

SmiTools - Fatty spew

Avoiding fatty spew on leather

In this SmiTools on fatty spew you can learn about its background, where it comes from, and what can be done to prevent its formation.

Introduction

On processed leathers it is sometimes observed that, over time, an undesired white milky film appears on top of the leather. This white layer often gives rise to debates on its origin and causes, and in some cases leads to a claim for damages.

The phenomenon described is called 'fatty spew'. The possible sources of fatty spew may be of diverse nature, they are similar in one respect. They always originate from high melting point substances.

What is fatty spew?

All fats have a tendency to migrate through the leather when they are not irreversibly fixed to the matrix. Free saturated fatty acids, as all other substances, are sensitive to the influence of temperature. One of temperature's effects is that it can change a substance's appearance. The reason for the white layer on the grain is the high melting point, which is about 60°C to 70°C for all of the substances causing fatty spew. Below this temperature they begin to solidify but remain undetectable to the eye.



Since they are not part of a larger structure, but free, they tend to cling to one another. With decreasing temperatures this tendency to form larger structures and change their appearance increases. Like water turning into ice, the fatty acid crystallizes when its temperature is lowered beyond a certain point. This point indicates the temperature where the fatty acid changes its structure to crystalline, becoming opaque and milky to the eye.

The most common origin of fatty spew is the migration of natural fat. At the surface the fat reaches the end of its migration, settles, and crystallizes, resulting in a white layer. This mechanism does not act instantly, but represents a gradual process requiring a certain length of time. A similar phenomenon can be observed on chocolate after longer storage and/or temperature changes.

This mechanism also applies to all other substances, other than natural grease, that have a high melting point.

A quick way to determine if the white film is fatty spew and not dirt, salt or fungus is to hold a flame of a lighter close to the affected area for a short time. In the case of fatty spew, it will easily melt and disappear. In all other cases it remains visible.

What is it made of?

In general natural fats and oils consist of triglycerides. These components are esters of glycerol and three (mainly different) fatty acids.

For the understanding of fatty spew it is important to look at the presence of specific fatty acids in the natural fat of the skin. The most problematic ones are the longer carbon chain saturated fatty acids which are solid at room temperature but could crystallize overtime:

- C14 (myristic acid),
- C16 (palmitic acid)
- C18 (stearic acid)

A large amount of fatty acids of even lower saturation degree is present in relevant amounts (e.g. linoleic acid, oleic acid), but these substances are liquid at room temperature and will therefore not crystallize at the temperatures humans are subjected to.

Where does it come from? - animals

Bovine hides contain 2-4% natural grease of which 40-50% is unsaturated. Sheep and pig skins can contain much higher levels of natural grease x%. An average composition of sheep fat contains up to 30% natural grease, of which two third (67%) consists of saturated fatty acids.

Some of the natural triglycerides are subject to hydrolysis. Hydrolysis can easily occur under acidic or alkaline conditions and also through enzyme activity.

If we now look at the melting point of e.g. a triglyceride containing one saturated and two unsaturated acids it will have a melting point at room temperature ($\pm 20^{\circ}\text{C}$). When a saturated fatty acid gets split off (thus becoming a free fatty acid) it will, in consequence, have the melting point of a saturated fatty acid ($\pm 60^{\circ}\text{C}$) and after time may form the white layer.

During hydrolysis of natural fat in the skin 1-2% of fatty acids may get released. In bovine hides, about half are saturated and thus 0,5-1% free saturated fatty acid can be expected to appear. The risk for this occurrence is higher when the hides have been insufficiently degreased, or perhaps well-degreased, but poorly washed or drained.

Where does it come from? - oils

All natural oils contain free fatty acids and a certain portion of them is present in their saturated form.

The typical level for free fatty acids (saturated and unsaturated) in vegetable oils amounts to $\pm 1\%$, for animal oils to $\pm 4\%$ and fish oils have up to 15%.

Part thereof is the problematic free saturated fatty acid.

The typical level for saturated fatty acids in vegetable oils amounts to $\pm 10\%$, for animal oils to $\pm 30\%$, and fish oils have up to 25% of the total and combined amount of free fatty acids.

It is impossible to give a simple formula to estimate the free saturated fatty acids for all products. Basically: Sulfated oils have higher levels than sulfited oil. Synthetic fats have the lowest levels.

What role play fatliquors?

All products based on natural fatliquors are based on triglycerides. Triglycerides are esters based on glycerol and three, possibly different, fatty acids. The raw materials already come with a certain spread in the amount of free fatty acids they contain. Hydrolysis of part of the esters during the production of fatliquors is unavoidable and some free fatty acids will always be found in any end product made containing natural oils.

Free fatty acids often are an essential and necessary ingredient and addition of fatliquors to impart handle and leather character.

Even in fatliquors made of natural ingredients only, the numbers of free saturated ingredients are too small to pose any risk of visible crystallization.

Analysis

The amounts of spew are most of the time too small to have them chemically analyzed for their origin. An FT-IR analysis can at best give an inconclusive idea of the spew's composition.

How can it be prevented?

Prevention of fatty spews is directly related to its possible origins in the hide's natural grease or, in some cases, to the fatliquors chosen.

Hides

Most hides have in common, that the fat is unevenly distributed over the surface and throughout the cross section.

The parts of the back where the kidneys are located, are the most likely places to show a problem. The area along the backbone is critical as well.

On force-fed stock one can more easily encounter problems because of their higher fat content, than with hides from animals raised in a more natural manner.

Unsuitable storing conditions are another possible cause for the deterioration of natural fats and all problems associated with it. Most fatty spew are therefore to be traced back to insufficient degreasing and the presence of excess natural fat in the skins.

When processing raw hides it is helpful to use already degreasers and emulsifiers in early steps of the process. Non-ionic products are usually the chemical base, although their use should be carefully understood since it may affect the leather's final properties, such as with waterproofed articles. The same applies to use degreasers and emulsifiers in the following steps of the process.

When in doubt about the quality and thoroughness of the degreasing, it is advisable to have the wet blue's fat content analyzed.

Fatliquors

Another, less likely cause when the right products are chosen, could be excessive fatliquoring, or the wrong application of a fatliquor.

Although fatliquors cannot contribute to any form of visible spew formation, certain guiding rules are yet advised to observe.

- Fatliquoring needs to be complete, well-exhausted and evenly done in the whole cross section.
- Water hardness can lead to problems in this respect since many anionic emulsifiers are sensitive to the higher amounts of Ca^{2+} and Mg^{2+} ions that cause water hardness. The fatliquor's emulsifiers will form a water insoluble precipitate with these ions and lose their essential emulsifying capacity. The same applies to the use of neutralizing agents containing calcium acetate should. If they are used, thorough washing is required afterwards.
- Excessive amounts of fatliquors are to be avoided for many reasons. Maximum softness today does no longer only depend on the quantities applied, but equally much on the products chosen. Ultra soft leathers can be made even with reduced quantities. For the sake of preventing fatty spews an optimum balance can be found by checking to which extent the amounts applied can be reduced.
- Splitting the total amount of fats into several smaller additions promotes its penetration and even distribution. Pre-fatliquoring is recommended, but adding the main fatliquor in two equal steps when larger %-ages are to be applied, creates safety later on – and better softness in addition.

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- Proper emulsification of the fat blend is a must: mix the products slowly with three times the amount of water (at 60°C) just before the addition to the drum. Doing so long before the addition is likely to destabilize the emulsion and cause uncertainties of the emulsion's stability.
- The process temperature should remain stable during the process. Higher temperatures support the distribution, uptake and gradual fixation of the oils. Particular attention must be drawn to temperature's effect on exhaustion and fixation, since it minimizes the risk of excess external fixation of unexhausted oil upon their acidification. To minimize this risk further, fixation should not be done in one addition, but in two or three.
- Biocides can help to prevent break down of the fats. Care has to be taken with the application conditions, because non-ionic emulsifiers deactivate certain biocides. It is not sufficient to rely on the biocides that may be present in the fat liquors since, for prevention of the breakdown's effects, the biocides should mainly act on the leather's surface. Biocides as a fattiquors ingredient penetrate into the leather cross section along with the fat and will lack the external protection of those added after fattiquoring. Besides this the biocides in fattiquors are only meant to protect the fattiquor itself during storage.

Storage

Low storage temperature of leather favors the formation of white fatty spew, based on the saturated free or esterified fatty acids. Therefore in wintertime there is more of a chance for a complaint.

Higher storage temperature favors the formation of darker colored fatty spews. Migration to the surface can occur, caused by excess of oils and fats.

Humid conditions favor microbiological activity. Natural fats present in the hides and in fat liquors are suitable as feeding material and under extreme tropical climatic conditions an appropriate biocide has to get used.

Others

An additional source might be found in certain finishing waxes, but could also be found in shoe polishes.

But since this SmiTools discusses the visibility of fatty spews on crust leathers those causes are not further elaborated on.

Remedies

Once fatty spews have appeared, not much more than trying to wipe them off can be done. The appearance of fatty spews is a temperature-time process and its appearance cannot be predicted. This makes it such a tricky problem. Perfectly fine crust can over time develop the white layers, even after it has been finished, making the leathers unusable. When the spew only appears after finishing, very little can be done. Crust leather can be wiped with solvents or mineral oils. However, in most instances this effect will only be temporarily.

Conclusion

The amounts of free unsaturated fatty acids contained in normal bovine hides is too small to cause fatty spews. The same is true for fattiquors. Most fattiquors do contain free unsaturated fatty acids as chosen ingredient or byproduct from the raw material and its processing. The amounts found in well-made quality fattiquors are so small that most of them are caught inside the matrix before reaching the leathers surface. Only through massive precipitation stemming from very wrong and careless processing enough oil might be deposited on the leather's surface for the formation of some visible spew.

The main cause for fatty spew lies in the very nature of skins with a very high content of natural grease, such as sheep and pigs, where large sufficient quantities of free unsaturated fatty acids can become available and migrate to the leather's surface.

Thorough degreasing and washing at the both the early and later stages are effective and durable protection against the undesired effects caused by the remnants of the skin's natural grease.

Last but not least we would like to mention that all components of a fattiquor are needed for the proper softness, even the saturated ones.

Smit & Zoon degreasing agents and fattiquors are developed with this knowledge in mind. With our knowledge of our fattiquors' composition, behavior and application we can help and advice you on their right use in relation to fatty spew .

Contact Smit & Zoon for further information

The information given in this SmiTools is just a short synopsis on the topic. We would be glad to help you further in case of questions, the sharing of information or help with choosing the right wet-end products for your application. Please feel to contact our Leather Service Centre or your usual relation within Smit & Zoon.