

The mechanism of aqueous degreasing, and the custom designed surfactant

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The degreasing of hides and skins can be considered state of the art. Excluding the use of solvents, the most effective water-based products are nonylphenol ethoxylates (NPEs).

However, the degradation products of NPEs exhibit high aquatic toxicity and are biological accumulative. For this reason, the European Union has prohibited products containing NPEs in concentrations exceeding 0.1% by weight for the majority of applications with effect from 2005 (Directive 2003/53/EC).

The more eco-friendly method would be a water-based process employing fatty alcohol ethoxylates (FAEs). Unfortunately, the result of this water-based process is often unsatisfactory. This is particularly so for very greasy sheep and pigskins, and in addition the technique can be uneconomic.

To date, no alternative surfactant has matched the outstanding cost-performance ratio of NPEs for industrial use. Consequently, it is recognised that worldwide there is a technical, economical and environmental need for a new and effective degreasing agent.

The degreasing mechanism

Until now, the degreasing of hides and skins has been viewed as four stages:

1. penetration of the surfactant into the pelt,
2. dissolving the grease,
3. transport of the grease into the external float,
4. formation of a stable emulsion of the grease (at least temporarily) in the process float to separate the grease from the skin.

Despite this broad understanding, the exact degreasing mechanism has not been fully understood. However, as a result of investigation¹, the degreasing mechanism has been revealed in detail.

1. penetration of the surfactant into the pelt,
2. dissolving the grease - *by the formation of a nanophase*,
3. transport of the grease nanophase to the surface of the pelt,
4. conversion of the nanophase into a macroemulsion as it is released from the pelt into the degreasing float.

In a conventional sheepskin degreasing process, this nanophase

was seen to occur, but proceeded by two other phases:

- A LOWER PHASE: this mainly consisted of water, and an upper phase mainly consisting of grease.
- A MIDDLE PHASE: this consisted of water, grease and the main part of the surfactant.

These phases were almost clear, but could be seen using a microscope under visible light. Under high magnification a nanosponge-like structure can be seen with a cavity diameter of less than 50 nanometres (5x10⁻⁸ m, 1/1000 of the thickness of a human hair), being illustrated in *Figure 1*.

Furthermore, these nanophases - containing water, grease and surfactant - show a sponge-like structure with an immense inner surface and stability over a wide temperature window. This leads to an outstanding capability for absorbing and dissolving grease and fat under varying conditions of temperature and pH as shown in *Figure 2*.

Figure 1: What is a Nanophase?

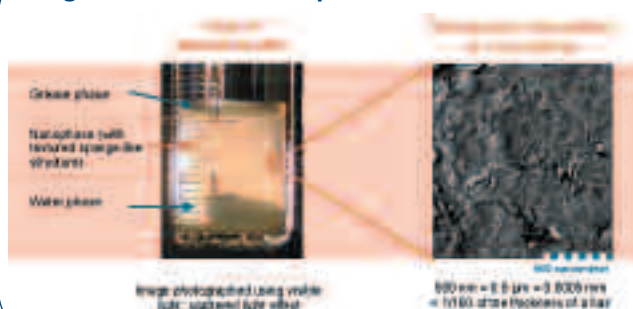


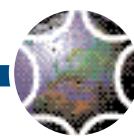
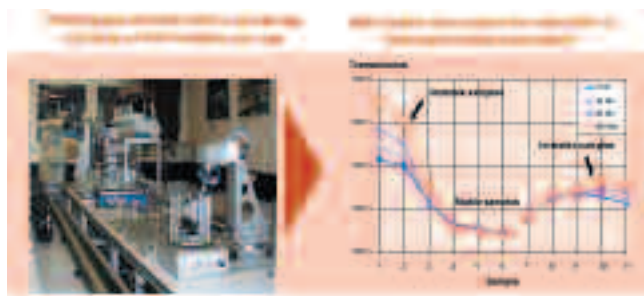
Figure 2: The Properties of a Nanophase?

- Nanophases containing water, grease and surfactant show:
 - A sponge-like structure with an immense inner surface (like a microfibre towel)
 - Stability over a wide temperature window



Outstanding capability for dissolving grease and fat under varying application conditions



**Figure 3: High-Throughput Screening of Surfactants****Figure 4: Degreasing of Pickled Sheep Skins (I)**

Profile of an effective and environmentally safe surfactant

An ideal surfactant needs to achieve the following requirements:

- ability to form nanophases during application,
- ability to form stable macroemulsions,
- low eco-toxicity,
- ease of biodegradation without aquatotoxic metabolites,
- ready-to-use characteristics,
- low foaming.

In addition, a base product is required as a single alcohol component for reasons of cost and quality in production. Ideally, this surfactant would be applicable across the full spectrum of raw materials as hides and skins, and process stages where degreasing is required.

During a development program 5,000 candidate surfactants were tested. Following homogenisation at 37°C, the homogeneity and phase separation between water and oil was automatically measured by light transmission and refraction measurement. This is illustrated in *Figure 3*.

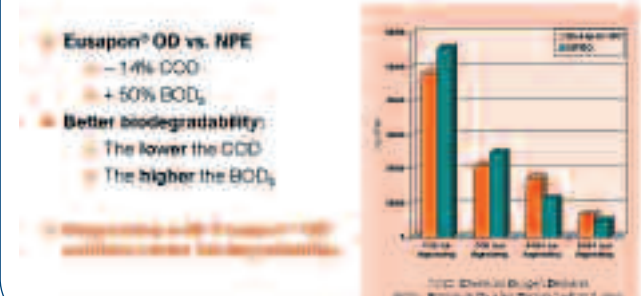
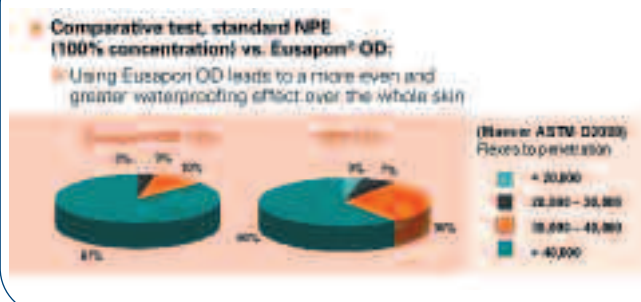
As a result of this program, a new surfactant² has been produced.

Degreasing performance

SHEEP SKIN PROCESSING:

Comparative trials with this product and a standard NPE in the degreasing of sheepskins revealed greatly superior fat extraction and a better phase separation of the float. This is shown in *Figure 4*. Moreover, only half the quantity of product was required compared to the NPE.

Furthermore, the biodegradability of the residual degreasing

Figure 5: Degreasing of Pickled Sheep Skins (II)**Figure 6: Cattle Hides Beamhouse (II)**

float is much better. This is demonstrated by a lower chemical oxygen demand (COD) and a higher biological oxygen demand (BOD₅) as shown in *Figure 5*. During both sheep and pigskin processing, superior grease extraction, and improved physical properties and dyeing shades were provided.

FUR PROCESSING:

Wool degreasing has always presented a problem in fur processing, resulting in the form of yellowish wool and dull dyeing. However, the trials provided an exceptionally clean wool whilst requiring only 40% of surfactant compared to the NPE.

CATTLE HIDES:

In the manufacture of waterproof leathers conventional surfactants have a negative influence upon repellency. However, if less surfactant is used then the dyeing becomes more uneven. In the trials the new surfactant was 2.5 times more efficient in grease removal than the standard NPE. Comparatively, the waterproofing performance was improved in terms of water penetration and uniformity across the hide as illustrated in *Figure 6*, and the dyeing was more regular.

Degreasing technology is often problematic, and the effects of poor grease removal and distribution on leather in terms of both appearance and technical performance are well known. New insight into the mechanism of degreasing shows that a new approach can be taken within the arena of aqueous degreasing agents. In particular, the investigation has provided a new flexible surfactant for leather manufacturers, with the ability to meet responsible environmental demands.

Legend

1. Development: BASF in co-operation with the University of Cologne, Germany (working group headed by Prof. R. Strey).
2. Product: Eusapon® OD by BASF