New Generation Emulsifiers for the Leather Industry

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Abstract

Emulsifiers of different chemical structures are used in many processes of leather making. In the present paper we would like to present on the use of amine oxide based surfactants in various stages of leather manufacturing, like in soaking, degreasing and wool washing. Amine oxide based emulsifiers can be applied over a high pH range, including at cationic conditions. They are free of sulfur compounds, alkoxylates or fatty alcohols, and can be used alone or in combination with other kind of emulsifiers. Also from the point of view of sustainability there are important advantages, what can especially be explained in terms of biodegradability and excellent general efficiency.

Keywords: amine oxide, surfactant, degreasing, wool washing

1. Introduction

Emulsifiers are widely used in different stages of leather manufacturing. Regarding the use of surfactants in different processes of leather making, especially high quantities are used during the production of small skins, for degreasing and in wool washing. In bovine leather, relatively high quantities are used in soaking, but also in other process steps. In Fig. 1, the average usage of emulsifiers in different leather processes is depicted (Canicio and Reetz, 2003)

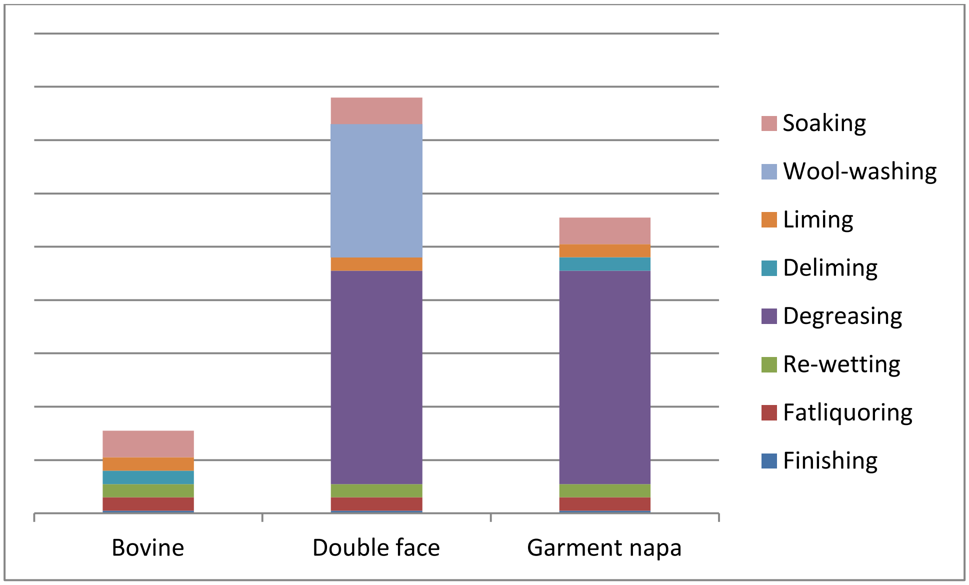

Fig. 1. Usage of surfactants for leather processing, relative amount

In Tab. 1., an overview over the chemical nature of the surfactants used in leather production is given.

Anionics	Non-ionics	Cationics
Sulfonates/Sulfates (sulfated alcohols or alkylethers, sulfosuccinates, ABN, sulfonated esters, secondary alkane sulfonates)	Polyethers (fatty alcohol ethoxylates (FAEO) (Candar, and Eryasa, 2005), propoxylates, mixed alkoxylates)	Alkyl quaternary compounds
Phosphates (alkyl or alkylether phosphates)	Alkylpolyglycosides (APG, (Segura et al., 1997)	Esterified alkyl quaternary compounds (esterquats)
Carboxylates (polymers or soaps)	Fatty acid alkanolamides	Imidazoline derivatives

Tab. 1. Chemical structure used as surfactants for leather

Normally, non-ionic surfactants are used for the emulsion of natural fat or oils used in fatliquoring and also for general cleaning, therefore this class of emulsifiers is especially important in soaking, degreasing, fatliquoring, or for improving the penetration in finishing formulations. Anionic surfactants, on the other hand, play an important role for thorough cleaning of dirt, dung or other non-desired, not purely oily substances. Consequently, anionic surfactants play an important role in formulations for wool-washing or soaking. Furthermore, there are special anionic surfactants, which display very high efficiency in particular applications, such as the stabilization of dispersion in liming, or the removal of unbound Cr in re-wetting. Cationic emulsifiers, on the other hand, are limited to special applications, such as acid degreasing or as component in top fatliquoring.

The use of amine oxides (AO) in leather making has so far not been reported. These environmentally friendly surfactants, due to their unique properties, have been used since many decades in formulations for personal care, home and industrial care, as well as for textile auxiliaries. The total output of AOs in Western Europe is about 20 kt/year representing less than 0,7% of the total production of surfactants (Cesio, 2011).

AOs are used at active concentrations between 0.1 and 10% in consumer cleaning and personal care products, mostly in conjunction with other surfactants. They function as foam stabilizers, thickeners and emollients, emulsifying and conditioning agents in liquid dishwashing and laundry detergents, liquid hard surface cleaners, with minor uses in personal care products like shampoos or hair conditioners (SIDS, 2007). AOs are insensitive to water hardness, have a stabilizing effect on foam and are especially mild to skin (Kosswig, 2012 and Smith et al., 1991).

At neutral or alkaline conditions, AOs behave as non-ionic surfactants, although with the strong dipole moment on the NO-group they may also be seen as a Zwitter-ionic. At acidic pH-conditions, on the other hand, AOs are protonated thus representing a transition to cationic emulsifiers.

In the current study we would like to show the results of our investigations regarding the use of AO based surfactants in the various stages of leather processing. Apart from demonstrating their good performance, we would also like to discuss the use of AO for leather from a more global perspective of overall sustainability.

2. Experimental

Leather trials have been made using AOs alone and together with other co-emulsifiers. Always, for the sake of comparison, reference surfactants of wide industrial importance have been used. Basic information on the trials done are compiled in Tab. 2

Table 2. Leather trials with AOs, overview

	reference	co-emulsifier	bath pH
Soaking	anionic	anionic, non-ionic	8…9
Liming	anionic	anionic, non-ionic	9..12
Acid degreasing	non-ionic, pseudo-cationic	-	3…4
Degreasing	non-ionic	non-ionic	6.5...7.0
Wool washing	anionic, non-ionic	anionic	6…7

For soaking/liming trials the following basic recipe has been followed:

Raw material: salted Turkish bovine leather

	%		ºC	min	pH/comment
Pre-soak	150	water	25		
	0.5	Garmin CTH			
	0.2	sodium carbonate			
	0.2 a.m.	beamhouse surfactant		10' run, 60' rest	
		drain, wash			
Main soak	100	water	25		
	0.2	Perdol 802			
	0.2 a.m.	beamhouse surfactant			
	0.05	Garmin CTH		o/n 5' run, 50' rest	9.0…9.5
Liming	80	water	28		
	0.7	Perdol 816		30'	
	0.2 a.m.	beamhouse surfactant		30'	
	0.7	lime		30'	
	1	Na-hydrogen sulfite			
	0.8	Na-sulfite		60' run, 60' rest	
	1	lime			
	0.8	Na-sulfite		60' run, 60' rest	
	1.3	lime			
	0.4	Na-sulfite		o/n 5' run, 60' rest	

deliming, pickle and tanning according to standard recipe

For degreasing trials, the following recipe was used:
Raw material: pickled sheep skin, pH = 1,8, % based on pickled weight

			ºC	min	pH/ comment
Depickling	100	water	30		
	2.5-4	PELLUPUR MP3 drain, wash, flesh, weigh		2*20+30	5-5,5
Degreasing	3.5 a.m.	Degreasing agent	38	90	
Degreasing	10 a.m.	Degreasing agent	38	90	
	50.0	water	38	30	
	+50	water	38	30	
	+100	water	38	30	
		drain, wash			

Pickle and tanning according to standard recipe

Trials with acid degreasing were done as follows:
Raw material: pickled Turkish sheep skin, pH = 1,8, % based on pickled weight

	%		ºC	min	pH /comment
Presoak	1:20	Water	25		
	0.5	Peramit ML/N			
	0.5	Garmin CTH		10' run, 120' rest	
		drain			
Main soak	1:20	Su	25		
	1	Peramit ML/N			
	0.5	Garmin CTH		20, o/n 5'/60'	
		drain, wash			
		shearing, fleshing			
Degreasing	1:7	Water	39		
	2 a.m.	Degreasing agent			
	1	Peramit ML/N		30	

Bating and pickle according to standard recipe

Wool washing trial were done using a simple recipe as follows:

Raw material: pickled Turkish sheep skin, pH = 1,8, % based on pickled weight

Pre-soak	1:20	water	25		
	0.35 a.m.	Surfactant			
	0.5	Garmin CTH		10	60' rest
		drain			
Main soak	1:20	water	25		
	1	Perdol SCC			
	0.35 a.m.	Surfactant			
	0.5	Foryl FRC			
	0.5	Garmin CTH		60	o/n turn 5'/55'
		drain, wash			
		Shearing, fleshing			control wool whiteness

The AO component used in this trials is a commercial product of Pulcra Chemicals having a chain-lengths of C12-18.

3. Results and discussion

3.1. Trials in Soaking and Liming

When used as soaking agent, an AO based beamhouse surfactant shows a similar water-uptake, softness and cleanness as a standard anionic soaking agent (ASA) widely used in tanneries. Importantly, after liming, where the same AO based agent has been used, the pelts are cleaner and have less hair roots. In wet-blue the leathers treated with the AO based beamhouse surfactant show a better openness, i.e., less wrinkles, and again less hair-roots. In Fig. 1, the more flat leather structure with the use of AO based surfactant is seen. Thus, it is clear that AOs help to get a more balanced soaking, with sufficient opening what is a ideal preparation for further process steps.

Table 3: Results in Soaking. Scores 1(bad)-10(excellent)

Soaking agent	% weight gain	Cleanness	Softness	Hair roots	Openness
ASA	34	9	9	7	6
AO	35	8	8	8	8

Figure 1. wet-blue with soaking using ASA (left side) and AO (right side)

3.2. Trials in Degreasing

Degreasing trials were performed on skins of various origin, using AOs vs. a FAEO based degreasing agents. In Tab. 4, results of trials with English domestic and Turkish pickled skins are presented. Relative effectiveness was calculated as: η = % residual Extract Ref. (FAEO) / % residual Extract AO where values > 1 mean that AO is more efficient than the reference product. Both degreasing agents were applied using the same active matter.

The results in Tab. 4 indicate, that the degreasing efficiency of AO based degreasing agents is similar to the efficiency of FAEO based degreasing agents. Notably, the FAEO tested is a very efficient degreasing agent which is widely introduced in the tannery industries. Similar results were also obtained under similar trial conditions, with skins of various origins, and using different reference degreasing agent.

Table 4. Results degreasing trials

	Prod.	% residual extract			η – rel. efficiency		
		neck	back	tail	Neck	back	tail
English domestic	FAEO	10.6	5.2	12.4			
	AO	6.7	4.6	10.3	1.6	1.1	1.2
	FAEO	5.0	6.5	5.3			
	AO	5.8	4.7	4.2	0.9	1.4	1.3
	FAEO	3.3	3.2	6.2			
	AO	2.8	3.5	8.3	1.2	0.9	0.7
	FAEO	9.0	6.9	4.1			
	AO	10.3	10.2	4.8	0.9	0.7	0.9
	FAEO	5.6	4.2	4.1			
	AO	2.4	4.0	5.7	2.3	1.1	0.7
	Avg				1.4	1.0	1.0
Turkish	FAEO	4.1	4.5	5.4			
	AO	4.3	5.9	5.6	1.0	0.8	1.0
	FAEO	3.3	3.3	2.8			
	AO	5.3	5.1	4.9	0.6	0.6	0.6
	FAEO	3.1	2.4	3.5			
	AO	4.7	1.5	5.1	0.7	1.6	0.7
	FAEO	5.1	1.6	2.8			
	AO	6.1	1.4	2.1	0.8	1.1	1.3
	Avg				0.9	1.0	0.9

Furthermore, the possible synergistic effects of AOs with non-ionic degreasing agents was investigated in various leather trials. In some trials, pronounced synergistic effect have been found. However, at this stage it is too early to give a quantification the results obtained.

When tested in acid degreasing, AOs showed similar results as pseudo-cationic (CDA) and again as a FAEO based non-ionic degreasing agents. It has to be pointed out that with the pKa value of ca. 4.1 for a C12.6 average chain length AO (Kirk Othmer, 2001), at the pH of acid degreasing (pH 3-4) at least 80% of the N-atoms are in cationized form. This is surely the reason why AO can work well in cationic degreasing.

Table 5. Results of trials of acid degreasing

	% residual extract			□ - rel. efficiency		
	neck	back	tail	neck	back	tail
CDA	2,8	3,2	4,5			
AO	4,8	4,6	3,5	0,6	0,7	1,3
FAEO	3,6	3,1	2,8			
AO	4,5	4,2	2,7	0,8	0,7	1,0

3.3. Trials in wool-washing

As a preliminary trial for checking the possible efficiency of AOs we checked the emulsion of a wool grease sample we had extracted from Turkish sheep wool. In this trial, AO was compared with three different anionic wool washing agents, which are normally applied for wool washing for sheep. The test was done with the same a.m. of surfactant, using 1g a.m. of surfactant per g of wool grease. As clearly seen in the picture below, which was taken after 24h, the AO sample was superior in emulsion efficiency as compared with the other tree products.

Figure 2. Emulsion tests with three anionic wool washing agents (S1-S3) vs. sample of AO (new)

In a next step, we tested a AO based wool washing agent. Making a full leather washing trial on Australian salted skins, we found that with the AO containing wool washing agent the wool is whiter, more open, and less greasy. Interestingly, the touch of the wool gets significantly softer, a fact which is also known from the use of AOs as conditioners in hair care. This can be probably explained in term of the pseudo-cationic nature and bonds which are created between the AOs and the anionic surface of the keratin thus partially covering the keratin by AO molecules.

Figure 3. Wool washing trial with AO containing wool washing agent (left) vs. traditional wool washing agent.

4. Sustainability consideration

Regarding sustainability, it should be mentioned first that ca. 80% of the AOs produced in the EU are based on renewable, oleochemical resources (Patel, 2003). This is a relatively high ratio, for ethoxylated alcohols it oscillates at around 60%, for alkyl ether sulfates at 70%. Thus, from the raw material usage point of view, AOs do show a high degree of sustainability.

As far as the environmental impact is concerned, AOs do exhibit a very good bio-degradability (García et al, 2007). This is illustrated in Tab. 6, where typical results for the OECD 301b test of various types of emulsifiers potentially important for leather formulations are compiled. In the mentioned test method, ultimate biodegradation is assessed by the release of CO2 during 28d of biological degradation. A degradation of over 60% is referred to as easy biodegradable.

Table 6. Typical results for OECD301b for emulsifiers used in leather products (Sanderson et al, 2009)

	% degradation
Fatty alcohol C12-14 2eo sulfated	99
Fatty alcohol C16-18 sulfated	91
AO C12-18	89
Fatty alcohol C16-18 14eo	86
Phosphor ester C10-12 2eo	83
Phosphor ester C8-10	79
Alcansulfonate C13-18 sec.	73
Lineal alkylbenzen sulfonate	65
Sulfosucciante C16-18	62
Nonylphenol 9eo	7

In ecotoxicity studies AOs show a moderate performance. Normally, LC50 values ranging between 1 and 10 are reported, depending on the species and the chain length of the AO (Sanderson et al, 2009). This figures would be comparable with cationic structures, like esterquats, but lower than with, e.g., many ethoxylated alcohols.

Finally, AOs are reported to be very mild to skin (Kosswig, 2012). This makes them interesting for formulation of care products, but surely is not an disadvantage when used for leather chemicals.

Very important is surely also cost. It has to be pointed out that the cost of AOs is in line with other high-end emulsifiers. The advantages in application do justify the use of this sophisticated chemistry for high-quality leather articles.

5. Conclusion

AOs can bring significant advantages in various process steps in leather application. When used in soaking and liming, cleaner leathers with less wrinkles may be obtained. In degreasing, thorough and secure degreasing is obtained under different application conditions. In wool-washing, AOs bring about excellent wool whiteness and cleanness, together with softer wool. Furthermore, AOs show a good bio-degradability and are surely an interesting topic for further investigations.

6. Literature

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