

Degreasing: Both effective and green!

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Conventional surfactants or surfactant systems for high efficient degreasing often suffer from poor ecotoxicological profiles. Therefore, the most efficient systems for industrial cleaning have to be replaced soon. The more eco-friendly replacements often do not give the expected result regarding environmental and performance criteria. Additionally, the requirements for auxiliary materials will be even more strict. Some of the long-time used auxiliaries are not available for the formulator any more. More surfactants, i.e. higher concentrations have to be used which finally leads to increased material costs.

The end-user will not accept these higher material costs just to obtain the same final cleaning result. The goal is to clean hard surfaces effectively with the minimal effort and according to the legal framework. The optimum would be to get all this also at reduced material costs. In order to meet all requirements, we have to abandon traditional formulation strategies and focus on new materials which are able to provide the required physicochemical properties. Ideally, these new additives should even fulfil future requirements concerning sustainability in order to be successful as cleaning enhancers.

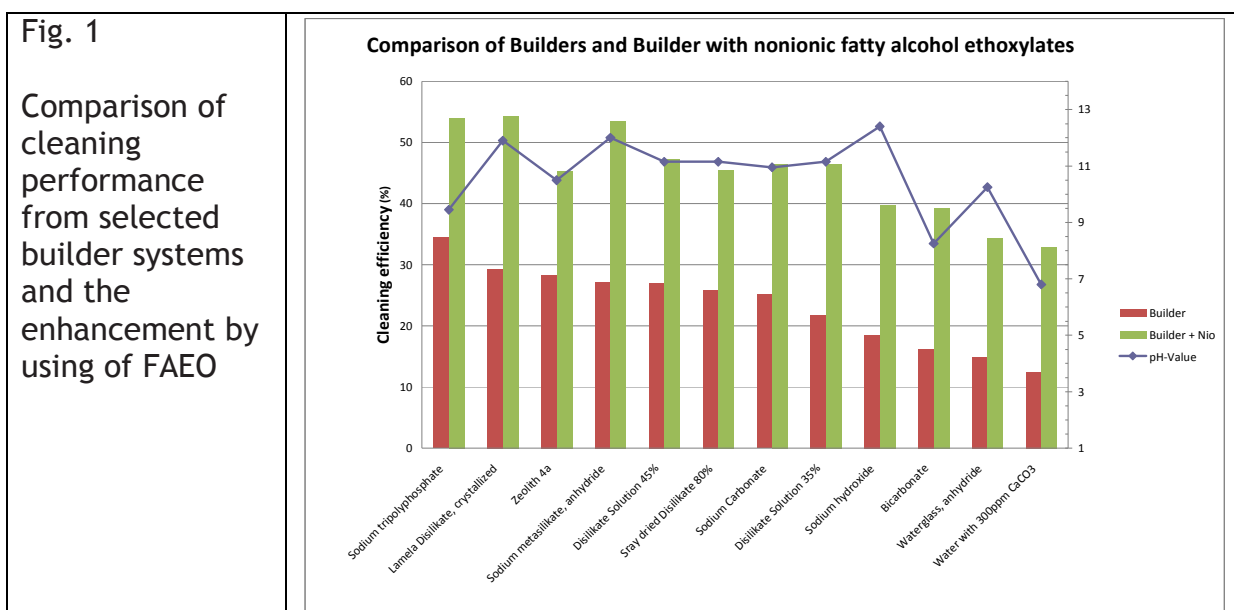
In our paper, details will be presented on how to formulate industrial cleaners effectively using a novel cleaning enhancer. According to our tests, a newly developed sorbitan ester combines excellent cleaning performance with a good ecotoxicological profile and low foam behaviour. The new formulations will be compared with traditional degreasing products in respect of efficiency and ecotoxicological profile.

Introduction

Formulating efficient cleaning systems depends on combining several surfactants. Each have a specialized function, e.g. for penetration, disconnection and transportation of the dirt. Via such street-smart combinations, enhanced surfactant efficiency will create the optimal results. More efficient surfactant formulations provide desired results giving broader possibilities concerning pH values and the builder system.

Typically, degreasing formulations are based on strong emulsifiers supported by a builder system to take off incrustations. If this greasy dirt consists of easily emulsifiable components, no additional boosters are necessary to achieve good cleaning results. Under most practical conditions, the dirt usually contains additional non-soluble materials, like pigments and salts as well as polymerized fats that enclose other particles and minimize the cleaning efficiency. To provide good efficiency also in everyday cleaning challenges, additional actives are needed to boost the performance for heavy cleaning conditions.

For particle-containing dirt, an appropriate builder is needed, which can be supported by a specific pH value if necessary. The cleaning efficiency depends considerably on a proper dispersing capacity. The cleaning performance of some selected builders, with and without a non-ionic surfactant, is summarised in Fig. 1. In this work, eight different contaminations were evaluated [1]. A cleaning efficiency of only 12-35% was achieved when single builders were used separately. By the addition of a simple non-ionic surfactant, a linear fatty alcohol ethoxylate (C12E7), the performance was enhanced up to 55% of cleaning efficiency. This shows nearly a duplication of cleaning performance, but this is still not sufficient. It will be shown that only a properly selected surfactant combination can provide the expected reward for the hard work of cleaning.



Let us first discuss traditional and modern surfactant systems for aqueous degreasers in more detail. The basic surfactant of degreasers is the fatty alcohol ethoxylate as shown in Fig. 1. To enhance speed and efficiency of the cleaning process, ionic or other non-ionic surfactants can support the fatty alcohol ethoxylate. Street-smart surfactant combinations can fill the performance gap for critical conditions.

Anionic surfactants as additives support the disconnection of dirt and enhance the emulsifying power; however, they show higher electrolyte sensitivity and need more mechanical support due to the weak dispersing efficiency as compared to cationics. Since especially industrial degreasers need a high amount of builders, anionic surfactants are not the component of choice.

The cationic surfactants are less affected by high amount of builders. They also support the wetting ability [2] of non-ionic surfactants and were well known as good performers in respect of dispersing and emulsifying [3]. Therefore, they have been used in degreaser formulations up to now. Considering the current legal situation, the most efficient cationic surfactants do not fulfil the requirements of ultimate degradation conditions. The traditionally used PEG-Cocomonium derivatives are not fast enough in biodegradation according to EU regulation EEC 648/2004 and show also some effects on aqueous toxicity. This is caused by the raw material source, the amines respectively the ethoxylated amines. Depending on the concentration used, in the end these cationic boosters cause an unfavourable labelling of the final cleaner.

Surfactants that provide similar performance as the cationic surfactants, but with a better ecological profile, are amphoteric surfactants. They give a comparably good dirt retaining performance as the PEG-Cocomonium derivatives. Amphoteric surfactants lead to excellent results since they exhibit properties of anionic and cationic surfactants depending on the pH value. Short chain amphoteric, especially the amphopropionates, show excellent electrolyte stability and a good solubilising performance for fatty alcohol ethoxylate in high builder containing degreasers [4].

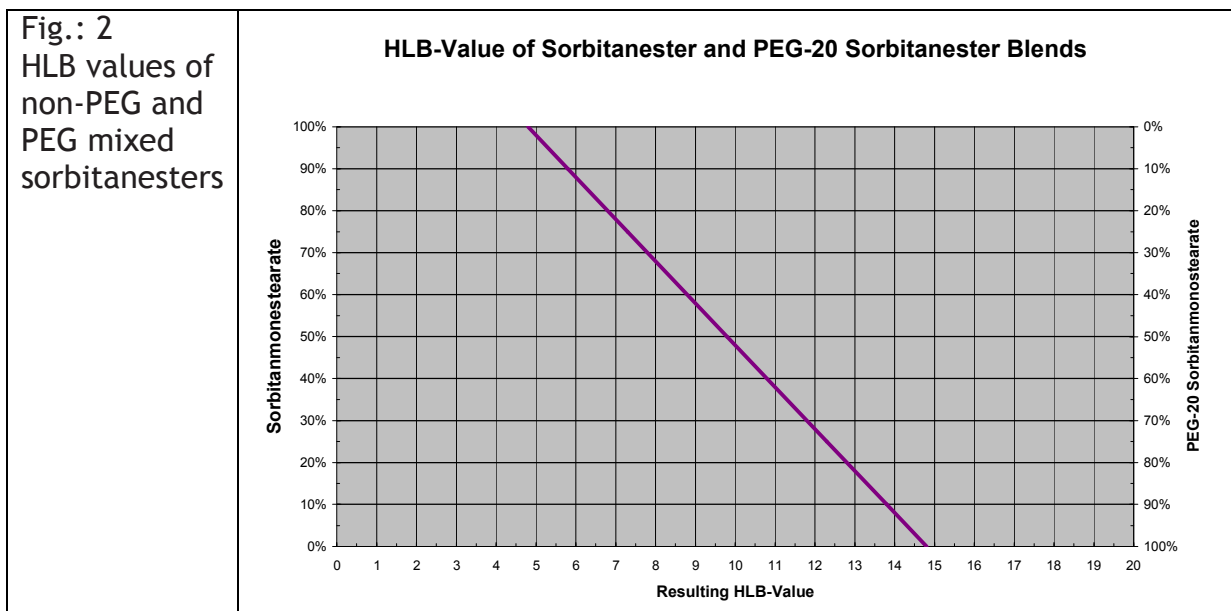
Similar characteristics as the amphoteric belong to the alkylaminoxides, although they belong to the class of non-ionic surfactants. They are chemically more resistant than amphoteric surfactants. Due to some toxicity against algae, their use concentration without additional labelling of the final products is limited. Alkylaminoxides with an alkyl chain length above 12 carbon atoms have to be labelled as the ethoxylated amines mentioned above.

Sugar-based surfactants are also used as cleaning booster for fatty alcohol ethoxylates. In general, they have a better environmental profile compared to amine based surfactants. Three major groups can be distinguished: esters, acetals and amides. The largest and oldest group of sugar surfactants are the esters, first of all the sucrose esters and sorbitan esters were used as mild emulsifiers in industrial applications since 1940. Alkylpolyglucosides (APG) belong to the group of acetals and were used since the 1980s in industrial applications. Very similar to the APGs are the amides, especially the N-alkylglucamides. They were used since the 1990s as mild co-surfactant in household products. [5]

Large quantities of APGs are used in alkaline formulations because of their exceptional electrolyte stability compared to all other available surfactants [6]. This enabled the use of high builder concentrations that can break up incrustations.

As mentioned above, the overall cleaning efficiency of builders is limited, and even the systems containing APGs can not provide the highest efficiency. Combined with FAEO, the performance is already acceptable, but not as good as combinations with cationic surfactants. Finally, the formulator has to decide whether he prefers the ecological or the efficiency approach. Up to date, the efficiency is often preferred over environmental issues.

Sorbitan esters are known for a long time as established and mild emulsifiers. Traditionally, only long chain fatty acids, from mono-laurate up to tri-stearate, were used. Standard sorbitan esters are in general not water-soluble and are often made more hydrophilic via ethoxylation. For the emulsifying work, the hydrophilic and the hydrophobic sorbitan esters are mixed up to the required HLB value and the solubility in various systems can be achieved. As depicted (Fig. 2), the resulting HLB value is a linear function.



This is a well known tool for selection and adjustment of solubility and emulsification properties of organic emulsifiers. The surface activity which is needed for cleaning efficiency can not be predicted or adjusted by blending of two similar structures. In general, the ethoxylated esters with the same alkyl chain length give higher surface tensions than the corresponding esters (Tab. 1). This shows that additional ethoxylation of sorbitan esters makes them more soluble, but not more surface active. Design of higher interface active sorbitan esters is only possible by modification of the structure.

Tab. 1: Comparison of surface tensions of 1% aqueous solutions

Alkyl Chain (Sorbitanmono...)	Sorbitanester [mN/m]	PEG-20 Sorbitanester [mN/m]
Laurate	28	36
Palmitate	36	40
Oleate	30	41
Stearate	46	43

The rather old group of sorbitan esters was just recently rediscovered as ecologically valuable raw materials which makes them more attractive. Recently, a sorbitan ester has been developed which suites the requirements of cleansers [7]. Its first application was the use as efficiency booster in floor cleaners for nanostructured tiles. Here the wetting dynamics could be enhanced noticeably [8]. This sorbitan ester is based on a short alkyl chain length; meanwhile, it is commercially available as TEGOTENS® SD 100. By a comparison of all available sorbitan esters according to their HLB-value and surface tension, it can be seen (Fig. 3) that the most suitable surfactant in respect of cleaning properties should be found at the shorter alkyl chain length.

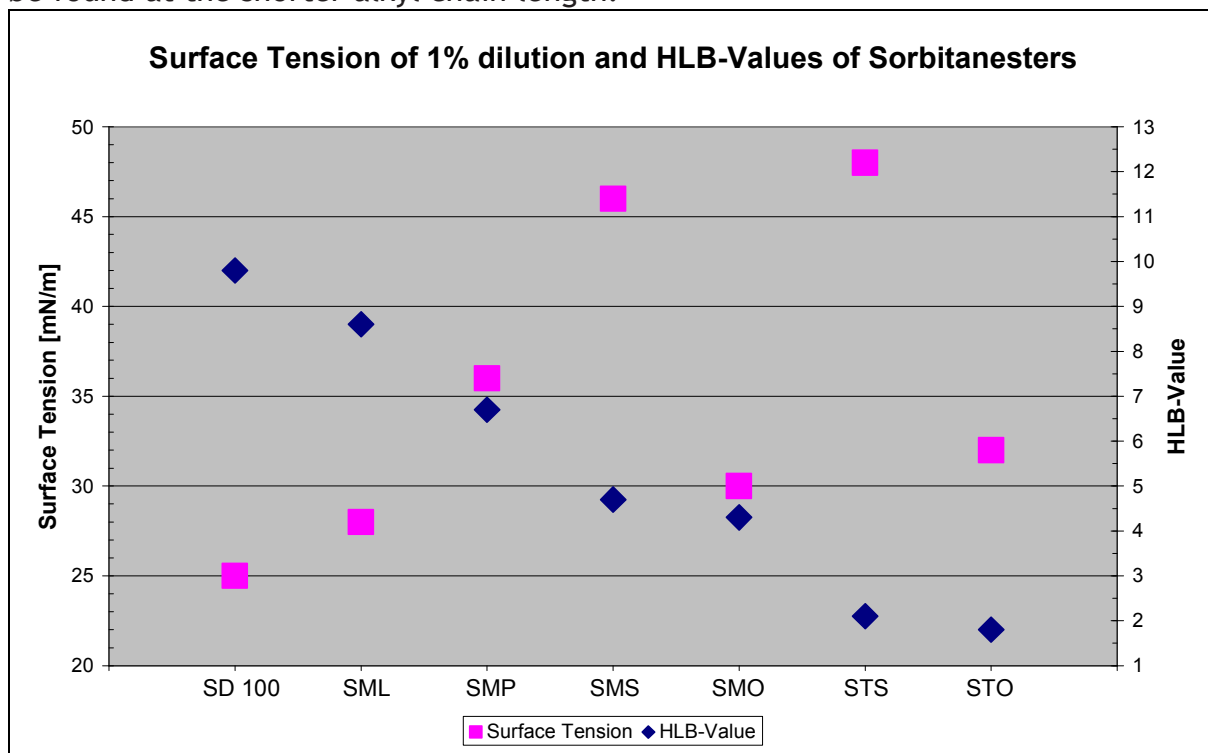


Fig. 3: Surface tension of diff. sorbitan esters plotted ag. HLB value (SML=Sorbitan monolaurate, SMP=Sorbitan monopalmitate, SMS=Sorbitan monostearate, SMO=Sorbitan monooleate, STS=Sorbitan tristearate, STO=Sorbitan trioleate)

Cleaning properties, however, was not the focus of the development in the 1940s, the early years of the original sorbitan esters. At that time, all sorbitan esters with

an alkyl chain below the sorbitan monolaurate (C-12), did not provide enough emulsification power for the major applications. Nowadays, the focus is more technical applications, where ecological alternatives are necessary to fulfil upcoming legal requirements. Furthermore, the industry is looking into renewable resources and alternative manufacturing processes. Additionally, the sorbitan esters can be manufactured not only by chemical synthesis, but also by biocatalytic processes, which are more energy efficient. [9]

A similar scenario we have already observed for the industrial use of APGs. They were also known since 1893 and got their industrial use 90 years later. As mentioned already, their cleaning performance was not sufficient to replace the PEG-Cocomonium derivatives. Therefore, they were not able to replace the traditional surfactants in the last 25 years, in spite of their positive environmental impact and the more and more strict legal requirements. Mainly in industrial applications cost/use performance is the main focus. Successful replacement can only take place when the efficiency of the ecological alternative is more or less on the same level as the traditionally used systems.

Some preliminary work shows that by adding the new sorbitanester derivatives to cleanser formulations, the wetting dynamics on surfaces can be enhanced drastically. Wetting of surfaces, especially microstructured ones, could be enhanced by 30% during a 3-5 seconds contact time [4]. Therefore, the original surfactant system could be improved to fulfil the requirements concerning wetting dynamics of an industrial floor cleanser. Some years before, PEG-Cocomonium derivatives had to be used to achieve similar performance [2]. A direct comparison of the fat-removing capacity of the surfactant system has been carried out. The main reason for combining these additives with fatty alcohol ethoxylates in degreasers are the wetting and the dispersing performance. However, for optimal results, we have developed a specialized version of short-chain sorbitan ester as a modern alternative in order to achieve the performance and at the same time focusing on ecological behaviour of the ingredients.

Verification of surfactant efficiency

The surfactant blend REWOPOL[®] SC 200 is based on fatty alcohol ethoxylate for emulsification of the dirt, and was enhanced by a unique alkaline-stable cocamidopropylbetaine. This CAPB adds good dispersing properties with an acceptable ecotoxicological profile. The performance of the combination of these two workhorse surfactants can be enhanced in respect of dynamic wetting by the new sorbitanesquioctanoate, TEGOTENS[®] SD 100. All three ingredients provide at least a comparable cleaning performance as traditional surfactant blends. As the traditional mixture of PEG-Cocomonium derivative and fatty alcohol ethoxylate (FAEO), this amphoteric/ non-ionic surfactant system can be blended with all kind of surfactants. Even with anionic surfactants, the efficiency is not affected like in

the traditionally used systems. This provides the formulator more freedom of choice concerning the ingredients.

The efficiency of degreasing depends on the individual cleaning conditions and have to be tested in each case. Our approach is more directed towards the surfactant properties to optimize the selection of surfactants, and therefore we minimize the influence of mechanical and temperature conditions. Ideally, only the physicochemical properties of the surfactant mix should influence the result of degreasing efficiency. Temperature and mechanical actions are seen to be only additional to the efficiency of the tested formulation.

Cleaning Method

On a clean stainless steel plate (5x10 cm), five droplets of 50 µl condensed milk, containing 10% fat (12% sugar, 10% C16-18- fat, 8% proteins, 0,5% inorganic salts), were applied and allowed to dry for 24 hours at room temperature (approx. 23°C) until a solid residue is obtained. Considering the available test substances, condensed milk contains most of the critical solids when dried on surface. Therefore, the results depicted here are of practical relevance and can be repeated easily. Each treated plate is added to the ready-to-use dilution of the individual degreaser formulation to be tested. The efficiency can be documented by pictures taken every 10 min. Finally, the plate will be rinsed under a smooth jet of water for 5 seconds.

The time of releasing of the fatty residues is monitored up to 60 minutes. The optical results and the behaviour in the liquid, i.e. whether the residue is emulsified or only disconnected, are monitored additionally by this method. The final results are the appearance of the plate after being rinsed with water and the drying time. The cleaning performance is evaluated by the following wordings:

Table 2

Y: Removal of Droplets					X: Visible Residues of Fat after Rinse				
0%	25%	50%	75%	100%	100%	75%	50%	25%	0%
No	Some	Half	Most	All	All	Some	Partial	Traces	Non

Useful for comparison is the behaviour of water by this method

- No droplets are removed (approx. 10%)
- Fatty residues are all visible (approx. 95%)
- The solution is clear and the disconnected droplets are agglomerated at the bottom

By this comparison, the additional performance of surfactants can be visualized with justifiable effort. Because mechanical influence does not alter the results, the penetration through the degreaseable film can be monitored easily and the

performance of each surfactant formulation can be optimized quickly. Temperature and mechanical performance will be added anyhow under the conditions practical applications.

Efficiency results of surfactant blends

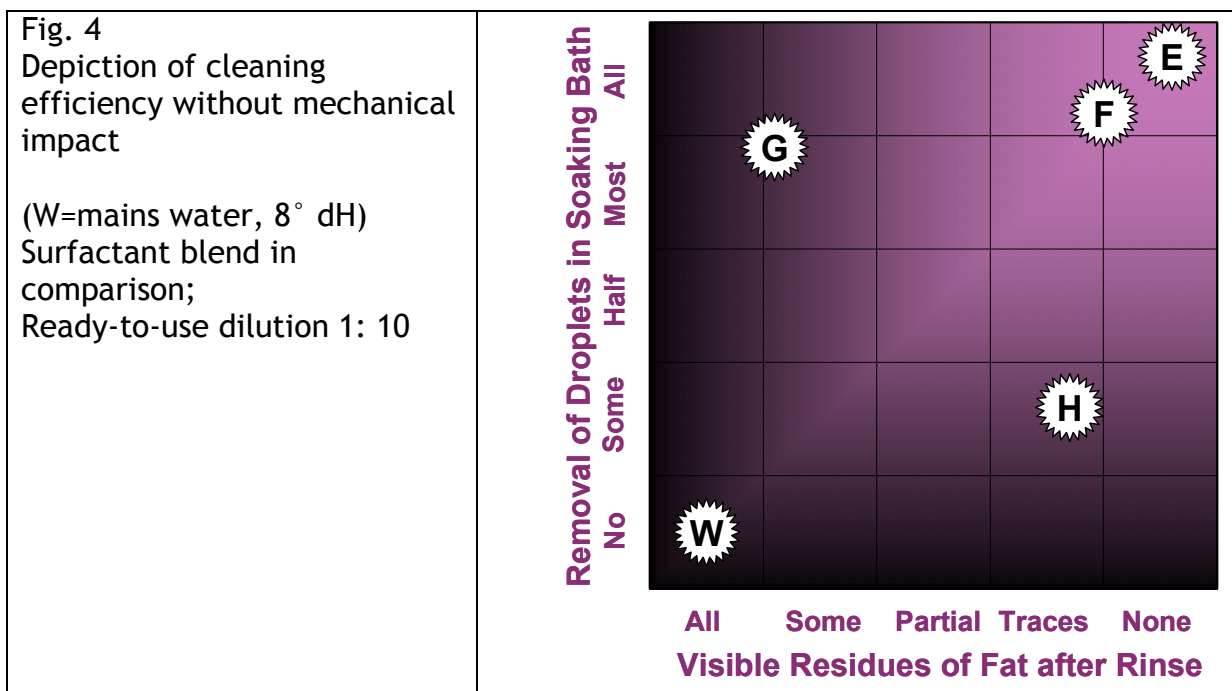
The cleaning efficiency of several model surfactant systems has been tested by using the formulations given in Tab. 3.

Table 3

Test formulations	E	F	G	H	W
REWOPOL® SC 200	6.0				
EO-QAC / FAEO		6.0			
EO-QAC/EO-Amine/ FAEO			6.0		
CAPTM-QAC/BG				6.0	
Water	84.0	84.0	84.0	84.0	100
Tetra potassium pyrophosphate	10.0	10.0	10.0	10.0	

EO-QAC / EO-Amin = PEG-(5-15) Cocomoniumchloride + PEG-(5-15) Cocoamine
 CAPTM-QAC /BG = Cocamidopropyltrimethylammoniumchloride + Butylglycol

For visualizing the results, a diagram is used where the efficiency of various solutions can be easily compared (Fig. 4). It is quite obvious that even REWOPOL® SC 200 has an advantage over various traditionally used dilutable degreasers.



Besides the performance, the good ecotoxicological behaviour is advantageous for the labelling of the formulations. Also the usage of solvents can be minimized by such an optimized surfactant system. The use level of builders can be reduced which also leads to a lower pH value and minimized corrosion behaviour of the cleaners.

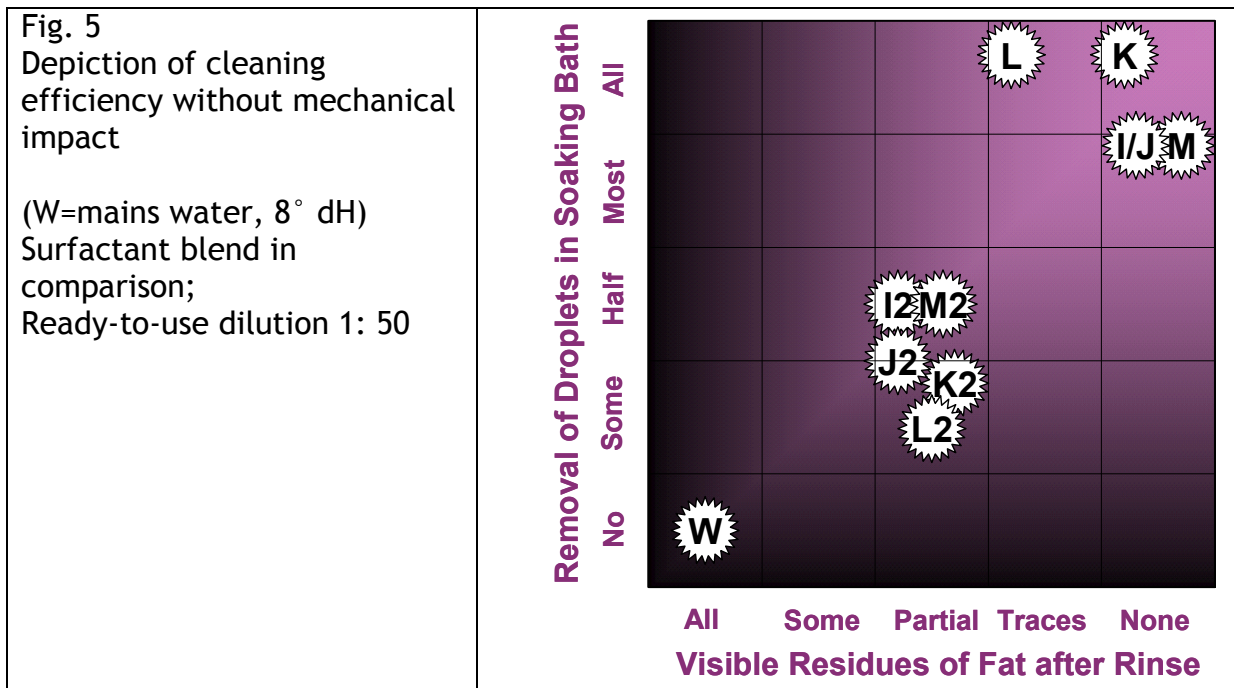
Further test formulations (Tab. 4) were selected to show the influence of builders onto the new sorbitan ester surfactant TEGOTENS® SD 100. The builders were limited to the modern systems, because here the cost/performance relationship is more difficult than in traditional systems.

Table 4

Test formulations (at 6% active surfactant)	I	J	K	L	M	I-2	J-2	K-2	L-2	M-2
TEGOTENS® SD 100	1.0	1.0	1.0	1.0	1.0	-	-	-	-	-
EO-Quat / FAEO			3.4					4.5		
EO-Quat/EO-Amine/ FAEO					2.0					3.0
CAPTM-Quat/BG				3.4					4.5	
REWOTERIC® AM K SF 40	5.0					7.5				
TEGOTENS® G 826		4.0					6.0			
C9-11 Pareth-8	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Methylglycine diacetic acid	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Water	87.0	88.0	88.6	88.6	90.0	85.5	87.0	88.5	88.5	90.0

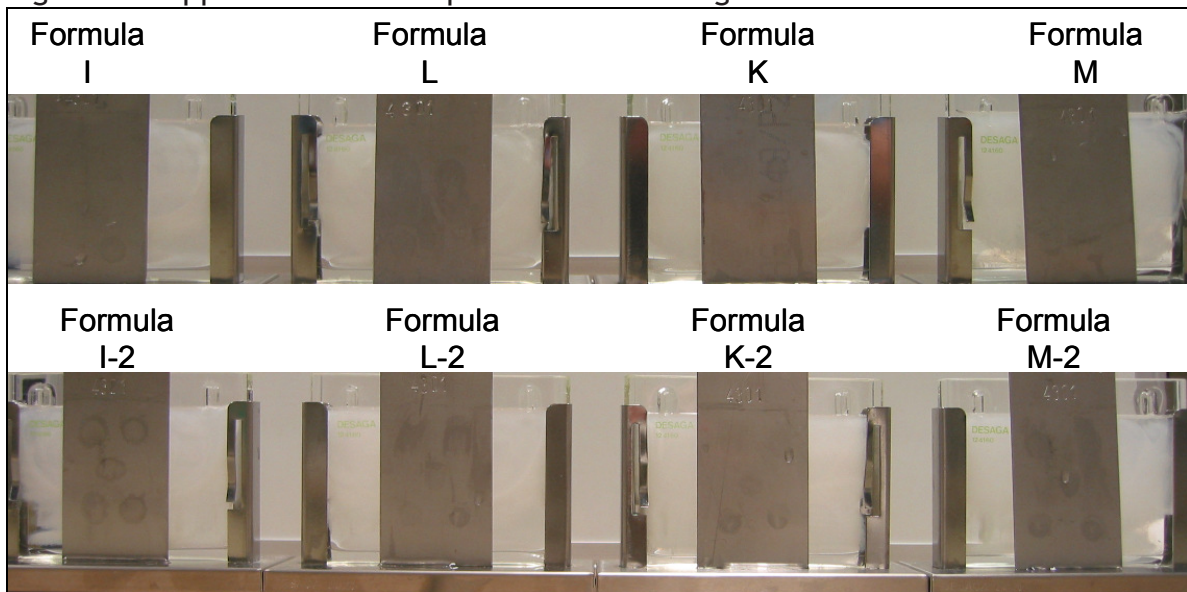
EO-Quat / EO-Amin = PEG-(5-15) Cocomoniumchloride + PEG-(5-15) Cocoamine
 CAPTM-Quat /BG = Cocamidopropyltrimethylammoniumchloride + Butylglycol

In Fig. 5, the boosting effect of TEGOTENS® SD 100 in traditional and modern surfactant systems is also quite obvious. All traditional or modern surfactant blends could be enhanced in cleaning result by adding the new product TEGOTENS® SD 100. This is also visible at the very high dilution rate of 1:50 used here, which means a final use level of about 200 ppm active booster in the ready-to-use cleaner.



In the photos shown in Fig. 6, the enhanced degreasing properties of the various surfactant blends are clearly visible. The efficiency results of the REWOPOL® SC 200 and TEGOTENS® SD 100 from these laboratory tests could be confirmed already under industrial conditions. Therefore, a novel surfactant system or a booster for the enhancement of cleaning speed of traditional surfactant systems, respectively, is now available to the formulator.

Fig.6 Final appearance of test plates after soaking and rinse of a 1:50 dilution



Summary

The traditional degreaser systems require the additional performance of cationic surfactants to achieve the optimal cleaning performance. Unfortunately, the most efficient cationic surfactants exhibit some ecotoxicological weaknesses that limits their use in traditional formulations. In the past, some replacements were presented that are not able to provide the full spectrum of efficiency. Mostly the cost/performance limits a broader usage and finally for critical conditions, e.g. heavily removable dirt, they fail and do not meet the expectations of the user.

REWOPOL[®] SC 200 is a new surfactant system for modern degreasers that fulfils the requirements of efficiency, cost and ecological behaviour. Enhanced by a novel wetting enhancer (TEGOTENS[®] SD 100), this already well known amphoteric/non-ionic surfactant blend achieves the same or even higher efficiency than current or traditional degreasers. By using REWOPOL[®] SC 200 it is possible to avoid the use of ingredients with a negative aqua toxicological impact and reduce the content of solvents for this broad application.

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References

- (1) D. Jourbert, R. Gresser, J.P. Cuif, Properties of builders, in: Handbook of Detergents, Vol.82 (1999) 511-558
- (2) N. Richter, J. Peggau, H. Kuhn, F. Müller., New surfactant systems for soil removal on micro and nanostructured surfaces, Tenside Surf. Det., 40 (2003) 202-207
- (3) F. Müller, J. Peggau, S. Arif, Special Purpose Cleaning Formulations, in: Handbook of Detergents, Vol. 128 (2006) 261-278
- (4) F. Müller, J. Peggau, H. Schramm., How to boost floor cleaners, in: Jahrbuch für den Praktiker 2007, S. 200-205, Verl. f. chem. Ind., H. Ziolkowsky, Augsburg (2007)
- (5) H.S. Bevinakatti, B.K. Mishra, Sugar derived surfactants, in: Design and Selection of Performance Surfactants S. 1-50 (1999)
- (6) Europäische Patentanmeldung, EP 1 130 026 (2001)
- (7) Deutsche Patentanmeldung, DE 102004036067 (2004)
- (8) G. Thie, 2nd WING Entwicklung neuer Tenside zur Enthftung von Kontaminationen, Status Seminar (2004)
- (9) O. Thum, Biokatalyse - Eine nachhaltige Methode zur Herstellung von Emollientestern; 54. SEPAWA Kongress, Würzburg, 10.2007, Conference Proceedings, S. 173-177 (2007)

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