journal* will continue to publish some of these technical presentations in the coming months. Some of the industry issues presentations, if not published, may be available directly from the presenters or contact the ALCA office for details.

Next years program will continue this diversity of new technologies, global trends and issues reports. **Mark your Calendars now for next years Annual Convention, returning to Oglebay Resort, Wheeling, WV, June 22-25, 2016.**

I want to thank the many people that make this *Journal* possible and available in both print and the electronic (ezine) formats. For the electronic *JALCA* subscribers, log-on to alcajournal.com or use the link at our website leatherchemists.org.

Your comments and suggestions are strongly encouraged and most welcome – send to jalcaeditor@prodigy.net

Robert F. White
Journal Editor

June 2015

Diagnosis, Prevention and Treatment of Fatty Spew in the Tannery

by
Ricardo A. Tournier*
Consultant,
Uruguay

Abstract

A comprehensive review of the possible causes and mechanisms of fatty spew formation is presented, together with a guide to remedial treatments for the defect. Best practices and trouble-shooting guidelines are provided that can be used for the prevention and systematic treatment of fatty spew on the tannery floor. The free fatty acid content of individual leathers can be used for routine assessment of the risk of spew events occurring at any stage of production, as well as the likelihood of fatty spew forming in crust and finished leather. A systematic approach to grading leathers according to their free fatty acid content is presented. This method can be applied on a routine basis in a production line, and/or prior to sending customer shipments.

Resumen

En este trabajo se resume la composición química de las eflorescencias grasas en cueros, posibles mecanismos de formación, fuentes de generación y tratamientos varios para mejorar cueros con eflorescencias. Se exponen los mejores procedimientos para evitar su formación así como una guía práctica para investigar las causas de su aparición ante un evento concreto. Se propone el análisis rutinario del contenido de ácidos grasos libres en cueros individuales, como forma de detección temprana del riesgo a eflorescencias grasas. Este método se puede aplicar sobre cueros semi terminados o terminados, en la línea de producción y/o previamente al envío de los cueros a los clientes.

Introduction

Spew (also spue[1]) is an exudate material that migrates from the inner to the outer surface of leather. Although it may be different colors, it generally occurs as a whitish dust or film on the leather surface. The defect is more visible, due to the effect of contrast, on dark-colored than on light-colored leather, and is at its worst on black leather.

The most damaging situations arise when spew appears in finished leather goods. In these cases the costs of claims can be very high. New cars with black leather seats covered with spew, and stains of spew on black leather coats and jackets, boots, shoes and briefcases are painful examples of this problem encountered over years of leather manufacturing.

In the history of leather making, spew has been a constant headache for technicians. Everything may be running well in a tannery and suddenly a spew event occurs, ringing alarm bells. In the best-case scenario, the spew occurs on the shop floor; otherwise the problem makes itself felt as a phone call or claim from an angry customer.

Spew can be of several different types, with different appearances and origins.[1,2] It can take the form of crystallized substances on the leather surface; these crystals can be of fatty matter, inorganic or organic salts, sugar or sulfur. It may be powdery, amorphous, resinous or gummy; it may be composed of polymers or amorphous sulfur. Mold (fungi) can grow on the leather, producing a whitish bloom or round white spots on the leather surface.

The most undesirable and frequent form of leather spew is fatty spew, which only appears on crust or finished leather and is generally first detected by customers or users. It is very difficult to eliminate. Although it is apparently possible to clean it off with a cloth, it can resurface after some time. It is difficult to track the source or root cause of fatty spew, and it is difficult to reproduce the defect, even when samples of the same piece of spewed leather are studied.

Many research studies on fatty spew have been published in leather journals over the years, but they have not been comprehensive enough to help leather technicians to cope systematically with the problem when it arises on the factory floor. This paper reviews the physical, chemical and biological factors and mechanisms involved in fatty spew formation. It deals with diagnosis of the causes of this defect and its prevention, mitigation and remediation. A practical guide to

* Corresponding author e-mail: tournric@adinet.com.uy
A Technical Note received May 5, 2015, accepted for publication June 10, 2015.
Author LIFELINE at end of this manuscript.

the investigation of real life fatty spew events on the tannery floor is provided, to serve as a quick reference guide for tannery technicians. The paper refers mainly to leather produced from bovine hides, but its findings and recommendations can also be applied to sheepskin, goatskin and pigskin hides, finished or unfinished, whether tannage is vegetable, chrome or other.

This article is divided into seven sections:

Section 1. Chemical composition of fatty spew
Section 2. Fatty spew types and formation mechanisms
Section 3. Possible sources of fatty spew generation
Section 4. Investigation of fatty spew events on the tannery floor
- A. Traceability
- B. Systematic guidelines for the identification of fatty spew causes

Section 5. Fatty spew prevention
- A. Best practices to avoid fatty spew problems at key points
- B. Monitoring fatliquors to prevent fatty spew

Section 6. Early detection procedures
Section 7. Fatty spew mitigation

SECTION 1. CHEMICAL COMPOSITION OF FATTY SPEW

Background

Fatty spew is formed by fatty matter contained in leather. Naturally occurring oils, fats and waxes (lipids) are composed mainly of a mixture of glycerides. Glycerides are esters derived from a condensation reaction between glycerol and fatty acids (FA), and occur as monoglycerides (MG), diglycerides (DG) and triglycerides (TG), according to the number of FA attached to the glycerol moiety. The attached FA molecules can be all the same, or all different, as shown in Figure 1.[3]

This figure shows a triglyceride containing one molecule of a saturated FA, palmitic acid (C16), a second molecule of a monounsaturated FA, oleic acid (C18), and a third FA molecule of triunsaturated alpha linolenic acid (C18).

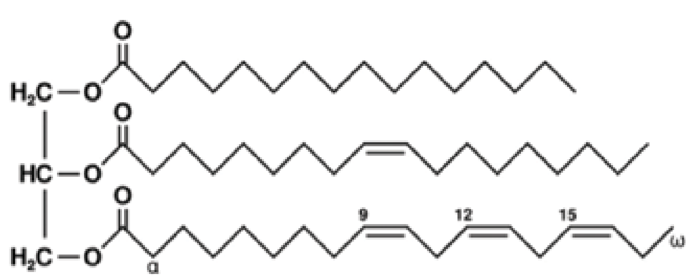

Figure 1. Triglyceride molecule with three different fatty acid molecules attached.

Fatty spew occurs when glycerides and/or free fatty acids are present in high concentrations in localized areas of the leather. In these circumstances, spew is liable to form. The fats may be present as triglycerides (TG), or may have been subjected to hydrolysis in which case the TG molecules are converted to glycerol and fatty acids (FA).

Among the wide range of different TG found as components of natural animal and vegetable fats and oils, it has consistently been found that fatty spews in leather are mainly composed of palmitic, stearic and oleic compounds. Palmitic acid is a C16 saturated FA, stearic acid is a C18 saturated FA and oleic acid is a C18 monounsaturated FA (see Figure 1).

TG Hydrolysis

TG are readily hydrolyzed by alkalis, acids or enzymes, leading to the formation of glycerol and free fatty acids. Since alkalis, acids and enzymes are used at different stages of the leather making process, it is critical to monitor all the steps very carefully to minimize TG hydrolysis and extract as much natural fat as possible from the raw hides and skins.

For example, when soaking salted hides in a bath containing sodium carbonate, a significant amount of foam is usually formed due to sodium soaps generated from free fatty acids (FFA) and solubilized proteins, present in the raw hides, which act as surfactants. These FFA most probably result from the action of bacterial lipases that hydrolyze natural fat in the salted hides (see Section 3). Raw hides with these characteristics tend to produce spew once converted into leather if best practices are not followed in subsequent steps (see Section 5). In raw stock where fat degradation has occurred, it is likely that some collagen has also been degraded to some degree, with negative consequences for the resulting crust leather. Therefore, it is essential to identify the origin of the raw hides and closely monitor the production stages of this leather.

Animal Fat

The main fat extracted from bovines is beef tallow and the main oil is neatsfoot oil, obtained by boiling the feet and shinbones of cattle.

Fat from warm-blooded animals normally has a high melting point (MP), becoming hard when cool, but neatsfoot oil remains liquid at room temperature (generally taken to be 20ºC), reflecting its lower MP. The relatively slender legs and feet of animals like cattle have adapted to maintain flexibility at much lower temperatures than those of the body core. In contrast, tallow extracted from adipose tissue surrounding the kidneys has the highest MP.

The different MP of beef tallow and neatsfoot oil reflects different ratios of high and low MP constituent FA in their TG. The MP of triglycerides decreases with decreasing carbon chain length of constituent FAs and with increasing degree of unsaturation. Table I shows the MP of different TG containing different ratios of palmitic, stearic and oleic FA.[4, 5]

Table II. shows that, in beef tallow TG, the combined content of palmitic and stearic acids is higher than in neatsfoot oil, and, conversely, the percentage of oleic acid is higher in neatsfoot oil.

Throughout the text and tables, percentages are expressed on a dry weight basis except where otherwise specified.

The main constituents of raw neatsfoot oil are shown in Table II. Roughly one third of these TG have high MP, and two-thirds have low MP. Winterization brings down the content of TG with high MP by cooling down raw oil and filtering out crystallized TG. Also small amounts of high MP FFA are removed, if present.

Fat Content of Raw Hides

Total fat content in fresh bovine hides is very variable, often in the range 2 to 5% of fresh hide weight. In goat skins the fat content varies from 3 to 10% and in sheep and pig skins it may be as high as 30% or more.[7]

TABLE I
Melting Points of TG containing different ratios of palmitic, stearic and oleic FA.

Triglycerides P - palmitic S - stearic O - oleic	Melting Point (MP) ºC
OOO	-12
OOP	18
OOS	23
OPS	31
OPP	34
POP	36
OSS	38
SSS	55
Oleic acid	13-14
Beef tallow	35-55
Palmitic acid	63
Stearic acid	70

According to Koppenhoefer (1978),[8] fatty matter in fresh steer hides is distributed in two clearly differentiated layers:

- The epidermal layer, containing approximately 1% of total lipids, composed of phospholipids, cholesterol, waxes and a small amount of FFA.
- The corium layer, containing 1 to 11% of total lipids, composed mainly of TG. The wide range of possible fat contents in corium contrasts with the narrow variation in the epidermal layer. The lipids in the corium are found as fat cell deposits for energy reserves. Maximum amounts are found in well-fed animals; thus the fat content differs greatly from one animal to another within the same category. The TG in corium are chemically similar to those found in the subcutaneous fat (adipose) layer and are consistent with the beef tallow composition shown in Table II.

Fatliquoring Materials

Fatliquors have traditionally been associated with fatty spews, but they are not always necessarily the main cause.

Fatliquors are oils, fats and waxes, synthetic or natural, plus auxiliary products, prepared so that they become emulsifiable in water and are suitable for lubricating leather in a water float.[9] According to Covington (2009), "The primary function of fatliquoring is to prevent the fiber structure resticking during drying; [the secondary function to soften the leather]."[10] There is in fact a third function, that of improving strength.

A wide variety of fatliquors can be made from numerous raw materials, including:

- Raw animal oils and tallow from mammals, chicken, fish, etc.
- Raw vegetable oils, including castor oil, soybean, palm, and sunflower oil

TABLE II
Fatty acids content of TG in tallow and neatsfoot oil.

Product	Carbon chain	Beef Tallow [6]	Raw Neatsfoot oils [5]	Sulphated neatsfoot oils [5]
Palmitic acid	C 16	24-26%	14 to 21%	23 to 39%
Stearic acid	C 18	14-19%	4 to 7%	5 to 8%
Oleic acid	C 18 : 1=	43-47%	45 to 60%	32 to 54%

- Mineral oils, mainly coming from the petrochemical industry
- Other fats and waxes of natural or synthetic origin.

Except for the petroleum derivatives, these oils, fats and waxes are all mixtures of different glycerides.

The leather industry normally employs partially sulfated or sulfited fatliquoring oils. The so-called sulfo fraction is the emulsifying agent, which keeps neutral oil suspended in solution, thereby enabling it to penetrate the leather. The neutral oils acts as the actual lubricant.[10]

Fatliquor manufacturers buy large quantities of raw oils that must be of uniform composition, purchase after purchase. However, significant variations occur. Oils used in leather manufacture are also in demand in the food industry, so when prices rise, or there is a shortage, manufacturers may change or dilute their usual raw oil with a substitute, to keep costs down. Tanneries need to ensure that quality and the effect of the agents on leather is maintained. Increasingly stringent ecological regulations may oblige manufacturers to change the composition of emulsifying agents, for example, and this will require changes in production processes.

A variety of natural and synthetic products whose composition is not known by the leather technician are included in fatliquors, a fact that must be monitored by the tanner. Tanneries must be aware of the variability among oil and fat sources and must have efficient quality controls to check the uniformity of the oils received.

Fatliquors may introduce glycerides and FA into the leather that may promote spew formation. Below, a method is proposed to evaluate fatliquors in order to manage outcomes (see Section 5B).

Heidemann (1993) warns that under drastic sulfonation conditions a certain amount of FFA may be formed.[11]

Waite (1999)[9] reported that FA exist in fatliquors containing natural oils in four states:

1. Esterified with higher alcohols or glycerin (lower alcohols are also used nowadays)
2. Free and non-neutralized
3. Neutralized with alkali other than ammonia
4. Neutralized with ammonia.

FA esters of lower alcohols are obtained by transesterification of animal or vegetable oils. The most commonly used are methyl esters, and to a lesser degree ethyl esters, of FA. Depending on whether the raw oils were winterized or not, methyl palmitate and stearate, with MP such that they may produce spew, may be present (see Table III).

TABLE III
MP of Esters.[12]

	ºC
Methyl palmitate	32-35
Methyl stearate	37-41
Methyl oleate, liquid	No data
Ethyl palmitate	24-26
Ethyl stearate	34-38
Ethyl oleate	-32

As can be observed in this table, oleate esters are liquid at room temperature (usually understood as around 20º**C**) while palmitate and stearate esters are not.

Taking into account the previous statements, we emphasize the need for quality control and standard protocols for evaluating incoming fatliquors in the tannery.

Section 2. Fatty Spew Types and Formation Mechanisms

Commonest Types of Fatty Spew

Numerous authors report that there are three types of fatty spew, comprising mainly:

- FFA, with MP above 60ºC
- TG, with MP below 45ºC
- Mixtures of both, with MP between 45 and 60ºC

The most serious problem in tanneries is spew involving FFA, that is, with MP above 45ºC.

Contrary to what one might assume, FFA spews generally occur at temperatures below 20ºC and high ambient humidity, while glyceride spews appear at around 40ºC in dry environments, as discussed.

Probable Mechanisms of Migration of Fats in Leather

Mitton and Pankhurst (1957)[13] published an interesting and comprehensive article on spew formation in different types of degreased sheepskin leather.

Their paper discusses some theoretical mechanisms that promote spew formation:

1. Development of monomolecular or thicker films of fats and oils, covering the surface of leather fibers.

2. Evidence that fats, below their melting points, can migrate to superficial fibers.

3. Chromatographic effect, such that mobile phase fats move through stationary solid fibers. Differences in fats' partition coefficients result in the separation of the different components.

In addition to the three hypotheses in Mitton and Pankhurst (1957), we propose two more:

4. Fatty spew development may be driven by the gradient of differential sizes, lengths and types of collagen fibers through the thickness of leather.

5. Probable influence of chemicals used during leather making, different gradients of which become attached to collagen fibers.

Since Mitton and Pankhurst's research work is so interesting, their main observations, findings and conclusions are presented below:

- *Different tanneries experienced different amounts of spue from the same fatliquor, suggesting that factors other than fatliquoring played some part in the process of spue formation.*

- *Temperature variations had a strong influence on the appearance and disappearance of spue.*

- *Changes of temperature during storage were more important than steady storage temperatures themselves in determining the risk of spue formation.*

- *Both triglycerides (TG) and fatty acids (FA) migrate through leather, but at room temperature at least, TG moves faster than FA.*

- *This differential migration of TG and FA is greater in chrome-tanned than in vegetable-tanned leather.*

- *From the mixture of natural fats in leather, at least two distinct types of fatty spue can be formed: FA spue and TG spue, which appear under different conditions.*

- *FA spue forms at low temperatures and is favored by high humidity. It disappears if the temperature is raised and may disappear slowly if the humidity is kept low.*

- *FA spue quickly vanishes at 40ºC and forms only slowly at 0ºC.*

- *TG spue forms at high temperature and is inhibited at low temperatures; it is favored by low humidity, and may disappear slowly if the humidity is high.*

- *TG spue forms quickly at 40ºC and vanishes only slowly at 0ºC.*

- *While fat content in the leather is not of great importance in determining whether or not spue will form, the fat content does determine whether spue will be light or heavy.*

- *Under experimental conditions, TG spue was much heavier than FA spue, although the leathers as a whole contained similar amounts of each type of fat. This does not mean, however, that TG spue is necessarily commoner or more troublesome in commercial leathers than FA spue; indeed, complaints of spue are usually made in cold weather, and this suggests that FA spue is usually the more troublesome.*

- *Sulphated fatliquoring oils do little or nothing to hinder spue formation; indeed, since they accelerate the migration of FA and TG, they may, in the early stages of storage, promote it.*

- *If, owing to poor penetration of fatliquor, any considerable excess of fat is deposited on and near the grain, crystallization of this fat* in situ *may form spue.*

- *Heavy spue was produced on the grain surface in experiments where all the fat applied was initially on the flesh side, and this spue can only be the result of migration.*

Recent Research Findings

There is a 40-year gap in the literature on fatty spew research from the 1957 study until modern studies from 2000 on, as noted also by Naviglio (2001).[14]

- Experimental results obtained by Naviglio (2001)[14] and Tomaselli et al. (2003)[15] show a change in the palmitic/stearic ratio between the initial fatliquor and that extracted from spewed leathers. The authors suggest that enzymatic hydrogenation of unsaturated fatty acids present in finished leather (mainly oleic) may take place, increasing the presence of stearic acid and thus promoting the appearance of spew.

- Zengin and Afsar (2010)[16] studying sheepskin fatliquoring with natural fat emulsions found that the degree of unsaturation (i.e. number of double bonds) in natural fat was higher than in the fatliquor emulsion. The authors suggest that a saturation process took place "by chemicals like an oxidizing agent or other effects which were used in [the] leather making process."

- Wang et al. (2011)[17] studied leathers fatliquored with oils containing large amounts of FA methyl esters. The authors conclude that these esters, mainly palmitic, stearic and oleic methyl esters "are the main components that cause fatty spew defect in leather."

Tournier (unpublished data) found significantly different behavior in several comparative tannery trials of production lots. Leathers from the same wet blue lot were retanned, dyed and fatliquored; then some of the hides were dried in a toggle drier only, and others in a vacuum drier followed by hanging up to air dry. Vacuum dried leathers developed higher FFA content than toggle-dried (see Table IV). The most significant difference was found for bellies.

The following facts and hypotheses may contribute to explaining these findings:

- Backbone and butt areas have a denser fiber structure than bellies and cheeks, and thus have lower water content in the wet state.

- Bellies and cheeks take more time to dry because they have a greater amount of water to be evaporated. In contrast, backbones and butts —where the fiber structure is more closely intertwined, and the water content of the wet leather is lower— dry sooner.

- Toggle-drying took 4-5 h.

- Vacuum drying followed by hang drying took 12-14 h, allowing a longer time for reactions than toggle-drying.

TABLE IV
Mean FFA content of leathers with different types of drying.

	FFA % dry leather		
Drying	**Backbones**	**Bellies**	**Cheeks**
Toggling	1.2	1.7	1.6
Vacuum	1.2	2.7	2.1

- During drying, chemicals (e.g. formic acid) in interfibrillar water become more concentrated, turning the pH more acidic, and the emulsified TG can then be hydrolyzed more easily into FFA.

Further research is needed to confirm and clarify these theoretical explanations.

Since FFA spews are the commonest and most harmful form of spew, it is necessary to avoid FFA generation by hydrolysis of TG. Bacterial and fungal action, aqueous media with high or low pH, and low pH of leather and/or high difference index are the main factors promoting hydrolysis.

SECTION 3. POSSIBLE SOURCES OF FATTY SPEW GENERATION

Raw Material

When spew patches of approximately specular appearance — i.e. showing bilateral symmetry— appear in specific areas of hides, they are probably due to a concentration of natural fat in that area of the live animal, and this may provide clues to the underlying cause of the problem (see Figure 2).

When poorly preserved salted hides are stockpiled for periods longer than 6 months, natural fat adhering to the flesh side can penetrate toward the corium, causing local increases in the normal grease content of the corium. The rate of grease penetration increases with increasing temperature. These phenomena can produce specular spew. Hides must be prefleshed prior to salting in order to remove adhered fat, and cool storage conditions are to be preferred

Figure 2. Near-specular spew pattern

The natural fat content of raw hides has increased over the years because of changing methods of cattle breeding and feeding. Selection of cattle breeds that give marbled meat (meat with higher amounts of intramuscular fat), grazing on rangelands complemented with grains and supplements, and the extended use of feedlots or feed yards are partly responsible for this.

Fatliquors

If spew is evenly distributed over the leather, the cause may be related to fatliquoring:

- Fatliquors did not penetrate evenly throughout the thickness of the leather
- Improperly prepared emulsions
- Fatliquors containing FFA
- Fatliquors with excessive amount of methyl esters of saturated FA
- Fatliquors precipitated on the surface
- Excessive amounts of fatliquors
- Cationic fatliquors
- Fatliquor migration during drying.

There are cases where, during vacuum drying, fatliquors that are improperly fixed migrate from the grain side through the thickness of the leather, accumulating on the flesh side with the help of temperature, vacuum and water vapor transport. If these pieces of leather are not immediately hung up to air-dry and instead, they are piled up hot, flesh to grain, TG from fatliquors will migrate from the flesh of one piece to the grain of the next. This can be a factor producing spew.

If the pieces of leather are piled up grain to grain, it will mitigate the problem but it is not a solution, because due to the irregular shape of leather pieces, there will always be some flesh sides touching grain sides promoting fat transfer. In these cases, spew will show the contour of the adjacent leather piece, as shown in Figure 3.

In Figure 4 there is a close-up showing spew with the pattern of vacuum upper mesh. If those leathers are hung up immediately after leaving the vacuum hot plate, generally the fats accumulated in the flesh side will be reabsorbed into the leather during final drying.

Finding fatliquor on the flesh side after vacuum drying should alert the technician to the fact that something is amiss with the fatliquoring. Perhaps some of the fatliquor is not appropriate for vacuum drying; the amount is too great; the emulsion was not properly prepared; fixation was insufficient; etc. The solution of this problem will have a direct impact on the cleanliness of vacuum dryer meshes.

Lipases

Lipases are enzymes secreted by fungi, bacteria and yeast. They catalyze the hydrolysis of TG to glycerol and FFA. Lipase is also secreted from the pancreas, hence it is present in pancreatic bate. Lipases are now being made available to the leather industry for degreasing pelts in the soaking process. This is a very useful application of enzymes, since degreasing with solvents is currently banned. Nevertheless, since their action produces FFA, it is important to know how much of these FFA - whether unmodified or as metal soaps - is carried into the leather in subsequent operations.

Figure 3. Spew showing leg pattern.

Figure 4. Spew showing upper mesh pattern.

The use of lipases requires stringent follow-up monitoring in order that the solution of a degreasing problem does not create other problems, such as clogging of felts in wringing machines or appearance of spew on leather.

Mold

If spew shows in circles of different sizes, it is highly probable that it is due to fungal colonies (mold) whose extracellular lipases have hydrolyzed fatliquor TG present on leather. Figures 5 and 6 show spew resulting from the action of mold.

Since fungal spores are ubiquitous, care must be taken to avoid the environmental conditions that promote mold growth. These include:

- Absence or low levels of appropriate biocides after retannage and fatliquoring

- Too much time in the wet state before drying, exacerbated by hot weather. Factors to be taken into account may include long weekends, official holidays, strikes, and errors in logistics such as failure to comply with 'first in, first out' (FIFO) protocols, etc.

- Partially dried crust leather stockpiled for too long a period

- Crust or finished leather accidentally wetted or stored in an excessively humid environment

- Among vegetable tannages, catechol tannins are more susceptible to fungal attack than pyrogallol tannins.

Microcrystalline Waxes

Microcrystalline waxes are refined mixtures of solid, saturated aliphatic hydrocarbons from the petroleum refining process. They have a fine crystal structure and their melting points fall into different ranges, with the lowest range being 54 to 76ºC. These waxes are widely used as touch auxiliaries in the finishing process. If these waxes are used to excess, a light uniform spew patina may be formed.

Other Finishing Auxiliaries That Can Give Rise to Fatty Spew

These include polyethylene glycol esters of fatty acids, mainly of palmitic and stearic acids, with melting point above 65.5ºC, and amides of palmitic and stearic acids, which are also used as topping oils. As with microcrystalline waxes, excessive use of these substances can lead to the formation of a light patina of spew.

Section 4. Investigation of Fatty Spew Events on the Tannery Floor

A. Traceability

Detailed records of all movements of a product throughout the production process help, among other things, to:

a. Identify the main cause or causes that generated a claim (internal or external) and to

b. Determine, by precise dates, times and locations, which goods must be recalled, and which are "safe."

In a tannery that aspires to be world-class, each hide must be marked with an appropriate code in order to trace its history. The mark must be placed in the least valuable part of the hide, such as the cheek. If the tannery is selling finished leather as sides (half hides) both cheeks must be marked. Hides and pelts must be marked as early as possible, ideally immediately after being removed from the animal in the slaughterhouse, or otherwise in the tannery at the prefleshing stage.

Figure 5. Spew due to single fungus colonies.

Figure 6. Spew due to extended fungus colonies.

Marking each piece of leather implies time and labor costs that in the short term may appear superfluous, but traceability is essential to preventing problems later on.

B. Systematic Guidelines for the Identification of Fatty Spew Causes

In the event of a sudden, unexpected outbreak of spew, the following practical guide can be used to identify the root cause.

1. Confirm the fatty nature of the spew

Apply moderate heating in the affected zone using a match or a hot air blower if available. If the powdery deposit vanishes, this confirms that it is fatty spew.

2. Determine the approximate melting point

Determine whether the spew is composed mainly of free fatty acids or of triglycerides (see Section 2).

3. Analyze spewed leather samples

Determine total fat (grease) content (as percentage), FFA content (%), pH and differential pH index. Compare with Table V in Section 6A.

4. Analyze spew samples

Tests may be carried out by a specialized external laboratory on samples taken from spewed leather. These may include analysis of natural fat extracted from limed pelts by soxhlet extraction.

5. Analyze fatliquor samples

Determine stearic and palmitic acid contents of fatliquors used in the leather. If fatliquor sediment is formed at 4-5ºC, analyze sediment.

6. Collect data on:

- Approximate date of first batches in which the problem first occurred.
- Quantity and extent of affected pieces and batches of leather.
- Examine traceability records for the affected hides and check whether shop floor practices actually complied with the standard procedures (formulas and routes).
- Check standard procedures for compliance with Best Practices at Key Points, as provided in Section 5A.
- Check chemical analysis records for leather (especially for fat and FFA contents) before and after the date when batches were first affected, and the date of reception of raw materials used.
- Check for mold on wet blue, wet retanned and fatliquored leather, and on humid or unevenly dried crust.
- Check for changes in fatliquor supplier, composition and formula concentration.
- Check for increased use of formic acid as a fixation agent in dyeing and fatliquoring. Excessive acidification at these stages can be detrimental.
- Check for excessive use of cationic topping oils.
- Check for excessive application of microcrystalline waxes during finishing.

7) Cause and Effect Analysis (CEA)

With all this data, perform a Cause and Effect Analysis (Fishbone Diagram) and proceed to identify the two or three most probable causes of the spew event.

8. Three-factor two-level experiments[18]

With, for instance, the three most probable causes, **two-level experiments** should be performed with 3-factor design to evaluate the effects of three different factors, each set at two different levels.[18] This method was used by Tournier et al. (2007)[19] to study the most probable causes of a grain abrasion problem on the shop floor of a tannery (not at laboratory level, but at production level). To evaluate the effect of each experiment the different options mentioned in the **Early detection procedures** in Section 6 can be used, and the intensity of spew can be graded from one to five.

More details about this method are given in **Annex 1.**

9. External laboratory

In addition to advanced physicochemical analyses, an external laboratory can provide the technician with an independent viewpoint that is not influenced or limited by the internal paradigms of a particular tannery.

Diagnosis of probable causes

A practical guide to the identification of the most and least likely causes of spew follows.

Begin with the determination of the melting point of the spew (Figure 7) (see also **Commonest types of fatty spews** in Section 2.) Based on observation of how the spew develops on the surface of the leather (whether uniform, patches on certain areas or round spots), Figures 8, 9 and 10 suggest what could be the main cause of the problem.

This information can also help in designing the CEA (Fishbone Diagram), see Figure 7.

Section 5. Fatty Spew Prevention

A. Best Practices to Avoid Fatty Spew Problems at Key Points.
To minimize the likelihood of a spew event occurring in the tannery, good practices are essential at several key points of the process:

1. Close inspection of incoming raw material. Beware of salted hides that have not been prefleshed, especially if they were not properly salted or they have been in stock for more than 6 months.

Figure 7. Identification of fatty spew Melting Point.

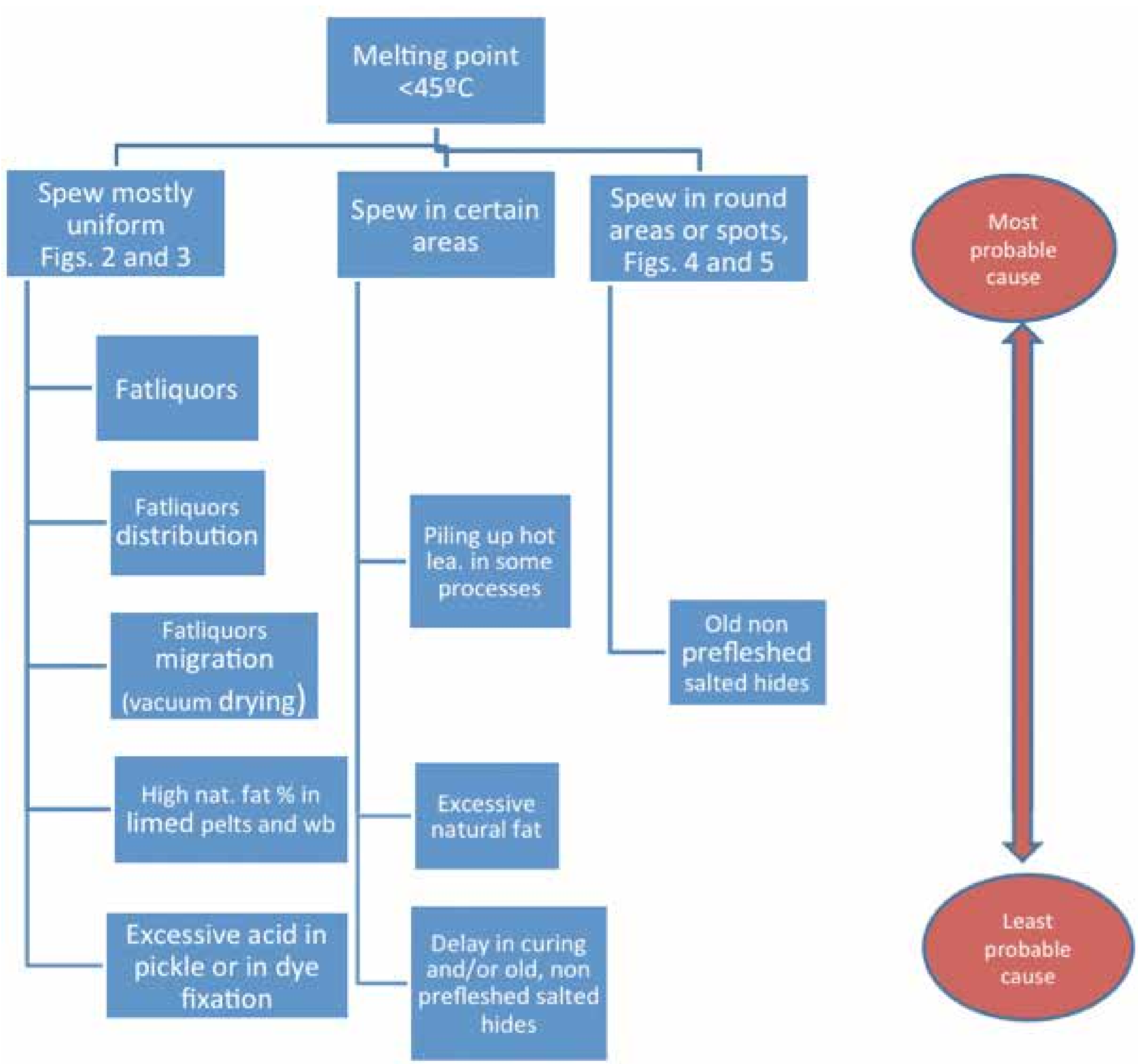

Figure 8. Causes related to MP <45ºC.

2. Efficient pre-fleshing of raw hides, whether they are soaked immediately or preserved for a short or long period. This is mandatory in order to avoid spew appearance in crust and finished leather. Below is a list of measures that must be taken to maximize the efficiency of pre-fleshing.

As much fat as possible must be removed, and the sooner the better.

It is useful to pay attention to the following:

- Proper adjustment of the fleshing machine.
- Automatic regular sharpening of the cutting blades. Sharpen knives after a fixed number of hides (every 100 or 150 heavy steers, for instance, depending on the knife material). This should not be left to the criteria of the operators. Saving money at this point can be a mistake.
- Spot inspection of outcoming hides.
- Proper cleaning of the fleshing machine after each working period.
- Daily checking of knife height; replace knives when the height is 8 – 9 mm.

Important note: If because of fleshing machine failure or other reasons, fresh hides cannot be pre-fleshed, these hides must be labeled as "At risk of spew." They must not be used for the manufacture of critical items and/or sale to valued customers.

3. Soaking, liming and degreasing
Efficient surfactant products should be used to ensure less than 1% of natural fat in limed pelts (dry limed weight basis).

Note that the knife cylinders in the fleshing machines are covered with smashed grease. Some of this paste adheres to

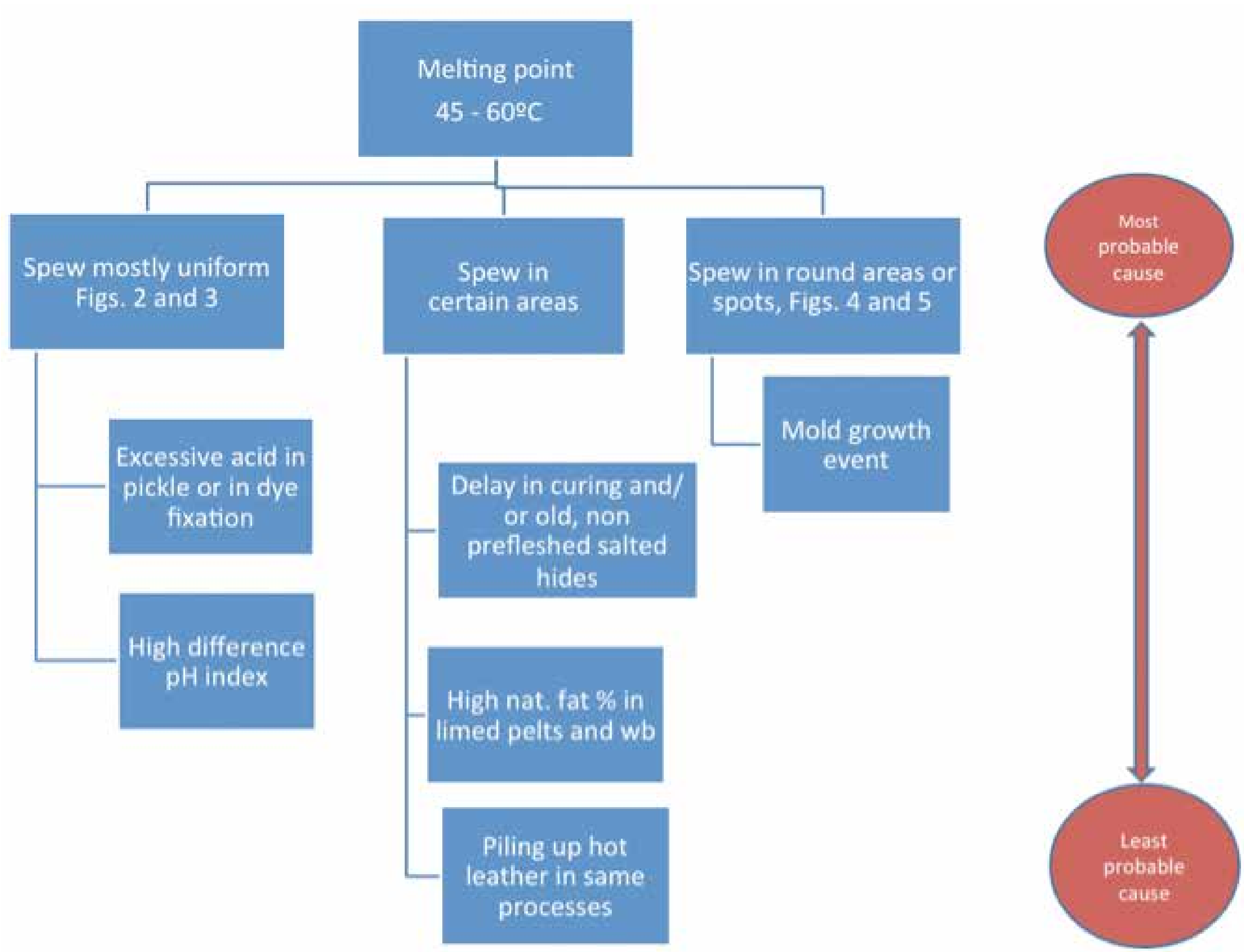

Figure 9. Causes related to MP 45 – 60°C.

and is carried on by fleshed hides. The soaking stage must therefore be preceded by thorough washing with surfactants.

4. Routine laboratory monitoring of limed pelts, to track and keep a record of fat content (%) in each production lot. This will help to detect and correct surfactant composition and dosage, particularly if consistent variations in fat content are observed. Care must be observed, when taking samples for the laboratory, not to include connective tissue from the flesh side, as this may give erroneous results. Values should be recorded on a chart. To be on the safe side, natural fats in limed pelts should preferably not exceed 1% on a dry weight basis.

5. Deliming and degreasing, emphasize defatting during the deliming process, using efficient surfactant products, to ensure less than 0.5% of natural fat in wet blue hides (dry weight basis).

6. Routine laboratory monitoring of wet blue hides, to track and keep record of the fat content (%) in each production lot. Free fatty acid analysis of the extracted fat may also be performed. It is understood that this is in addition to normal routine sample analysis of wet blue production lots. The tannery laboratory should take into account, in its results, whether fatliquor was added during chrome tannage. For wet blues that have not been pre-fatliquored in the tanning stage, natural fats should not be higher than 0.5% on a dry weight basis. If a fatliquor was added during tannage, the result of soxhlet extraction must be deducted from the added amount; this assumes that the leather took up all the active material.

7. Ensure a good level of fungicide in wet blue hides, to assure absence of mold development.

8. Ensure thorough neutralization before retannage. The resulting pH of leather must be above 3.6, with a difference index well below 0.7 (see Section 6A.)

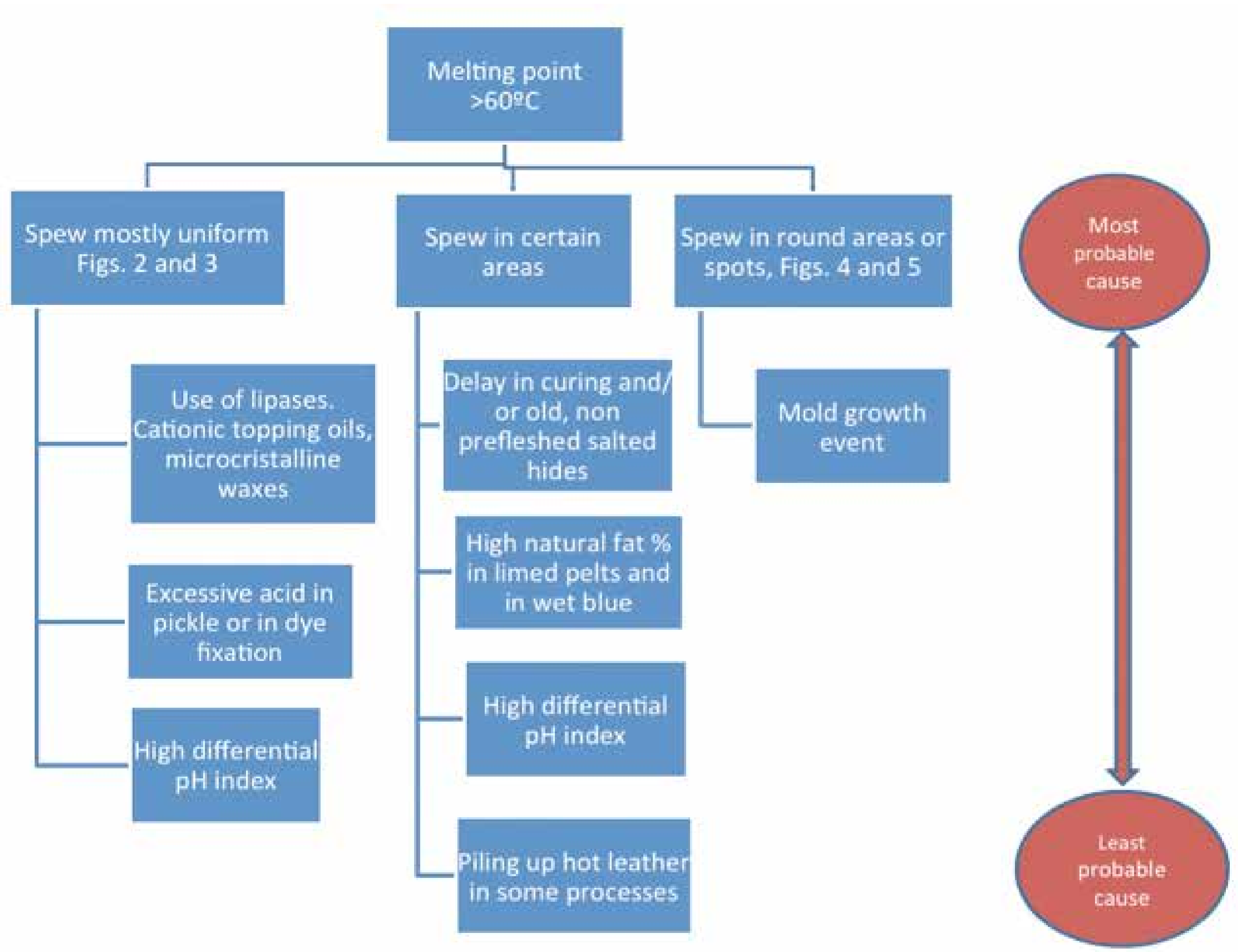

Figure 10. Causes related to MP > 60°C.

9. Good level of fungicide in retanned and fatliquored leather, to ensure at least 2 weeks' absence of mold in wet leather. Add the fungicide together with the fatliquor. In general the active ingredients of fungicides are oil soluble, and will remain in close contact with the material to be protected.

10. Control of incoming fatliquors, to ensure absence of free fatty acids, see Section 5B. Use winterized oils and synthetic fatliquors.

11. Do not over-fatliquor leather.

12. Do not over-acidify with formic acid in the fixation steps. Use other auxiliaries in conjunction or instead.

13. Proceed to dry out leather without delay.

14. In drying steps, cool hides before piling them.

15. Routinely determine total fat content (percentage) in crust samples. See Section 6.

B. Monitoring Fatliquors to Prevent Fatty Spew

In addition to standard analysis procedures for fatliquors, the following quick and easy procedures are recommended:

- Take two samples of oil from the original container after thorough homogenization, preferably by mechanical means.
- Let the two samples stand for several days, one at room temperature and the other in a refrigerator (approximately 4ºC).
- If solid sediment is formed, there is likelihood of spew appearing. Spew tends to occur in leather shipped from warm climates to cooler destinations.
- If no sediment forms, keep the sample as reference for future shipments or to compare with other drums or containers.

Sedimentation in fatliquors is undesirable because any sediment formed must be kept in suspension or heated to ensure homogeneity during use. Otherwise, there is a risk of fatliquor composition changing over the period of the process, as only the supernatant is used. If fatliquor forms a sediment at room temperature, the sediment is likely to be composed of undesirable fatty acids (palmitic and stearic) or their derivatives.

Considerable amounts of FFA may be released from processed oils.[11]

Schindler Method[20]

Modified Schindler liquid-liquid separation, as described in Tancous (1974, 1986)[21,22] consists in shaking an aliquot of a fatliquor with a water-ethyl ether mixture. The hydrophilic compounds remain in the aqueous phase; separate the phases, evaporate the ether, dissolve the remaining oil in alcohol and let stand for several days. If fat crystals develop, the fatliquor is likely to cause spew problems. This method allows for further analysis of the fat crystals and mixture by gas chromatography.

Oleoquim Method[23]

To minimize spew occurrence, there is an interesting proposal by Oleoquim (1991).[23] It is based on prior calculation of the total percentage of stearic acid on a dry shaved weight basis, taking into account the stearic acid content of natural grease present in shaved hides and stearic acid content in each of the fatliquoring oils to be used on the leather.

According to this publication, risk levels are shown in Table V.

SECTION 6. EARLY DETECTION PROCEDURES

A. Free Fatty Acids (FFA)

Based on practical experience of various spew events with MP > 45ºC, Tournier et al. (2014)[24] found a close relationship between FFA content and spew occurrence. They performed a large number of fat extractions from leathers belonging to same type of finished product, classified into three groups: having heavy amounts of spew, lightly spewed and without spew. They measured the FFA contents of the fat extracted from each group and expressed it in two forms: FFA as a percentage of dry weight of leather samples and FFA as a percentage of total fat extracted. With the results, they constructed Table VI. These authors have been more rigorous than SATRA (2006)[25] in that they predict No Risk of spew only at FFA contents of less than 1.5% of dry leather weight (rather than SATRA's recommendation of less than 2.5%).

They also found a strong correlation between high risk of spew occurrence and leather pH, at pH below 3.6.

To check the risk of spew in a particular batch of leather, it is advisable to take the samples to be analyzed from bellies of several hides, since in general the belly has a higher fat content than the rest of the hide, because of its open structure. Bellies also take longer to dry, because of their higher water content.

Cold Chambers

Cold storage of leather samples from production batches can enable early detection of fatty spew in the tannery. The use of an Environmental Chamber can be very helpful (see **Annex 2** for a detailed cycle). If the tannery does not have access to an Environmental Chamber, a refrigerator at 0ºC can be used. If the tannery stocks raw hides or wet blue leather in an industrial cold chamber at 4ºC, this can be used to stock samples from production batches for 1 month. Another alternative is purchasing or renting a refrigerated container for the temporary storage of samples of production lots. In any event, systematic rotating batch inspection procedures must be established for spew detection.

Fat and FFA

Measure and keep a record of fat percentage for each production lot. It must include FFA analysis of extracted fats, which must always be below 1.5% (see Table VI.) Keep a record of pH and difference index (see Section 5A, item 8).

Fat Bleeding Test

Bleeding is the transfer of materials exuded from leather to other materials that come in contact with it. Sandwich small pieces crust or finished leather between white PVC strips; expose to a temperature of 60°C and saturated humidity for 6 h. If there is no bleeding, this is reassuring; however, the presence of bleeding does not prove that spew will occur in the leather, but is a warning, and other tests must follow.

Modified Ollert Method

This method to test the tendency of leather to form fatty spew was first developed by Ollert (1989)[26] and later modified by Zauns-Huber et al. (1992).[27]

TABLE V
Risk of spew in relation to stearic acid content.

High risk of spew	Borderline	Low risk of spew
Stearic acid % > 1.2	1.2 < Stearic acid % < 1.0	Stearic acid % < 1.0

TABLE VI
Risk of fatty spew occurrence (with MP > 45°C) in relation with FFA content.

	High risk of spew	Borderline	No risk of spew
% FFA in leather, dry basis	> 2	1.5 - 2	< 1.5 (*)
% FFA in extracted grease	> 13	10 - 13	< 10

(*) SATRA[25] recommends < 2.5%.

It consists in subjecting a sample of leather to a steam flow that passes through its thickness from flesh side to grain side, then letting it cool and stand for 5 days at 25°C; then inspect for spew formation. For a more detailed description of the method see **Annex 3**.

This method can be used, not only by tanneries but also by manufacturers of leather articles, to test incoming leathers before cutting. The results are conclusive only for leathers with a high general potential to spew. In leathers with low potential or potential in only certain zones, a negative result does not guarantee that this leather will not spew.

Section 7. Fatty Spew Mitigation

Remedial treatment for spewed leather

Once fatty spew has formed inside the leather, it is very difficult to get rid of. Nevertheless, there are some procedures that can mitigate it or eliminate it at least temporarily.

Heating the spewed leather and quick cooling piece by piece (not piling them up) to room temperature. A hot air blower, a hot tunnel, plating machines, etc., can do the heating. This aims at melting the spew, returning it into the leather and crystallizing it there.

Spraying with a water emulsion of a low viscosity mineral oil followed by drying through a hot tunnel. This is aimed to mix high melting point spew with low melting point oil and interfere with new spew crystallization.

Swabbing with a cloth soaked in a fat solvent, to dissolve part of the spew and remove it, while returning part of it into the leather.

There are some products on the market for prevention or treatment of fatty spew in leather. Some of them may be based on dialkyl ethers,[28] Guerbet alcohols,[27] or other mixtures; each should be tested carefully to confirm they have the desired effect. Langmair and Madek (1990)[29] have also reported that non-ionic detergents may have a preventive action against spew.

If mold growth is detected in damp leather,[24] do not dry it. Wash the whole lot with a detergent that withstands 70°C, to melt stearic acid, and re-fatliquor adding a small amount of mineral oil to prevent crystallization of the remaining FFA. If the mold event is detected in crust or finished leather, this procedure is not recommended since rewetting these leathers will drastically affect quality, in addition of the extra costs of reworking.

CONCLUSIONS

Nowadays, sufficient knowledge is available for the control of fatty spew problems.

Leather processing takes many days and the raw materials are different and variable. Processes are highly dependent on labor practices, weather variability, correct performance of machines, etc. As a result, it is always possible for something to go wrong and a surprise bloom of spew to appear. Traceability is the tool that will help to track what might have happened. It will help to identify how many leathers are involved and where they are, whether in the production pipeline, or in transit, or in the hands of customers. Flow-charts and procedures described in this paper provide systematic methods for diagnosing, preventing and mitigating fatty spew in leather. We hope these will be useful as a ready reference for tannery technicians.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance of Lic.Victor Daniel Vera, ex CITEC, Argentina, in technical discussion and constructive criticism, and also Dr. María Rubino and Dr. Rafael Auras, both at Michigan State University for invaluable help in language corrections, paper structure and technical assistance. In addition I want to thank my colleagues Alvaro Castagna of ZENDA Leather, Uruguay, Germán Azzato, Jaime Velez and Juan Carlos Oclepo of SADESA GROUP International, and Juan Carlos Pérez of DAXILAN, Uruguay, for text corrections and helpful criticism. Finally I want to thank "Words of Science" for polishing the final draft.

REFERENCES

1. Leather Technical Glossary in Six Languages. Eduard Roether Verlag, Darmstadt, 1976.
2. Tancous, J. J.; Skin, Hide and Leather Defects. Second Edition. Lee Corporation, Cincinnati, Ohio, USA, 1986, p. 270.
3. http://en.wikipedia.org/wiki/File:Fat_triglyceride_shorthand_formula.PNG
4. Poré, J.; La Nourriture du Cuir. Société des Publications « Le Cuir », Paris, 1974.
5. Barandiarán, J.C.; Manual de Materias Grasas para Cuero. CITEC – INTI, pp. 17- 18 Argentina, 1993.
6. http://www.scientificpsychic.com/fitness/fattyacids1.html
7. Hollstein, M.; On the Problem of Fatty Spews on Leather. *Das Leder* **3**, 40-46, 1979.
8. Koppenhoefer, R.M., in O'Flaherty, Roddy and Lollar; Chemistry and Technology of Leather, Vol. 1, A.C.S. Nº 134, Krieger Pub. Co., New York, 1978, p. 50.
9. Waite, T.; in Leafe, M.K. (ed); Leather Technologists Pocket Book. Society of Leather Technologists and Chemists, East Yorkshire, UK, 1999
10. Covington, A.; Tanning Chemistry, The Science of Leather. RSC Publishing, Cambridge, UK, 2009, p. 392.
11. Heidemann, E.; Fundamentals of Leather Manufacturing. Eduard Roether KG, Darmstadt, Germany, 1993.
12. www.sigmaaldrich.com
13. Mitton, R.G. and Pankhurst, K.G.A.; A study of the Mechanism of Fatty Spue Formation. *JSLTC* **41** (4), 128, 1957.
14. Naviglio, D.; Mechanisms involved in the formation of fatty spues. *Leather*, May 2001, p. 44-48
15. Tomaselli, M., Naviglio, B., Naviglio, D. and Raia, C.; *Cuoio, Peli, Materie Concianti* **79** (2), 85-92,2003.
16. Zengin, G. and Afsar, A.; Use of natural fat emulsions in fatliquoring process and investigation of fatty spue formation. *Deri Bilim/Journal of Leather Science*, **4**(3), 6-15, 2010.
17. Wang, Y., Liao, X., He, Q. and Shi, B.; Determination of Fatty Spew on Leather by GC-MS. *JALCA* **106**, 179-183, 2011.
18. Lochner, L.H. and Matar, J.E.; Designing for Quality: An Introduction to the Best of Taguchi and Western Methods of Statistical Experimental Design. Quality Resources, a Division of The Kraus Organization Limited, NY, NY, American Society for Quality Control, Milwaukee, WI, 1990
19. Tournier, R., Avallone, C., Ruibal, J., Temkin, R. and Chinelato. C.; Estudio de causas que generan abrasión de flor en cueros vacunos. Tecnología del Cuero, *Revista de la Asociación Argentina de Químicos y Técnicos de la Industria del Cuero* **19**(63), 10, 2007.
20. Schindler, W.; *JSLTC* **14**, 34, 1930.
21. Tancous, J. J.; Skin, Hide and Leather Defects. Second Edition, Lee Corporation, Cincinnati, Ohio, USA, 1986, p. 337.
22. Tancous, J. J.; A study of fat spew by gas chromatography. *JALCA* **69**(2), 66, 1974.
23. Oleoquim Ind. Com. de Produtos Químicos Ltda.; Revista do Couro, *Associaçao Brasileira dos Químicos e Técnicos da Indústria do Couro, Brasil,* November 1991, p. 62.
24. Tournier. R, Castagna, A., Lado, F., Lucas, J.; Tecnología del Cuero, *Revista de la Asociación Argentina de Químicos y Técnicos de la Industria del Cuero*. **25**(87), 13-18, 2014.
25. SATRA http://www.satra.co.uk/spotlight/article_view.php?id=325 or SATRA Spotlight, March 2006, p. 14.
26. Ollert, H. A.; *Das Leder*. 1989, p. 256.
27. Zauns-Huber, R., Ruscheinsky, E. and Wolter, F.; Oiling leather using oiling component in combination with aliphatic alcohol. US Patent 5476517 A, Henkel KAA, July 18, 1992.
28. Zauns-Huber, R., Ruscheinsky, E. and Wolter, F.; Use of nonionic organic dialkyl compounds for preventing fatty spew on leather. US Patent 5468255 A, Henkel KAA, 18 July 1992.
29. Langmaier, F. and Mladek, M.; *Das Leder* **41,** 149-162, 1990.

ANNEX 1

Methods based on varying one factor at a time, while keeping the others fixed have long been used in tanneries. However, these practices are based on the assumption that it is possible to rapidly obtain accurate results on performance, which is not always true. Positive and negative interactions between a new factor and already existing ones can distort results.

Statistically designed experiments have been found to be useful in engineering development, as they can be used to improve product quality and process performance, leading to improved product sales and reduced manufacture costs.

These methods can be applied in a leather manufacturing plant. Two-level experiments with two- or three-factor design provide a simple method that can be efficiently used in tanneries. The authors recommend replicating the experiments to confirm results.

TABLE VII
Design matrix for a two-factor, four run experiment.

FACTOR SETTINGS				
TRIAL Nº AT RANDOM	**TRIAL Nº STANDARD**	**FACTOR A**	**FACTOR B**	**RESPONSE**
	1	1	1	Y_1
	2	2	1	Y_2
	3	2	2	Y_3
	4	1	2	Y_4

Table VIII
Response table for a two-factor, four run experiment.

RESPONSE TABLE							INTERACTIONS	
TRIAL Nº AT RANDOM	**TRIAL Nº STANDARD**	**RESPONSE**	**FACTOR A**		**FACTOR B**		**FACTORS AB**	
			Levels		**Levels**		**Levels**	
			1	2	1	2	1	2
	1	Y_1	Y_1		Y_1		Y_1	
	2	Y_2		Y_2	Y_2			Y_2
	3	Y_3		Y_3		Y_3	Y_3	
	4	Y_4	Y_4			Y_4		Y_4
TOTALS			Sum	Sum	Sum	Sum	Sum	Sum
NUMBER OF VALUES		4	2	2	2	2	2	2
AVERAGES		Avg Y	Av1	Av2	Bv1	Bv2	ABv1	ABv2
EFFECTS (difference)			**Av2 - Av1**		**Bv2 - Bv1**		**ABv2 - ABv1**	

Response Tables can be used to simplify the calculations. Two forms used in a two-level two-factor design are shown in Tables VII and VIII.[18]

ANNEX 2

Use of Environmental Chamber with the following cycles:

- 1 week at 0ºC and 95% relative humidity (RH)
- Inspection for spew
- 1 week at 30ºC and 30% RH
- Inspection for spew
- Day 1 at 30ºC and 30% RH; Day 2 at 20ºC and 40% RH; Day 3 at 10ºC and 50% RH; Day 4 at 0ºC and 60% RH; Day 5 at 0ºC and 70% RH; Day 6 at 0ºC and 80% RH; Day 7 at 0ºC and 90% RH; Day 8 at 0ºC and 95% RH
- Final inspection for spew

ANNEX 3

Leather samples were punched out in the shape of disks (155 mm in diameter) without conditioning. The opening of a 1 liter face-ground beaker (external diameter of 155 mm) filled with 300 ml of running water was then covered with these leather disks, with the grain side on top (outside). The leather was fixed with a clamping ring, after which the water was brought to the boil and kept boiling for 2 minutes. In this way, the leather sample was subjected to a predetermined thermal load, with steam escaping from the scars. The clamping ring was then removed, the leather disk covering the face-ground beaker was taken off and the water was poured out.

The droplets of water adhering to the walls of the beaker after the water had been poured out were left in the beaker, i.e. the glass was not additionally dried. The leather still moist from the steam treatment described above was then immediately transferred to the face-ground beaker, which was then sealed with a glass disk. The leather samples were then stored in the sealed beaker for 5 days at a temperature of 25°C. Finally, the sample was visually examined for fatty spew.

LIFELINE

Ricardo A. Tournier earned a degree in Chemical Engineering from Universidad de la República, Montevideo, Uruguay in 1968 and an MSc in Chemical Engineering from University of South Carolina, USA, in 1971. In 1974 he attended a Dyestuff Course at the Chemistry Department of Turin University and a Practical Course on hide tanning at Instituto “Baldracco,” Turin, Italy. Started in the leather industry in 1971 at Lanza Tannery, Uruguay, for 9 years. Later he worked for 20 years as Senior Technical Manager at Paycueros Tannery, a member of SADESA Group. From 2000 to 2012 he was Technical Assistant to the General Manager at Zenda Leather, Uruguay. His work on leather problems and defects has been published in regional journals. He is currently working as a freelance consultant.

Few people realize that Leather Making is the world's oldest manufacturing process, thus the world's oldest industry. Tanning—the process of converting hides and skins into leather—is also the world's first science. Also, because of the pure craftsmanship involved, tanning may well be the world's first art form.

Anyone who doubts that a sheepskin has up to 30,000 fibers per square inch has only to count them.

NOTHING TAKES THE PLACE OF LEATHER

INDEX TO ADVERTISERS