EXTENDED SURFACTANTS FOR LEATHER

I.Reetz [1,a] and A. Kilikli[1]

1 Pulcra Chemicals GmbH, Isardamm 79-83, D-82538 Geretsried, Germany

a)Corresponding author: Ivo.Reetz@pulcrachem.com

Abstract. Surfactants of different ionic nature are used in virtually all steps of leather production. In processes like soaking, degreasing and wool washing, tremendous amounts of surfactants are applied and to a great extent discharged into the tannery effluent. In order to improve the sustainability of leather processing, there is a constant search for more efficient, environmentally friendly emulsifiers, which give superior results already in smaller usage amounts. By introduction of propylene oxide based lipophilic linkers between the hydrophilic head and hydrophobic tail, the wetting and emulsion capability of a surfactant can be increased significantly. The resulting surfactants, so called extended surfactants have an extended tail, which reaches further into the oil phase without scarifying the water solubility, what would be the results when increasing the alkyl chain. Thus, the use of lipophilic linker changes the emulsion on a structural level. Extended surfactants have been found to be superior in various applications, including textile laundry or tertiary oil recovery. In the present work, the efficiency of various types of non-ionic and anionic extended surfactants is demonstrated in various stages of leather processing. Model surfactants with lipophilic extensions are compared to their analogues without extension. In many processes, significantly improved surfactant efficiencies are found making this group of molecules an interesting topic for further exploitation.

1. Introduction

Surfactants are widely used in different stages of leather manufacturing. Notably, 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 relative usage of emulsifiers in different leather processes is depicted. [1]

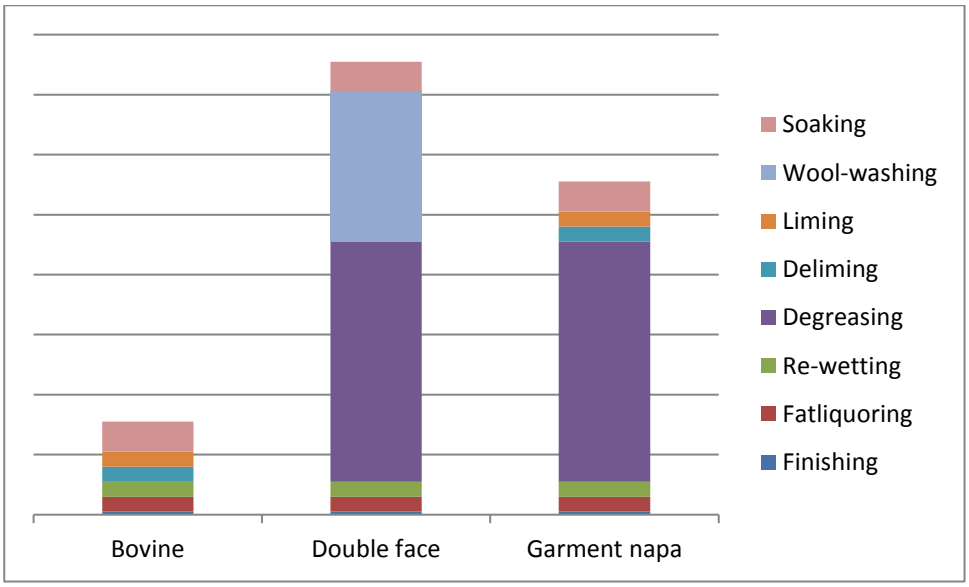


Fig. 1. Usage of surfactants for leather processing, relative amount

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

Table 1. Chemical structure used as surfactants for leather.

Anionics	Non-ionics	Cationics
Sulfonates/Sulfates (sulfated alcohols or alkylethers, sulfosuccinates, ABN, sulfonated esters, secondary alkane sulfonates)	Polyethers (fatty alcohol ethoxylates (FAEO) [2] , propoxylates, mixed alkoxylates	Alkyl quaternary compounds
Phosphates (alkyl or alkylether phosphates)	Alkylpolyglycosides (APG) [3]	Esterified alkyl quaternary compounds (esterquats)
Carboxylates (polymers or soaps)	Aminoxides [4], Betains [5]	Imidazoline derivatives

Non-ionic surfactants are normally used for the emulsion of natural fat or of fatty components in fatliquoring. Thus, 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. Cationic emulsifiers, on the other hand, are limited to special applications, such as acid degreasing or as component in top fatliquoring.

Extended surfactants contain a lipophilic linker unit in the surfactant molecule, which is positioned between the polar head and the non-polar tail group[6]. As a linker, propylene-oxide blocks are used. By many researchers and in different applications it was found that extended surfactants perform extremely well in the preparation of microemulsions, being the most successful surfactants for achieving ultralow interfacial tensions [7,8,9]. This fact is explained by their unique chemical structure. On one hand, the intermediate PO block gives a gradual change of polarity, what changes or smoothens the structure of the micelles[10]. On the other hand, the hydrophobic tail is made longer what increases the interaction of the surfactant tail with the oil phase and subsequently the structure in the latter. The use of PO blocks as lipophilic extension has a big additional advantage – the introduction of PO units renders the long hydrophobic chain, which is normally based on a long-chain alcohol, more liquid. Normally, emulsifiers based on alcohols with chains longer than C18-20 are not accessible since they are solid, have lower solubility and detergency. By propoxylation longer carbon chains can be made liquid, and the propoxylated block itself further increases the length of the surfactant molecule.

The use of extended surfactants, which can be of any charge, has never been described in applications for leather. In this work, extended surfactants are compared with their analogues without extension, adjusting the chain length of the hydrophobic tail in order to have similar HLB values. This gives a more direct information on the effect of the lipophilic extension in application.

2. Experimental

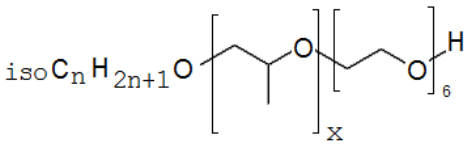
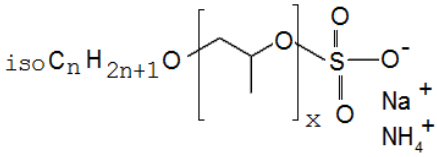
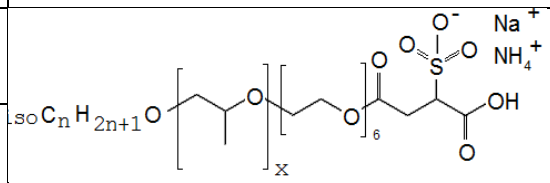
The surfactant samples used in this work have been synthesized starting from the respective iso-alcohols of ExxonMobil Chemical (Exxal 10, Exxal 11 and Exxal 13). Three types of surfactants with no (0), short (X) and long (XX) extensions have been synthesized and tested:

1. Nonionic surfactant based on ethoxylation: E0, EX and EXX

2. Anionic surfactant based on sulfation: A0, AX, AXX
3. Mixed non-ionic / anionic surfactant based on sulfosuccinate: M0, MX, MXX.

Details of the surfactants used depicted in the table below

Table 2. Samples of surfactants tested.
(*) Calculated molecular weight of surfactant (w/o) cation (**) HLB according to Davies[11]

Sample name	Chemical Structure	n	x	M_W(*)	HLB(**)	Basic Parameters
E0		13	0	460	2.8	OHV=128mgKOH/g, conc. 95%, pH(10%)7.4
EX		11	4	668	3.2	OHV=98mgKOH/g, conc. 95%, pH(10%)7.5
EXX		10	6	770	3.3	OHV= 88mgKOH/g, conc. 95%, pH(10%)7.5
A0		13	0	277	39.5	%SO3=6.0, conc. 32%, pH(10%)7.7
AX		11	4	484	39.9	%SO3=4.0, conc. 32.6%, pH(10%)7.8
AXX		10	6	586	40.1	%SO3=3.6, conc. 31.8%, pH(10%)8.2
M0		13	0	638	n.a.	%SO3=3.0, conc. 30.8%, pH(10%) 6.2
MX		11	4	846	n.a.	%SO3=2.0, conc. 30.7%, pH(10%) 5.6
MXX		10	6	948	n.a.	%SO3=2.0, conc. 30.9%, pH(10%) 5.7

Alkoxylation was done following the general alkoxylation procedure. Sulfation was carried out by reaction with amidosulfonic acid with further neutralization by NaOH 50%. In the case of the sulfosuccinate, reaction conditions of the reaction with maleic anhydride were chosen in order to give the hemiester (typical conversion 70-80%). Sulfitation was done with sodium disulfite solution 33%.

The wetting power of the samples was determined by EN 1772:2000, using solutions of 0.1% a.m. and standard cotton pieces. For a wetting test on leather, a drop test was used on standard hydrophobic leather, with 0.1% of a.m. solutions, monitoring the time to the full disappearance of the drop. Surface tension was measured according to DIN 53914:1997 using KRÜSS Tensiometer K11. Critical micelle concentration (CMC) was determined by plotting the results of surface tension = log(concentration), with the critical micelle concentration being the point of intersection of the two linear graphs.

Emulsion testing was done using 1g of animal triglyceride pre-emulsified with a given amount of surfactant. The mixture was placed in a cowles stirring unit adding 2ml of water during 2 min. Then, while stirring, 100ml of water were added slowly. The emulsions were checked after certain period of time. As an additional characterization, the particle size of the emulsions was measured using a Mastersizer Hydro

2000SM of Malvern Instruments. For this measurement, the emulsions were diluted in order to obtain results within the accessible zone for the intensity measurement of the scattered light, with all samples of one group being adjusted to exactly the same concentration. For degreasing trials, the following recipe was used: Raw material: pickled English domestic sheep skin, % based on pickled weight + 30%

	%		ºC	min	comment
De-pickling	100	water	30		
	10	salt		10	Bé >6
	2.0	sodium formate		20	
	2.0	surfactant			
	1.0	sodium bicarbonate		90	pH 4.6
		drain			take sample (#1)
Degreasing	100	water	35		
	2.0	surfactant		45	
	100	water	35	60	pH 5.0
		drain			take sample (#2)
Degreasing	100	water	30		
	0.2	surfactant		15	
		drain, repeat (2x)			take sample (#3 and 4)
		wash, pickle, Cr-tanning			

The degreasing trials were repeated totally 3 times and average values have been used for the calculation. Fat content was determined according to EN ISO 4048:2008. Soaking was tested using a dry salted Turkish bovine hide with the following general recipe (% based on salted weight).

	g/l		ºC	min	comment
Pre-soak	200	water	27		
	0.2	bactericide		60	
		drain			
Main soak	100	water	27		
	1	surfactant			
	0.3	bactericide		480	overnight turn 5min/h
		drain			

Wool washing trials were done using the following recipe: Raw material: pickled Australian sheep skin, % based on pickled weight

	g/l		ºC	min	comment
1st washing	1:10	water	30		
	1.0	surfactant			
		bactericide		60	60min rest
		drain, wash, centrifuge			evaluation #1
2nd washing	1:10	water	25		
	2.0	surfactant		30	overnight turn 5min/h
		drain, wash, fleshing			evaluation #2
3rd washing	1:10	water	37		
	3.0	surfactant		30	rest 30min, run 30min
		drain			evaluation #3

The sheep skins were assessed after each washing step. Also, the hair was cut and the fat content was determined. For the fatliquoring trials, the following recipe was used: Raw material: South German bull wet-blue, 1.4mm.

	%		ºC	min	comment
Washing	200	water	35	10	
		drain			
Rechroming	100	water	45		
	3.0	chrome sulfate 33% basic.		60	
	0.5	CORATYL® G			
		drain, wash			
Neutralization	100	water	35		
	2.0	sodium formate			
	0.5	sodium bicarbonate		60	pH 5.0
		drain, wash			
Fatliquoring	150	water	50		
	8	fatliquor		60	
	2	formic acid 75%		30	
	2	formic acid 75%		30	pH 3.4
		drain, wash, horse-up, vacuum			

The organoleptic properties were assessed in a scale 1(poor)-5(excellent). Furthermore, yellowness index was measured according to ASTM E313 after aging. Tear resistance of the leathers was determined according to DIN53.328 (IUP6).

3. Results and discussion

3.1 Simulation trials

Results of simulation trials carried out with the surfactant samples are displayed below.

Table 3. Results of determinations of surfactant properties.

	Surface tension 0.1% a.m.	CMC	Wetting power	Drop test
substrate	**solution**	**solution**	**cotton**	**hydrophobic crust**
conc. a.m.	**0.1%**		**0.1%**	**0.1%**
unit	**mN/m**	**mg/l**	**sec**	**min**
E0	28	40	17	5
EX	29	100	13	3
EXX	30	200	14	4
A0	33	100	31	77
AX	32	~180	16	23
AXX	31	~200	14	30
M0	28	200	82	51
MX	30	~500	68	37
MXX	31	700	64	39

Regarding surface tension, there is a general trend for a slightly increased surface tension with introducing the extension. Since the concentration used, 1g active matter/l, is in all cases above CMC, it is believed that this is simply due to the higher molecular weight by introduction of the extension. The critical micelle concentration itself is increasing, both when calculated on weight and molar base. This is normally explained by the fact that the extension is occupying some space on the interphase of the micelles, and for that reason the surfactant molecules are not packed as dense as without a spacer group.

As far as wetting power is concerned, the trend is very clear that the extension is helping to have a faster wetting of the standard cotton cloth, i.e., surfactant properties in the practical test are actually improved when introducing an extension. Also in the drop test on hydrophobic leather a much faster wetting was found. In fact, in both the wetting trials on cotton and the hydrophobic leather it was found that the difference in introduction of the lipophilic extension is much more significant than the fact whether it was a short or longer extension.

Furthermore, as an additional simulation, emulsion tests were run with different triglycerides from animal sources, using the nonionic surfactants E0, EX and EXX. The idea of these tests was that the stability of emulsions with the very fat of a skin may give conclusions on the performance of the very emulsifier in degreasing of this particular skin (Candar et al., 2005).

In many emulsion trials which had been done with freshly extracted sheep skin fat, it was found that the stability of the emulsions with the three surfactants tested is in fact not very different. In many trials, it was found that the longer extension EXX works better than the shorter extension EX. However, in many cases, the product without extension gives even more stable emulsions.

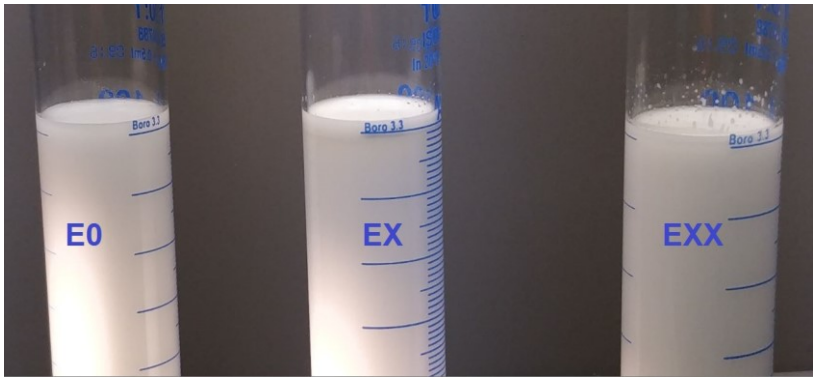


Fig. 2. Emulsion test with 0.5g surfactant /100ml

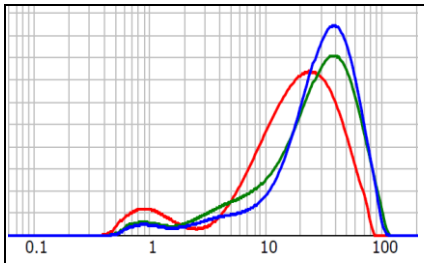
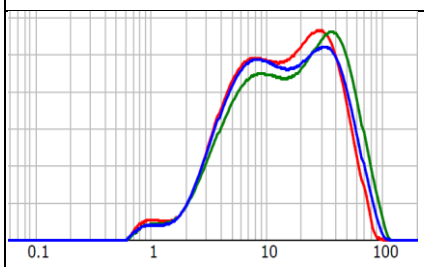
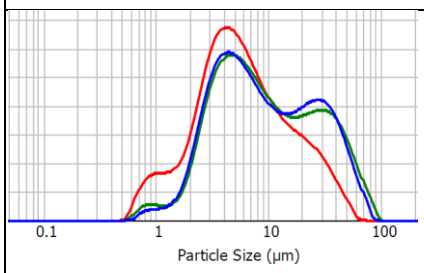
	C_{surf}=0.004 g/l, C_{surf}:C_{TGL} = 1:10
	C_{surf}=0.008 g/l, C_{surf}:C_{TGL} = 2.5:10
	C_{surf}=0.012 g/l, C_{surf}:C_{TGL} = 5:10

Fig. 3. Particle size measurement with system surfactant-triglyceride using **E0**, **EX** and **EXX**.

A similar behavior was also found when measuring the particle size of the emulsions. With the surfactant without extension, E0, the emulsion was found to be of smaller particle size. In this case, the concentrations used were far below the respective CMC of the surfactants. It can clearly be seen that with the Emulsifier E0, at the highest concentration a close to unimodal distribution is achieved at about 4µm average particle size. For the emulsion with the extended surfactant, there is still a pronounced portion of higher particle size of 30 µm. Again, the surfactant with the longer extension, EXX, gives better emulsions than the emulsifier EX with shorter extension, the maximum of the respective particle size curve being shifted slightly towards lower particle size.

Thus, in the different simulation trials in fact a very complex picture is found. General surfactant properties, like CMC or the stability and particle size of emulsions are not improved with the extension. On the other hand, in wetting trials on different substrates, cloth and leather, the extended surfactants behave better than the not-extended analogues.

3.2 Trials in Degreasing

Degreasing trials were performed using the three ethoxylated samples E0, EX and EXX. Notably, nonionic surfactants are the state of the art in degreasing, especially when degreasing is done on raw or pickled hides. In the trial, always halves of pickled skins where compared with each other. The efficiency was calculated as η = % residual fat / % initial fat, with at least three different results per sample. In all comparisons, the efficiency for the extended surfactant was found to be superior to the conventional surfactant. Furthermore, with the increase of extension, the efficiency improves.

Table 4. Result of degreasing efficiency, in %, and standard deviation.

Surfactant	η_{AVG}	DEV
E0	76	9
EX	82	6
EXX	86	8

3.3 Trials in soaking

Soaking was tried on a relatively dry and dirty salted bovine hide using the mixed nonionic/anionic emulsifiers M0, MX and MXX. Sulfosuccinates are a type of surfactants which are successfully used in many commercial soaking agents. It turned out that with the extended surfactant better cleanness of the skins on hair and flesh side was achieved with both types of extensions, in comparison with the skin, which was soaked using the surfactant without extension, M0. In fact, it was evaluated that the difference between the results with the two extended surfactants is minor in comparison with the difference to M0. This is demonstrated in the pictures below:

	Soaking with M0
	Soaking with MX
	Soaking with MXX

Fig. 4. Results of soaking with extended surfactants

3.4 Trials in wool-washing

Wool washing was tested with the sulfated samples A0, AX and AXX. For washing, often anionic surfactants are used, sometimes also in combination with non-ionic emulsifiers. In order to see the direct influence of the extension we decided to test the purely anionic types. As a reference, a commercially very successful wool washing agent of our portfolio was used. Chemically, this reference product is also based on an anionic surfactant, and further contains environmentally friendly alkyl polyglycosides, which, apart from improving the eco-balance of the product are known to act synergistically in cleaning and degreasing operations (Segura et al., 1997).

As seen in the tables and Fig. underneath, the efficiency in wool washing is significantly improved with the introduction of the lipophilic extension, as compared with the same chain type without lipophilic extension. With the longer extension, the results are even better than with the commercial wool washing agent.

Table 5. Evaluation of results wool washing after washing steps #1-3

#	Parameter	Reference	A0	AX	AXX
1	Whiteness	3	2	2,5	4
	Cleanness	3	3	3	3
	Openness	3	2	3	4
	Touch	3	2	3,5	4
2	Whiteness	3	2,5	2,5	4
	Cleanness	3	3	3	3
	Openness	3	2	2	4
	Touch	3	2	2	4
3	Whiteness	3	3	2,5	3,5
	Cleanness	3	3	3	3
	Openness	3	2	2,5	3,5
	Touch	3	2	2,5	4
	Total score	100	79	89	122

Tab. 6. Results of Determination of fat content of hair after step #3

	Reference	A0	AX	AXX
Fat content hair (#3)	3,9%	6,0%	1,8%	1,5%

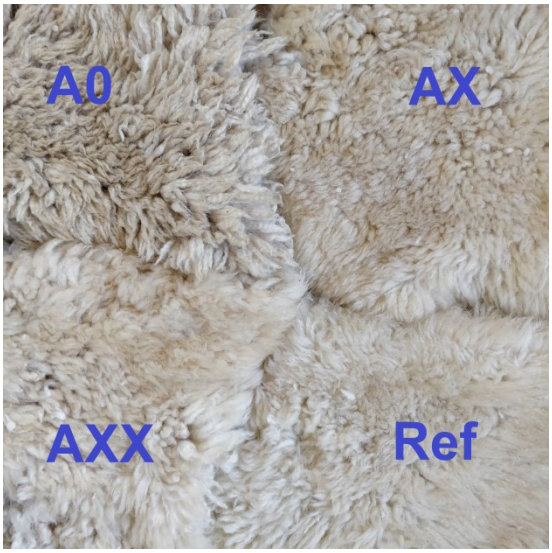


Fig. 5. Result wool washing after step #3

3.5 Trials in Fatliquoring

For fatliquoring, a very simple trial scheme was applied. To a sulfited fish oil of 90% a.m., 10% of a.m. of surfactant was added and the mixture was adjusted to a product concentration of 80%. The trial was done with the anionic/nonionic surfactants M0, MX and MXX, since this type of surfactants would be the most likely to be used in product formulations of state-of-the-art fatliquors. As a result, softness and tear resistance were found to be improved, when an extension was introduced, with the optimum being the shorter extension. The better softness is seen as an indicator for a better penetration of the fatliquor. Also, the improvement in tear resistance is interpreted in terms of a more homogeneous distribution of the fatliquor within the cross-section of the leather. The yellowing after thermal aging was measured as an additional simple means to follow the penetration of the fatliquor – the part of the fatliquor which is penetrated does not give yellowing on the surface. In this trial, too, it turned out that yellowing is reduced by the extension, i.e., the sulfited oil presumably penetrates better with the extended surfactants. Notably, the fish oil did not contain added antioxidants in order not to interfere with the results.

Table7. Results in fatliquoring with the use of extended surfactant.

Surfactant	Softness, score	YI (144h/100ºC)	Tear resistance N/mm
M0	3.0	29.5	55
MX	4.5	26.8	59
MXX	4.0	27.1	57

4. Conclusion

The virtue of extended surfactants was demonstrated using model substances with similar HLB's. In basic trials of surfactant properties, the extension did in many cases give similar or even slightly inferior results: emulsions were generally less stable and of higher particle size and the CMC values

measured where higher. On the other hand, when used in different applications for leather, all model substances with the extension actually behaved better than the homologues without extension. In degreasing and wool-washing, the longer extension was clearly found to work better than the short extension. In the trial regarding fatliquoring, the shorter extension was found to work better. Also in soaking the extended surfactants worked very well. Thus, the use of extensions in different types of surfactants gives an important improvement in efficiency in leather application, making it possible to test lower usage amounts and to improve the quality of the finished leather article.

An interesting further advantage of extended surfactants is the possibility to make use of longer carbon chain molecules creating surfactants which are otherwise not accessible due to their low solubility.

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