ZINC LAURYL ETHER SULPHATE, A NEW APPROACH TO SKIN CARE

Abstract

Combining skin cleansing with skin care is one main aim in modern cosmetics. The most common surfactant, sodium lauryl ether sulphate, has frequently been used in combination with anti-irritant agents in order to reduce its lipid-solvent effects. Magnesium or alkanolamine salt of the same surfactant have been claimed to perform detersion with lower irritation. A new ‘colloidal precipitation’ surfactant, formed by hydro-soluble zinc alkyl ether sulphate, shows very low irritation potential both alone and in combination with other tensioactives. Moreover, it has additional properties, bound to its capability to inhibit bacterial growth: it strongly reduces body odour without the use of common bactericides. Evaluations of its main cosmetic properties are described, together with the significant formulation requirements.

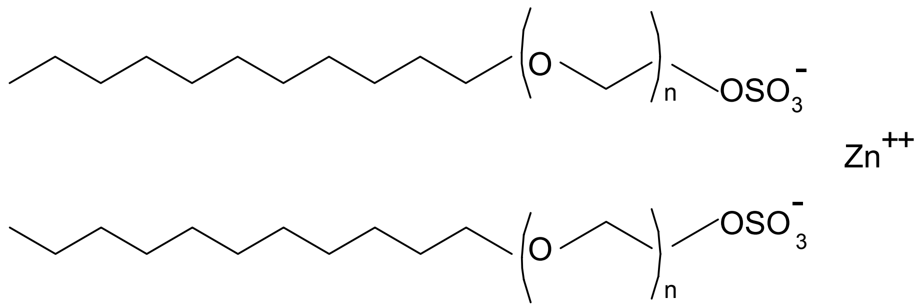
Introduction

In famous movies of the 30’, the leading actor, a young man, at the end of his working day grooms for the ”big encounter” by a series of hygiene procedures. Plenty of water and soap shower, mainly on the armpits. Cleansing operation probably followed by some more, aimed to improve the “deodorised” state, with long-lasting products, such as perfumed talc or eau de Cologne. Indeed, ‘true’ deodorants appear only in the sixties. They were presented in several cosmetic forms, modelled according to the specific site of use: a limited area, shaved or hairy, occluded, rich of sebaceous and sweat glands, warm, scarcely visible but able to send to the environment acute odorous messages, streamed by water vapour. Stick or roll-on, atomised liquids or aerosol, quick-drying creams, aimed to control bacterial proliferation and mask the capric-caprylic notes of sweat, deteriorated by oxidation. Since ever, the long-lasting deodorant action was clearly distinct from the previous cleansing action, effective but short-lasting. The appearance of acid aluminium salts, in the early seventies, added the sweat reduction effects to the action of antibacterial agents and perfumes. Their safety level is still today in a hot phase. All the weapons of deodoration were directed against bacteria or excessive sweating, with all the auto-prejudicial risks of scarcely refined instruments. Moreover, they have the evident contradiction of applying odour-fighting substances in the very moment of the least need, i.e. after washing, when body odour is very low. On the contrary, their effect fades progressively, while more needed. With the additional risks of using somehow aggressive substances, easily absorbed in skin sites with shunts for trans-dermal delivery. The deodorant cleansing, performed by antibacterial soaps or perfumed shower gels, has till now been considered little efficient on the long-term. Able, on the contrary, to increase the cutaneous intolerance to antibacterial agents and perfumes. Many solutions to tolerability problems in deodoration have been proposed: enzyme deviators, antioxidants, odour absorber based on organic zinc salts, slow release systems.

‘Compact’ deodoration

How to perform successfully three hygiene actions (cleansing, deodoration, antibacterial) without side effects? A possible answer is given by a new compound, meeting point of well known substances: zinc lauryl ether sulphate.
Its actions? A moderate reduction of sweating, long-lasting hindrance to bacterial action, cleansing at acidic pH, body-odour reduction. Its synthesis? It was enough to neutralize an alkyl ether sulphuric acid with zinc ions. The molecular structure is so represented:

STRUCTURE FORMULA



Zinc Coceth Sulfate
(n=3, mainly C12 alkyl chains)

Its properties are the synergic result of the characteristics of its components: detergency and foaming given by the anionic part, odour fighting, astringency and cutaneous tolerability from the cation and the acidity. Finally, dandruff control performed by the whole molecule.

Experimental Evaluations

The idea to couple a bivalent ion, known as skin beneficial and lenitive, with a classic foaming system is not new (for instance magnesium based actives). On the contrary, the (patented) solution to production problems has been innovative in our case. To evaluate experimentally its in-vivo efficacy has been a source of surprises. Indeed, zinc ions keep soluble in the finished products until diluted in water, during the foaming phase. Once on the skin, the formation of colloidal zinc hydroxide takes place, probably the leading factor of the cosmetic efficacy.
In detail the experimental results:

a) DETERGENT and FOAMING POWER

Similarly to all alkyl ether sulphates, Zinc LES shows good detergent properties. On the other side, its skin compatibility is surprising. A first measure of this parameter is given by the CMC value. Even if does not represent an absolute parameter, the comparison of CMC values among structurally similar surfactants allows to define a scale of potential cutaneous aggression. In our case we have:

$$CMC_{MgLES} \sim CMC_{ZnLES} < CMC_{SLES}$$

with a CMC value of 0.18 g/l for ZnLES. The linear structure of the alkyl chain allows high aggregation number in micelles. The detergent potential of this alkyl ether sulphate is indifferent to water hardness, while pH value has a major importance, for its high influence on Zinc ion solubility. Foaming ability parameter, bound to pleasantness of use, is till today a signal of the efficient depletion of superficial lipids. We have always associated unconsciously foam height to immediate efficacy. Alkyl ether sulphates, provided with high foaming power, soft and creamy foam, with compact, homogeneous and long-lasting structure, are the reference parameter in these cases. Modern formulation strategy is based on blends: we have therefore studied its foam behaviour both alone and in blends with other detergents at the following conditions: Ross.Miles Test : 20°C, water hardness 10 French degrees, 10% total active matters, Zn LES/other actives ratio = 8.5/1.5. Also in this case blends give excellent results (fig.1).

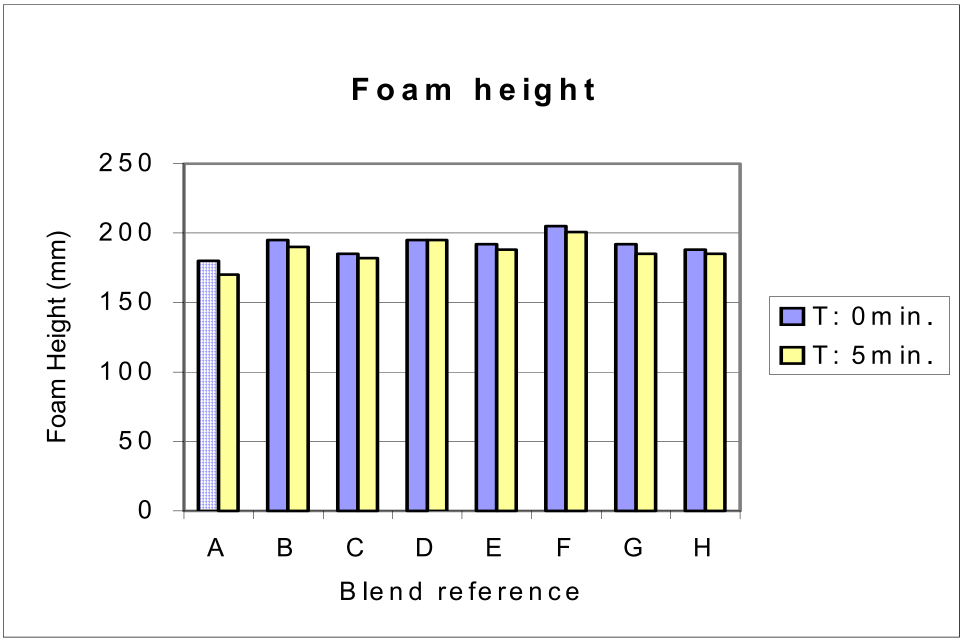


Fig.1

Blend ref.	Tab. 1 **10% Total Active Matters**
A	ZnCS = Zinc Coceth Sulfate
B	ZnCS (8.5% SAL) + Disodium Laureth Sulfosuccinate
C	ZnCS (8.5% SAL) + Disodium Cocoamphodiacetate
D	ZnCS (8.5% SAL) + Lauramidopropyl Betaine
E	ZnCS (8.5% SAL) + Sodium Lauroyl Glutamate
F	ZnCS (8.5% SAL) + Sodium Lauroyl Sarcosinate
G	ZnCS (8.5% SAL) + Sodium Cocoyl Hydrolyzed Wheat Protein
H	ZnCS (8.5% SAL) + Potassium Cocoyl PCA

Additives, such as Sodium Lauroyl Sarcosinate, Sodium Cocoyl Hydrolyzed Wheat Protein and Potassium Cocoyl PCA may be classified as tolerability improvers and foam enhancers. Results have been very encouraging (Fig.2) in blends with Magnesium based tensioactives, that further enhance mildness and skin respect. Blending ZnLES with the Magnesium salt gives a transparent system, even at pH 5.5. The highest foam volume is obtained at a 1/1 ratio.

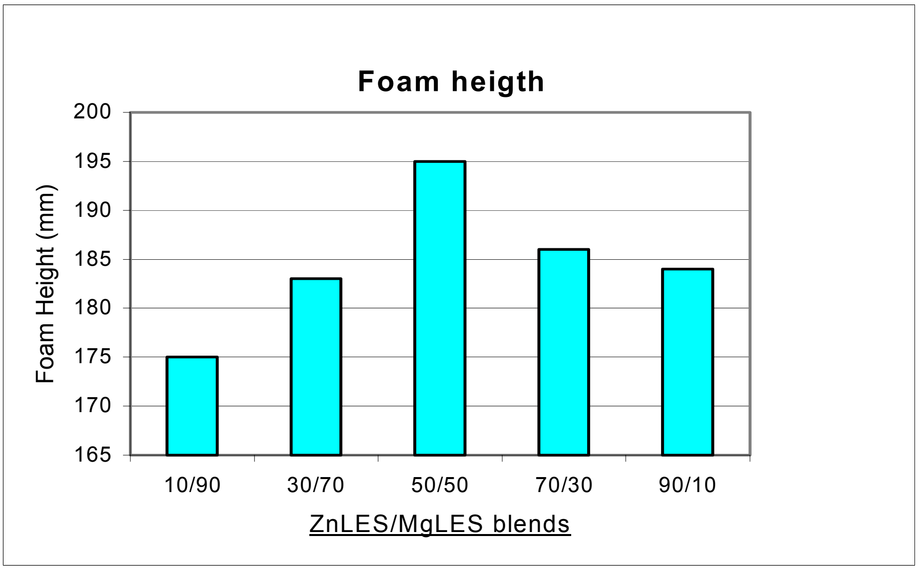


Fig.2

b) ODOUR CONTROL

Which are the main advantages bound to the use of Zn LES in cutaneous detersion? In other terms, which property of lauryl ether sulphates is modified by replacing sodium by zinc ions? The direct consequence of bacteriostatic and astringent power of zinc are illustrated by the experimental evaluation of the deodorant efficacy (Fig. 3) by a “Sniff Test” on 12 volunteers. For one week, before starting the trial, subjects washed their armpits with a non perfumed, bactericide free soap. At the eighth day volunteers used the test products instead of soap. Then, 6 and 24 hours after last application, a group of trained experts sniffed the armpits and gave an intensity score on a scale from 1 to 10. The tested products where:

A) Zinc Coceth Sulfate sol. 25% = 48%
B) Sodium Laureth Sulfate sol. 27% = 44%+ Triclosan (0.5%)
C) Zinc Coceth Sulfate sol. 25% = 44% + Disodium Capryloyl Glutamate sol. 39% = 3%

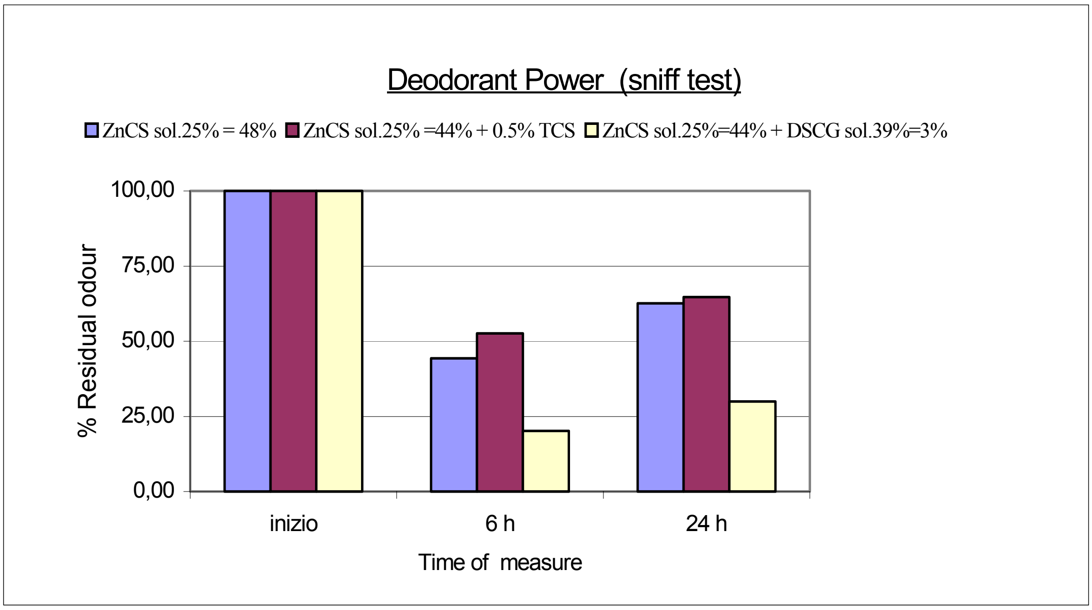


Fig.3

Tab.2

		ODOUR SCORE			Percentage Decrease	
SAMPLE	Times	Initial	6 h after last use	24h after last use	at 6 h	At 24 h
A	Average score	5.4	2.5	3.1	56%	37%
B	Average score	4.8	1.9	2.8	47%	34%
C	Average score	5.0	1.2	1.7	80%	70%

Zinc Coceth Sulfate shows efficient odour control properties. Moreover, its activity is comparable to that of 0.5% Triclosan (1) and further improved by blending with Disodium Capryloyl Glutamate.

Limits of use

90 enzyme or protein complex that are present in our body are regulated by the presence of Zinc. Since decades, Zinc derivatives are used for treating some cutaneous diseases (2) . Therefore, its use may be considered safe within the limits foreseen by the European law. Typical bacterial inhibition properties of Zinc, reported in the literature establish precise limits to soluble Zinc ions in cosmetics (Tab. III). Maximum concentration allowed for Zinc Lauryl ether Sulfate corresponds to 12.5% active matters: a commercial product at 25% concentration may be used up to 50% in a formula.

Tab.3 Zinc derivatives and EEC cosmetic norms		
Material	Reference	Limits
Hydrosoluble Zinc salts except Zinc sulfophenate and Zinc pyrithione	Annex III Part I, n.24	Max. 1% as Zinc
Zinco sulfophenate (or Zinc salt of 4-hydroxybenzensulfonic acid) or Zinc Phenolsulfonate	Annex III Part I, n.25	Max. 6% as anhydrous substance
Zinc Pyrithione	Annex V	Max. 0.5%
Zinc Oxide CI n.77947	Annex IV	
Micronized Zinc Oxide	No restriction	No restriction

c) ASTRINGENT POWER

The astringent and tonic action of Zn LES is the result of complex physico-chemical actions on the skin substrate. As for aluminium salts, sparingly soluble zinc salts are able to coagulate proteic materials and to form a protective layer. This mechanism could partially explain the efficacy in controlling bacterial growth. The use of zinc citrate in tooth-pastes and of zinc oxide in creams and lotions for irritated and abraded skin is based on these actions. As for hydro-soluble salts, no effect is reported. Then, how to explain the outstanding behaviour of the lauryl ether sulphate salt? The most probable phenomena are hydrolysis and carbonation. They may take place over the skin, during dilution with tap water, increased by the continuous reduction of Zinc ions concentration as insoluble hydroxide and carbonate (calamine). Indeed, the superficial activity of precipitated insoluble salts and Zinc oxide may be maximised only by the formation of a colloidal ‘sol’.

d) DANDRUFF CONTROL CAPABILITY

Dandruff, the most common and annoying scalp disease, induced by a disequilibrium of cutaneous homeostasis, is worsened by hyper-proliferation of saprophyte micro-organisms. Zinc Coceth Sulfate showed especially active in its treatment. Results of a comparison between zinc lauryl ether sulphate at 12% active matters and the sodium salt, at the same concentration but added with 0.75% Piroctone Olamine, gave comparable efficacy (3) on 16 subjects.

e) CELL TURN-OVER

Experimentally, alfa hydroxy acids effects on cutaneous renewal are measured by the speed of disappearance of a spot (visible under UV lamp) obtained by treating the skin with a solution of dansyl chloride. The comparison between the fluorescence intensity of the skin in the normally washed site (control area) and in skin treated with 48% Zinc Coceth Sulfate (25% sol.) in presence of 2% alfa-hydroxy acids shows a 28% increase of cell turn-over (p=0,001) (3b). When the same trial is carried out with the simple aqueous 48%solution of Zinc Coceth Sulfate, a 23% increase over the standard takes place (p=0,001) (3a).

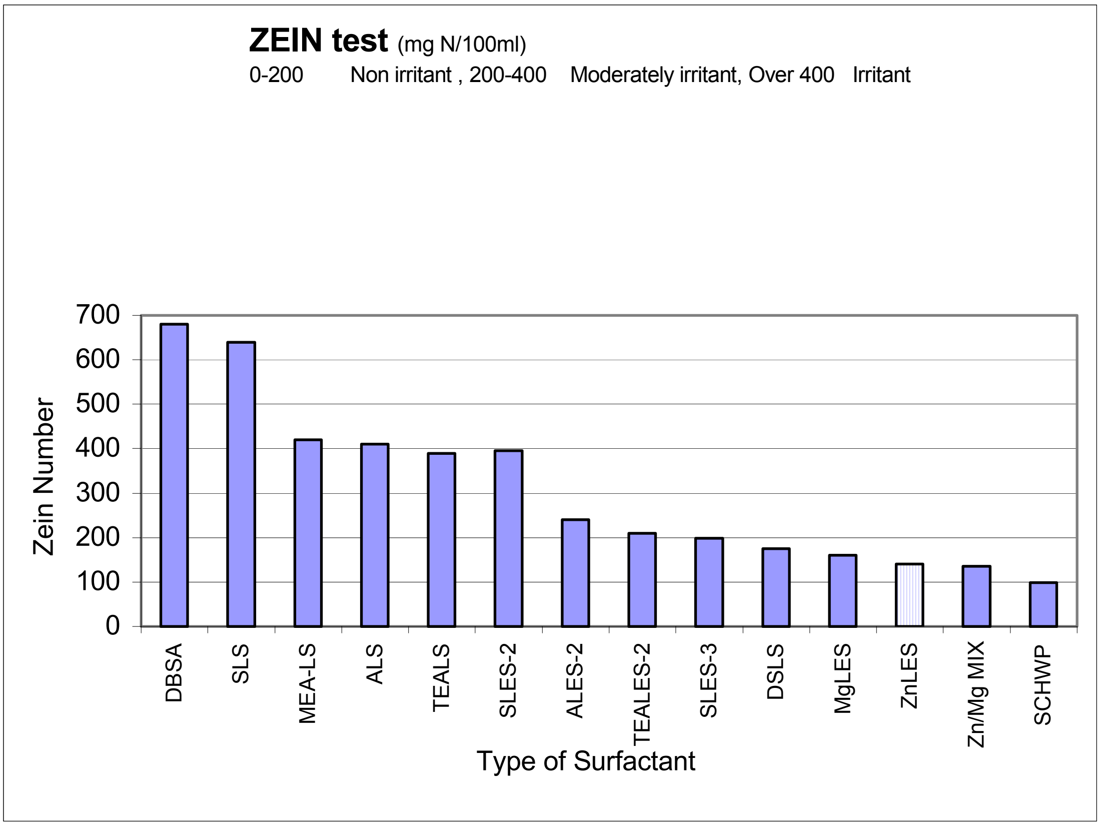
f) DERMAL INNOCUITY

Zinco LES is safe, as per the below described in-vitro and dermatological tests.

f1) Zein Test

Zein, a practically water insoluble cereal protein, when blended with surfactants undergoes a solvation process. A relationship between the irritation potential of a tensioactive and the amount of Zein dissolved in water is frequently demonstrated (4).

Fig.4



DBSA	Dodecylbenzen Sulfonic Ac.	TEALES-2	TEA Laureth-2 Sulfate
SLS	Sodium Lauryl Sulfate	SLES-3	Sodium Laureth-3 Sulfate
MEA-LS	MEA Lauryl Sulfate	DSLS	Disodium Lauryl Sulfosuccinate
ALS	Ammonium Lauryl Sulfate	MgLES	Magnesium Laureth-2 Sulfate
TEALS	TEA Lauryl Sulfate	ZnCS	Zinc Coceth Sulfate
SLES-2	Sodium Laureth-2 Sulfate	Zn/Mg MIX	1/1 Zn Coceth Sulfate/Magnesium Laureth-2 Sulfate
ALES-2	Ammonium Laureth-2 Sulfate	SCHWP	Sodium Cocoyl Hydrol. Wheat Protein

f2) Shelanski and Shelanski Test

Zn LES is void of any irritant and sensitising potential. Severe in-vivo trials have demonstrated this quality: as an example, the Shelanski-Shelanski test, carried out on 25 volunteers aged 18 to 70, with 5% a.m. solutions applied in 7 mm Finn Chambers. Treatment is repeated for four weeks, by applying a patch a week. Finally, a revealing patch evidences the possible outcome of sensitisation. Preliminary patches are maintained on the skin for 48 hours. Treated skin site is examined after 15', 1 h and 24 h from patch removal. The revealing patch is identically examined. Evaluation scores are given to the evidenced oedema and erythema, on the basis of their intensity (5).

f3) Toxicology and biodegradability
Non mutagenic , ZnLES passes the Ames test (6). It is also biodegradable: 83% decomposition in 28 days (7).

Use Details

As surfactant molecule, Zn LES is effective and stable. Some possible drawbacks may rise, concerning appearance and viscosity of finished products, that nevertheless are easily solved.

1) Zinc Precipitation and pH
Solubility of Zinc ion is strictly related to acidity. At pH higher than 5, product appearance turns from transparent to opalescent then to milky, according to Zn LES concentration. Opacity is initially uniform, then slowly (according to product rheology) zinc hydroxide precipitates and settles. Therefore, product pH should be adjusted around 4,5 before adding Zn LES. This value is well tolerated, as healthy skin usually has acidity values between pH 4.6 and 6.0. Product based on Zn LES work as acidity buffer and help maintaining the correct skin pH. Precipitation and consequent clouding are not always negative, if adequately controlled: opaque cream shower-gel at pH 6-7, stabilised by high thixotropy or by the presence of natural polymers (Xanthan gum) may be prepared.

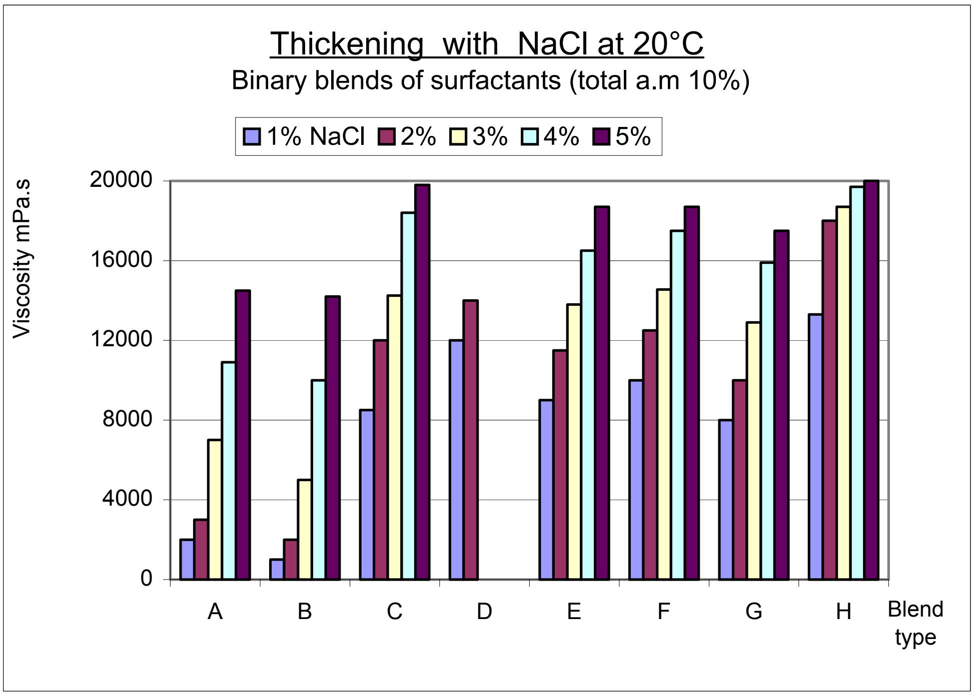


Fig.5

2) Thickening

A Zinc LES-based detergent is easily thickened: as all laurylether sulphates, it is very sensible to salts. As usual, alkylamido betaines increase its viscosity, but their use limit is only 1,5%. Higher amounts induce opacity even at favourable pH. We worked with a low total content of surfactants (10% SAL total) while keeping at 8.5/1.5 the ratio between Zn LES and the other additives. They belong to the category of 'ultramild' detergents (sulphosuccinates, betaines, glycine amphoterics) or to the 'anti-irritants' (interrupted soaps, glutamates, sarcosinates, protein derivatives) (graf.1). Composition of binary blends is reported in tab.1. Thickening behaviour with Potassium Cocoyl PCA (mix H) is very interesting: at 1% NaCl 10.000 mPa.s are reached. Ternary tensioactive blends using Zn LES/Mg LES 1/1 in place of Zn LES alone gave similar results (Fig.6), with the advantage of further increased mildness (ref. Zein Test).

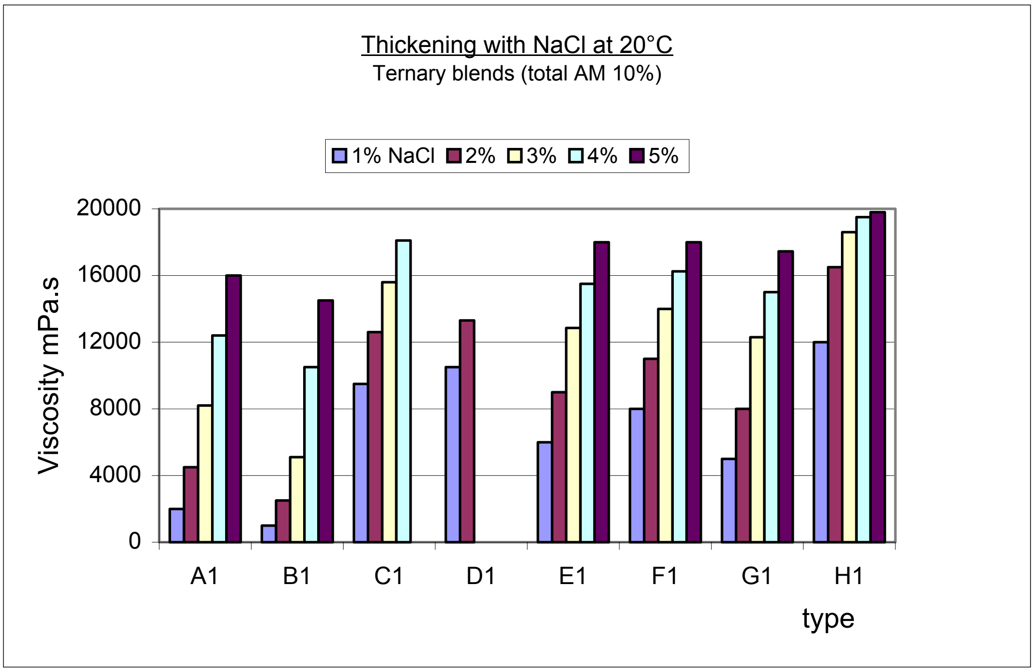


Fig.6

Applications

Possible uses of Zn LES are manifold: from deodorant shower products to anti-dandruff shampoos, from component of syndets at acidic pH to refreshing detergent emulsions (9). A general use is for 'cosmoceuticals' as long-lasting conditioner for irritated skin or for personal hygiene formulae with deodorant effect. Some possible formulae are here described.

Skin compatible detergent

One optimised ternary blends (short PZnZ) containing Zinc Coceth Sulfate, Sodium Laureth Sulfate, Disodium Cocoil Glutamate (DCSG) is described. In a preliminary study on transparency at variable pH, we fixed the total percentage of actives to 23%, while Zn LES was varied between the maximum allowed

concentration (50%) to a lower limit of 16%, laurylether sulfate (at 27%) between 32% and 52%, DSCG (at 39%) between 4.4% and 6.6%.
At pH around 4.5, all these systems are almost clear, while completely clarifying around pH 4. We should keep in mind, beside skin acidic pH, that pH 3.87 is the isoelectric pont of the hair and that by simple tenfold dilution an acidic pH increases of 1 unit. In another series of trials, with Zinc Coceth Sulfate (at 25%) 20% and SLES (at 27%) variable between 35 and 65%, limit pH for clouding was slightly increased (4.3-4.5). On this basis, we developed a multifunctional system, characterised by optimal foaming and high deodorant power in absence of antibacterial agents. Suitable for shower gels, it might be the starting point for the formulation of "medicated" shampoo. The most efficient thickeners for the blend at 40 mPa.s and pH 4.3 are here reported.

Base PZnZ (SAL 19%)

Sodium Laureth Sulfate 27%	48.1
Zinc Coceth Sulfate 25%	16.0
DSCG 39%	4.7

pH adjusted at 4.3, water to 100

VISCOSITY (mPa.s) (thickener %)

Low	Medium	High	**Type**
200 (2%)	6800 (4%)	11600 (6%)	NaCl
//	5600 (3%)	26800 (4%)	PEG-150 Distearate
1200 (3%)	7200 (5%)	//	PEG 120 Methyl Glucose Dioleate
600 (3%)	5200 (4%)	//	Cocamide MEA

The most efficient additive is Sodium Chloride, but also Laureth-3 and Cocamide DEA used in combination show synergic effect. When added at 3% respectively, with pH adjusted to 4,0 - 4,7, viscosity values 9.600 and 14.700 are obtained and clear systems. Some recipes were drawn from this basic blend, that are suitable for problem skin or for body odour control.

Conclusions

The age of functional skin cleansing is still amazing: after various structures of mild surfactants, the use of 'colloidal deposition' cations, opened by this new Zinc surfactant, offers elegant and complex formulation potential, allowing interesting blends and tailor-made cutaneous effects for sensitive skin and for restitution cleansing at low pH.

SHAMPOO for seborrheic skin
(SAL 20.1%) Ref SHG/AG8

BASE PZnZ	93.5
- Cocamide MEA	1.9
- Potassium Cocoyl PCA 38%	3.7
- Perfume	q.s to 100

CHARACTERISTICS

Clear	pH tq 4.4
Viscosity @ 25°C	6800 mPa.s

ACID SHAMPOO for aged skin
(SAL 18.0%) Ref. 12/AG8

BASE PZnZ	90.1
-Sodium Lauroyl Sarcosinate 30%	4.5
-PEG-150 Pentaerytrityl Tetrastearate PEG-6 Caprylic/Capric Glycerides	4.5
- Perfume	q.s to 100

CHARACTERISTICS

Clear	pH tq 4,3
Viscosity @ 25°C	7200 mPa.s

DEODORANT SHOWER GEL
(SAL 21.2%) Ref.13/AG8

BASE PZnZ	91.7
- Cocamide MEA	3.7
- Sodium Cocoyl Hydrolyzed Wheat Protein 28%	3.7
- Perfume	q.s to 100

CHARACTERISTICS

Clear	pH tq 5.1
Viscosity @ 25°C	4600 mPa.s

FOAMING CLEANSER for mycotic skin
(SAL 18.2%) Ref. 14/AG8

BASE PZnZ	92.2
- Potassium Cocoyl PCA 38%	4.5
- Acrylates/Steareth-20 Metacrylate Copolymer	2.4
- Perfume	q.s to 100

CHARACTERISTICS

Clear	pH tq 4.8
Viscosity @ 25°C	3200 mPa.s

Commercial Names – INCI Names

Acrylates/Steareth-20 Metacrylate Copolymer	ACULYN 22
Ammonium Lauryl Sulfate	SULFETAL LA
Cocamide MEA	PURTON CFM
Disodium Capryloyl Glutamate	PROTELAN AG 8 (DSCG 39%)
Disodium Cocoamphodiacetate	AMPHOTENSID GB 2009 SPEZIAL
Disodium Laureth Sulfosuccinate	SETACIN 103 SPEZIAL
Disodium Lauryl Sulfosuccinate	SETACIN F SPEZIAL PASTE
Lauramidopropyl Betaine	AMPHOTENSID B4
Magnesium Laureth Sulfate	ZETESOL MG
PEG-150 Pentaerytrityl Tetrastearate - PEG-6 Caprylic/Capric Glycerides	CROTHIX L
Potassium Cocoyl PCA	PROTELAN NMA/C
Sodium Cocoyl Hydrolized Wheat Protein	PROTELAN VE/K
Sodium Laureth Sulfate	ZETESOL LES 2 A
Sodium Lauroyl Glutamate	PROTELAN AGL 95
Sodium Lauroyl Sarcosinate	PROTELAN LS 9011
TEA-Lauryl Sulfate	SULFETAL LT
Zinc Coceth Sulfate	ZETESOL ZN

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