



The replacement of nonylphenol ethoxylates (NPEs) as degreasing agents in wet blue manufacture

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Alkylphenols (APs) are chemical compounds¹ used mainly to manufacture alkylphenol ethoxylates (APEs); APEs are primarily used in cleaning agents or as surfactants. APEs have been used for more than 50 years and are important to a number of industrial processes. This includes pulp and paper, textiles, coatings, agricultural pesticides, lube oils, fuels, metals, plastics, and leather. These industrial applications comprise 55% of the total APE market. Other uses are mostly in industrial, institutional, and household cleaning products.

The chemistry of nonylphenol ethoxylates

Nonylphenol (NP) is the most commercially prevalent member of the alkyl phenol family (*Panel 1*), accounting for approximately 85% of the total. NP is rarely used "as is." Rather, it is further reacted to produce nonylphenol ethoxylates and other less significant NP-based products. Due to their combined attributes of high performance and cost-effectiveness, NP derivatives have emerged as the preferred surfactant in numerous industrial processes and products, including leather.

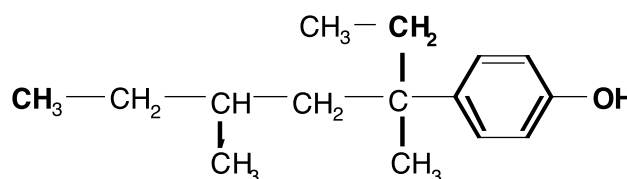
Nonylphenol ethoxylates (NPEs) are produced by the base catalysed reaction of para-nonylphenol with ethylene oxide. Lintelmann et al.² report that technical p-nonylphenol contains 22 isomers. The compounds formed with ethylene oxide are polymers with repeating 2-yloethoxyl units (*Panel 2*). The ethoxylation reaction yields an array of chain lengths, further increasing the number of isomers present in a single product.

The NPEs produced in commerce have numerous different CAS numbers, indicative of the branching of the nonyl group and its position on the phenol ring. These CAS numbers do not account for the degree of ethoxylation, though.

While it is reasonable to assume that manufacturers of NPEs use essentially the same starting materials and synthesis route, commercially available NPEs will have different properties due to differences in ethoxylation. These properties are related mostly to distribution of molecules with varying numbers of repeating 2-yloethoxyl units.

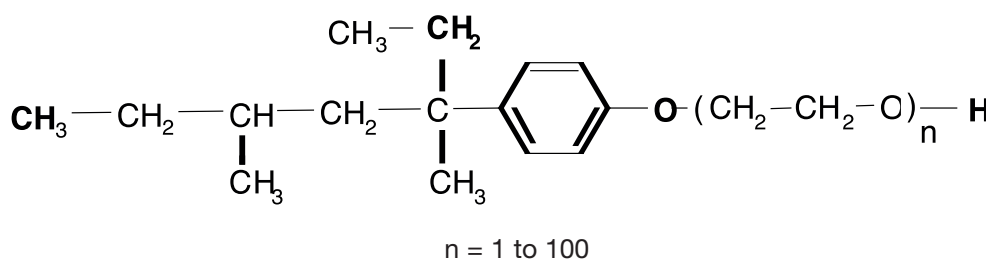
In NPE, the alkylphenol portion of the molecule contributes a

Panel 1: Nonylphenol



measure of hydrophobicity to the compound and accounts for its ability to extract fat from the hide matrix. The p-substituted long chain of ethylene oxide units imparts a hydrophilic character to the other end of the NPE molecule, assuring emulsifying activity. As the chain length is increased, so is the hydrophilic nature of the molecule and its emulsifying potential.

Panel 2: Nonylphenol Ethoxylate



Environmental and regulatory issues surrounding NPEs

The degradation of APEs in the environment has been well documented. Their degradation pathways include an intermediate decay to alkylphenol, creating some unique toxicity questions.

As APEs degrade, they shed ethoxylate units until the original alkylphenol precursor is revealed. The relative toxicity increases as this ethoxylate chain degrades. At the same time, as the ethoxylate chain gets shorter, the hydrophobicity of the molecule and the tendency toward bioaccumulation increase. ➤

About Buckman:

Buckman Laboratories is a long standing manufacturer and supplier of non-NPE surfactants to the global leather industry. The company has distributed five million pounds of non-NPEs over the past decade.



THE REPLACEMENT OF NPES AS DEGREASING AGENTS IN WET BLUE MANUFACTURE

There is significant evidence cited by various regulators that NPEs (and more specifically, their degradation products) are endocrine disruptors. The International Union of Pure and Applied Chemistry³ cite numerous references for their conclusion that the toxic metabolites of NPEs, including nonylphenol, produce an estrogenic response in a variety of aquatic organisms, resulting in a change in their sexual nature. More recently, Acevedo et al.⁴ reported that mice administered 4-nonylphenol had a higher breast cancer incidence and metastasis, and decreased latency than both controls and those administered estradiol (predominant estrogen).

The European Integrated Pollution Prevention and Control Bureau has labelled the phenolic degradation metabolites of NPEs as endocrine disruptors⁵ and highly toxic for aquatic environments. Consequently, the European Union has severely restricted the marketing and use of NPEs⁶ effective January 2005.

In the United States, The Environmental Protection Agency (USEPA) has proposed (69FR340) acute and chronic freshwater Water Quality Criterion for NP of 27.9 µg/l and 5.9 µg/l, respectively. USEPA expects to finalise standards in 2005.

Unlike the EU—as related by Hankey et. al.⁷ and Mihaich⁸—the USEPA's risk assessment concludes that the concentrations of both nonylphenol ethoxylate and nonylphenol are very low in the environment and do not exceed safe levels. Thus, the United States government has no existing or pending regulatory restrictions on the manufacture, processing or use of NPs and NPEs.

Whether the United States will ultimately adopt restrictions similar to the EU is still up for discussion. Individual States retain the right to adopt water quality standards that are more restrictive than the Federal criteria. However, regardless of the ongoing debate in the USA, the EU limitations are effectively limiting the use of NP and NPEs, especially for products destined for international commerce. This regulatory backdrop has paved the way for advancement of alternative chemistries for the past ten to fifteen years, as it will continue to in the future.

NPEs application in leather manufacture

In leather degreasing, the objective is to extract the natural oil and grease from the hide and into the surrounding float. One useful tool in measuring the suitability of a surfactant for this purpose is hydrophilic-lipophylic balance, or HLB. According to the IULTCS Glossary of Leather Terms, HLB is the "Relative simultaneous attraction of an emulsifier for two phases of an emulsion system. For example: Water and oil."

The widely referenced HLB scale⁹ runs from zero to 20. At the low end of the scale, surfactants have greater attraction for fatty matter and tend to stabilise water-in-oil emulsions. At the high end of the scale, surfactants are more hydrophilic in nature and tend to stabilise oil-in-water emulsions¹⁰.

Several leather researchers and specialty chemical manufacturers have independently determined that the optimum hydrophilic-lipophylic balance for leather degreasers is between 12 and 14. Within this optimum range, leather surfactants have moderate affinity for natural fat and grease, and have very good wetting and emulsifying properties. This makes them suitable for leather making.

For many years, NPEs have been the workhorse aqueous degreasers of the leather industry. This is due to their excellent balance of properties, including attraction for fats, wetting ability, emulsifying ability, and low cost.

The 8-mole and 9.5-mole nonylphenol ethoxylates with corresponding hydrophilic-lipophylic balances of 12.4 and 13.1 are effective leather degreasers¹¹. Their relatively high HLBs predict that each possess a comparatively high affinity for water, and thus a corresponding tendency toward forming stable oil-in-water emulsions. This pronounced ability to form stable emulsions is a significant attribute of these products.

Alternatives to NPEs

Alternative chemistries are available based on alkyl alcohol ethoxylates. These have excellent wetting properties and perform admirably in degreasing high-fat hides from feed-lot raised cattle.

Like the alkylphenol ethoxylates, these alcohol ethoxylates can be made from a wide range of alkyl alcohols, and with varying degrees of ethoxylation. The alkyl groups can be branched, but more commonly are straight-chained leading to the nomenclature of linear alcohol ethoxylates, or LAEs. As with their NPE counterparts, LAEs exhibit a wide range of attraction to fatty substances, wetting ability, and emulsification potential.

The LAEs offer an improved environmental profile over NPEs. For example, LAEs are far less likely than NPEs to blind fish gills and interfere with oxygen transfer. In addition, the relative biodegradability of LAEs is significantly greater than that exhibited by the more common NPEs, as indicated by the reduction in BOD and COD presented in *Panel 3*.

Panel 3: Comparative biodegradability of a LAE and a typical NPE

Time for biodegrade	NPE	LAE (Busperse 2094 HLB 12.5)
5-day BOD (g/g)	0.024	0.45
15-day BOD (g/g)	0.086	1.5
30-day BOD (g/g)	0.083	1.9
COD (g/g)	2.2	2.2
% Biodegradation 30 days	4%	86%

Several non-NPE surfactants as proprietary blends of linear alcohol ethoxylates and assists have been used successfully in leather manufacturing for the past 10 years. These products exhibit excellent detergency, wetting, cleaning, and grease removal characteristics, but contrary to their beneficial hydrophilic-lipophylic balance, they create only moderately stable emulsions.

These surfactants are especially useful where a lower level of emulsification is preferred. This may significant when a tannery's wastewater pretreatment and primary treatment facilities are specifically designed for grease flotation and separation, where the emulsion must be easily broken,

LAEs' leather degreasing performance

The relative effectiveness of linear alcohol ethoxylates vs. nonylphenol ethoxylates for leather degreasing have been studied, where the alternate chemistries produce results comparable to or superior to NPEs. Used in conjunction with commercially available lipases, outstanding degreasing is possible. The relative

**Panel 4: Performance of LAE (+/- lipase) for degreasing in comparison with NPE**

Chemistry	Product	Dosage	No. of Lots	% Fat in Wet Blue	% Fat std. dev
Nonylphenol ethoxylate	Comparative Surfactant	0.42%	72	2.0%	+/- 1.4%
Linear alcohol ethoxylate	Busperse 2196	0.55%	340	1.8%	+/- 1.4%
Linear alcohol Ethoxylate + lipase	Busperse 2196 + Buzyne 2103	0.60% 0.25%	93	1.5%	+/- 0.9%
Linear alcohol Ethoxylate + lipase	Busperse 2196 + Buzyne 2103	0.90% 0.25%	238	0.88%	-

Panel 5: Comparison of different categories of degreasing agents

Product	Description	% Fat* (60% moisture)	St. Dev.
Product A (0.2%)	synthetic fatty alcohol ethoxylate	1.3	(0.3)
Product B (0.2%)	nonylphenol ethoxylate	1.5	(0.1)
Product C (0.2%)	fatty alcohol ployglycol ether	2.4	(0.5)
[^] Busperse 2094 (0.2%)	blend of linear alcohol ethoxylates	1.0	(0.3)
[^] Busperse 2196 (0.2%)	blend of linear alcohol ethoxylates	1.4	(0.1)
[†] Busperse 7769 (0.2%)	blend of linear alcohol ethoxylates	0.7	(0.1)
[†] Busperse 7770 (0.2%)	blend of linear alcohol ethoxylates	0.9	(0.1)
[†] Busperse 7770 (0.1%)	blend of linear alcohol ethoxylates	1.1	(0.1)

[^]Products based on HLB12.5, where the emulsion must be easily broken.

[†]Products based on HLB12.2, that provide strong emulsion stability.

*average of three samples.

effectiveness of the two chemistries over an extended period, based on the same hide source is given in *Panel 4*.

The results show that 0.42% NPE distributed between the soak, lime, and delime reduced the extractable fats in the wet blue to approximately 2%. This value is a norm for US-produced full-thickness wet blue. Some wet blue manufacturers' products are consistently below this level, while many hover at about the 2% mark.

The slightly higher dosage of LAE at 0.55% slightly improves the degreasing, with a reduction in extractable fats to 1.8% on a 60%-moisture basis. As the level of LAE surfactant is increased, and with the incorporation of a stabilised lipase, the fat content of the wet blue is dramatically reduced. Depending on the combination of surfactant and enzyme used, the extractable fats are reduced to 1.5% and 0.88% on the same big packer hides.

The examples given in *Panel 4* were based on HLB values of 12.5. However, recent developments have created surfactants based around linear alcohol ethoxylate technology where the HLB value has been reduced to 12.2, but provide very strong emulsion stability.

The effectiveness of these products compared to commercial products is illustrated in *Panel 5*.

Moving forward: embracing "clean" technologies

The debate continues over whether NP and NPE represent a serious insult to the environment, but there is no longer any doubt about the direction of regulatory control. Increasingly, tanners sourcing wet blue are requiring that it be certified as NPE-free, but a wide range of alternatives now addresses their concerns about substituting NP/NPE technology with more environmentally desirable alternatives. 

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