Addressing sustainability with waterless formats in Home Care products

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PEER REVIEWED

Abstract

The need for alternative sustainable approaches to meet both the European Green Deal and today's society demands has been recognized by the home care industry, which has been challenged to respond with innovative eco-friendly cleaning solutions. Waterless formulations are a clear example of sustainable formats that cut back on single-use plastics and CO_2 emissions due to transport savings. Being surfactants the key ingredients in the formulation of super-concentrated waterless formulations, extensive research has been made around the phase behaviour of highly concentrated surfactant systems and the mechanisms behind aggregation processes, to select the best surfactant components that enable not only to meet the formulative requirements of hard surface and hand dishwashing cleaning compositions (stability, appearance, viscosity, etc.) but also to provide the excellent performance consumers are looking for.

Keywords

- Waterless formats
- Sustainability
- Concentrated surfactant systems
- Key ingredients
- Hard surface cleaning Hand dishwashing
- Home care: Laundry & Cleaning
- Peer Reviewed

INTRODUCTION

The European Union has enacted an investment plan to achieve the sustainability-related goals set by the European Green Deal over the next ten years. This investment plan is supposed to promote and facilitate an inclusive transition to a climate-neutral economy by 2050. As an approach to sustainable economic growth, this plan aims to help companies become leaders in clean products and technologies.
Moreover, connected with this green transition, waste-free lifestyles are becoming increasingly popular among consumers, who place special emphasis on the replacement of single-use plastics by refillable options.

To meet the demands of society, the Home Care industry is moving towards more sustainable solutions. Dilutable formats, concentrated products to be diluted at home by the consumer, are a clear example of an eco-friendly innovative cleaning option, which cut back on single-use plastics and carbon dioxide emissions associated with transportation.(1)

Many cleaning products contain water as a major ingredient, accounting for more than half percent of the composition. Since water is a common ingredient in everyone's home, why should these big water volumes be transported? Dilutable formats emerge as a result of this consideration. In addition, they manage to reduce plastic consumption through recycling the plastic package.

Figure 1 shows the idea behind waterless cleaning formats. A refill sample, which can be even a concentrate minidose or a water-soluble tablet, is placed in a plastic bottle that is subsequently filled up with water to obtain the standard diluted product ready to be used. The plastic bottle should be reused as many times as possible.

Among the different home care applications, waterless dilutable products for hard surface and hand dishwashing applications are especially innovative. In the next sections, the selection of the key surfactants to formulate these dilutable formulations and the performance that can be achieved will be discussed.

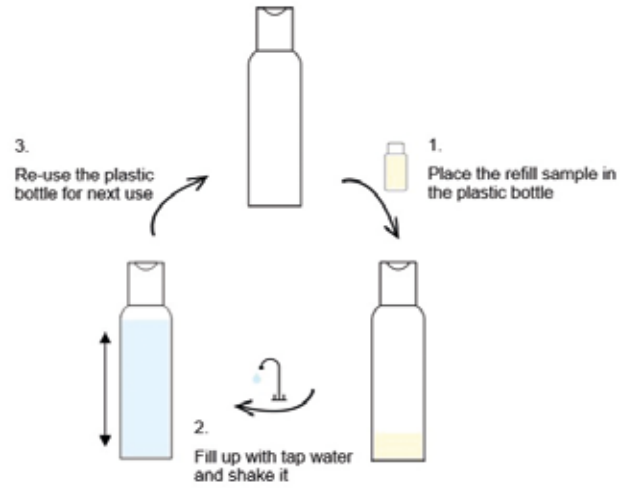


Figure 1. Representation of the idea behind dilutable waterless formats.

Ether carboxylates in dilutable acid and alkaline HSC

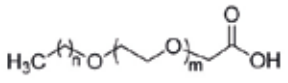
The scope of hard surface cleaning (HSC) products is very wide, it comprises any cleaning formulation to be used over a rigid surface. Since many different surfaces can be found, as well as many different types of soil, different cleaning products are employed for each application: bathroom cleaning compositions are different from kitchen ones, which also differ from window and glass cleaning compositions.

All household HSC formulations currently contain at least 90% of water, which means that high volume compaction could be achieved. However, the higher the compaction, the more challenging the formulation will be.
We have focused on selecting the main ingredients to formulate the most demanding refillable format for hard surface cleaners, which consists of a water-soluble 15 mL tablet of concentrated product to be diluted in a 750 mL bottle (corresponding to 1 to 50 dilution).

The most difficult task associated to these formats is to meet all the requirements of both the concentrate and the resulting dilution.

There are many technical requirements to fulfil: the stability and clear appearance of the formulations, the low water content of concentrates and their easy dilution of the concentrate in tap water; also a suitable viscosity of concentrates to facilitate their encapsulation, while being non-viscous once diluted; the incorporation of high levels of acid or alkali to reach the desired pH in dilution, and of course, to have a good performance in the diluted form. We have concentrated our efforts on selecting the best composition to meet the above mentioned requirements.

Taking all these features into consideration, alkyl ether carboxylic acid surfactants are envisioned as key ingredients for hard surface cleaning bathroom and kitchen concentrates. Kao Chemicals Europe produces this anionic family-type surfactants under the trade name of AKYPO. Figure 2 presents the chemical structure of alkyl ether carboxylic acids and their main properties.



- Active matter within 88-95%
- Low water content
- Stable in acid and alkaline solutions
- Good hydrotropy
- Versatile foaming ability
- Compatible with oxidizing agents
- Compatible with electrolytes
- Stable in hard water

Figure 2. General chemical structure of ether carboxylic acid surfactants, where n refers to the alkyl chain distribution and m to the ethoxylation degree, and the general properties that share this family-type surfactants.

Depending on the specific alkyl chain distribution and ethoxylation degree of the product, several ether carboxylic acids are available. Although they share the above-mentioned properties, they are different enough to cover a wide range of applications. The AKYPO LF range (Table 1) is particularly suitable for the HSC application, where low foam is preferred.

Chemical description	Trade name
Capryleth-6 Carboxylic Acid	AKYPO LF-1
Capryleth-9 Carboxylic Acid	AKYPO LF-2
Capryleth-9 carboxylic acid/Hexeth-4 carboxylic acid	AKYPO LF-4
Capryleth-9 carboxylic acid/Buteth-2 Carboxylic Acid	AKYPO LF-6

Table 1. Alkyl ether carboxylic acid range.

For bathroom formulations, where lime and scale deposits should be removed (2), one of the ether carboxylic products that gives the best performance, due to its good hydrotropy and cleaning ability, is Capryleth-9 carboxylic acid, sold under the trade name of AKYPO LF-2.

Apart from the surfactant, the developed composition, which contains less than 10% of water, is based on non-aqueous solvents and lactic acid, to reach a pH value of 2.5 in dilution.

The cleaning performance of the water-soluble tablet has been evaluated following the IKW Recommendation for the Quality Assessment of Bathroom cleaners (3). This method is used for the assessment of lime soap removal. It consists of cleaning a white ceramic tile that has previously been soiled with a black calcium stearate suspension.

Compositions are tested at specific contact times with the surface, and after the exposure time the solution is mechanically removed by using a wet sponge.
A visual assessment of the cleaning is performed following a standard scale defined by the standard methodology (3), expressed as an average cleaning percentage. The whiter the treated area is, the better the lime soap has been removed.

Figure 3 shows the surfactant factor relevance regarding the cleaning response. A comparative between the use of the ether carboxylic amphiphile (AKYPO LF-2) and a polyoxyethylene fatty alcohol (Deceth-6) is provided, concluding that there is a significant difference in favour of the specialty surfactant AKYPO LF-2.

Product in 1/50 dilution	AKYPO LF-2	Deceth-6	Composition
Cleaning ability 12 min contact time			>35% Surfactant >20% Lactic Acid Glycerine/Propylene glycol to 100% pH 2.5 in dilution
Visual assessment (%)	60%	5%	

Figure 3. Cleaning performance for bathroom cleaners for two dilutable formulations containing different surfactant ingredients: Capryleth-9 carboxylic acid (AKYPO LF-2) and Deceth-6.
Cleaning method: IKW Recommendation for the Quality Assessment of Bathroom cleaners (3).
Assessment: the white area corresponds to the surface that has been cleaned.

The cleaning ability of the developed formula containing ether carboxylic amphiphile is compared with a current market dilutable formulation and with a standard ready to use market product. In Figure 4 can be observed that the developed dilutable waterless formula performs at the same level as a regularly packaged ready to use product and is much more effective than a commercial dilutable product.

Product	Developed formula based on AKYPO LF-2 in 1/50 dilution	Market dilutable based on POE-Fatty alcohol in 1/50 dilution	Market ready to use based on APG as it is
Cleaning ability 15 min contact time			
Visual assessment (%)	90%	0%	80%

Figure 4. Cleaning performance of bathroom dilutable and ready to use cleaners.
Cleaning method: IKW Recommendation for the Quality Assessment of Bathroom cleaners (3).
Assessment: the white area corresponds to the surface that has been cleaned.

For kitchen formulations where baked-on grease and oily residues should be cleaned (2), one of the ether carboxylate products that we recommend is the Capryleth-9 carboxylic acid/Hexeth-4 carboxylic acid, sold under the trade name of AKYPO LF-4. In addition to surfactants, the kitchen developed waterless formulation, which contains less than 10% of water, is based on non-aqueous solvents and alkalis to reach a pH value above 10.0 in dilution.

For kitchen HSC dilutable formulations, the surfactant factor was significant again. The developed formulation containing a standard ethoxylated fatty alcohol as a surfactant ingredient

is not clear neither stable. Figure 5 shows the appearance of the same model formulation containing the ether carboxylate (AKYPO LF-4) in comparison to the Deceth-6 commodity, thanks to its compatibility with alkaline environments.

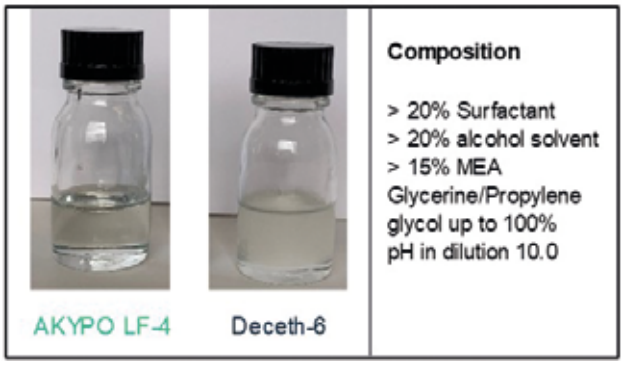


Figure 5. Kitchen HSC concentrate formulations' appearance at room temperature containing as surfactant ingredient AKYPO LF-4 on the left and Deceth-6 on the right.

The cleaning performance of the kitchen water-soluble tablet has been evaluated following the IKW Recommendation for the Quality Assessment of All-Purpose Cleaners (4).
This method simulates the removal of cooked or baked-on grease. It consists of the cleaning of a tough polymerized grease made of fatty acids, clay and carbon black, which has been baked on a white floor tile. Compositions are tested in a multi-track scrubbing device that mimics the scrubbing process as done by the consumer at home when using the product on tough soil.
A visual assessment of the cleaning is performed after every stroke, following a standard scale defined by the standard methodology (4). The number of strokes needed to fully remove the soil from the surface indicates the cleaning performance of the diluted product.

Results are described in Figure 6, where the cleaning ability of the developed formula is compared to both, current market dilutable product and a benchmark ready to use product. It can be observed that the developed formulation presents better cleaning performance than both, a standard ready to use product and a market dilutable product.

EO Glycerine esters in dilutable Hand Dishwashing

Consumers' demand for low-environmental impact products also apply to hand dishwashing products, therefore some market examples of dilutable hand dishwashing have been already launched.
In this application, regularly packaged formulations contain high surfactant concentrations (around 20-30 wt. %) to achieve the performance that consumers look for. The surfactant system usually consists of an anionic surfactant that confers good foaming ability to the formulation; an amphoteric surfactant that gives emulsifying and degreasing power, increasing also mildness to skin; and, finally, a non-ionic surfactant that improves the formulability and compatibility between all the ingredients.(5)
Unlike hard surface cleaners, here the highly concentrated ternary surfactant system makes formula compaction difficult, since surfactant aggregation at high concentrations can lead to

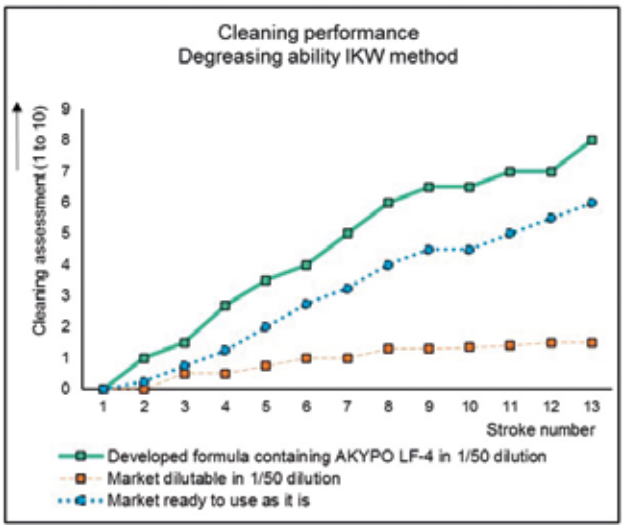


Figure 6. Cleaning performance of kitchen dilutable tablet containing AKYPO LF-4, compared with a market dilutable product (based on >30% of non-ionic surfactants) and with a ready to use product (based on APG).
Cleaning method: IKW Recommendation for the Quality Assessment of All-Purpose Cleaners (4).

highly viscous phases that makes the formulation impossible to manipulate. Here is where the non-ionic surfactant plays a crucial role, leading to appropriate viscosity/concentration profiles apart from improving ingredients compatibility and, therefore, formula stability. Consequently, we have specially focused on the selection of key non-ionic surfactants for the formulation of concentrated hand dishwashing products.

Taking this into account, ethoxylated glycerine ester surfactants are envisioned as key surfactants for hand dishwashing application. Kao Chemicals Europe produces this non-ionic specialty family-type surfactants under the trade name of LEVENOL and EMANON. Figure 7 illustrates the chemical structure of EO glycerine esters and their general properties.

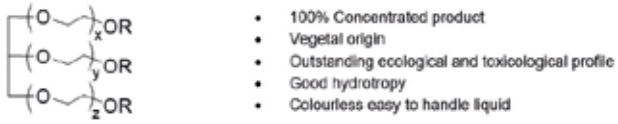


Figure 7. General chemical structure of OE-Glycerol esters, being n:x+y+z the ethylene oxide mols and R=R' or H, R': alkyl chain, and general properties shared by this surfactants family.

Depending on the specific alkyl chain distribution and ethoxylation degree of the product, several EO glycerine esters are available, Table 2.

Chemical description	Trade name
Glycereth-6 Cocoate	LEVENOL F-200
Glycereth-17 Cocoate	LEVENOL C-201
Glycereth-7 Cocoate	LEVENOL C-301
Glycereth-2 Cocoate	LEVENOL C-421
Glycereth-7 Caprylate/Caprate	EMANON XLF

Table 2. EO Glycerine esters range.

Although they share the above-mentioned common properties, their differences allow to cover a wide variety of applications. In this case, Glycereth-6 Cocoate (LEVENOL F-200) and Glycereth-7 Caprylate/Caprate (EMANON XLF) have been specially designed to have excellent hydrotropic properties and outstanding foaming ability in oil presence.
For this reason, their presence in waterless dilutable hand dishwashing formulations has been studied for two compositions containing the two typical surfactant systems:

1. Sodium laureth sulfate (SLES) + Cocoamidopropyl betaine (CAPB) + non-ionic surfactant. Being the optimised surfactant ratio of anionic/amphoteric/non-ionic surfactants (70/20/10), calculated taking the active matter of the sum as a whole. The pH of the system is of 7.0 approximately.
2. Sodium laureth sulfate (SLES) + Cocoamidopropyl amine oxide (AO) + non-ionic surfactant. The optimised surfactant ratio of anionic/amphoteric/non-ionic surfactants (74/16/10) is calculated taking the active matter of the sum as a whole. The pH of the system is of 5.0 approximately.

Other ingredients present in the dilutable formulations developed are ethanol and magnesium chloride. A more detailed description of the compositions can be found in EP2666848 (B1) — 20170906 Patent (6).

The viscosity profile and the formula stability and appearance of the two formulations, including the studied EO glycerine esters (LEVENOL F-200 and EMANON XLF), were evaluated in the concentrated formulation and upon the addition of water to dilute the concentrate. It is well-known that surfactant systems will present different phase structures (micelles, reverse micelles, hexagonal, lamellar and cubic liquid crystals, among others), with different physicochemical properties (viscosity, rheology, scattering, etc), depending on the main components concentration (7, 8).

Different physicochemical properties of both ternary surfactant systems have been measured at different dilutions, and different behaviours have been observed, which might be due to dissimilar molecular ordering with the solvent matrix as function of the surfactant molecules concentration.

Figure 8 shows how the viscosity of the surfactant system containing SLES/AO/EMANON XLF changes upon the addition of water, as well as the formula appearance. These two properties are especially important for the practical use of a hand dishwashing product. It can be observed that a clear and stable phase, with an adequate viscosity range for their use in application (200-2000cP), was obtained for the concentrate formulation as well as for the 1 to 2 and 1 to 3 dilutions, for both systems.

The existence of different phases is frequently illustrated by the rheological behaviour of the different structures.(9) Figure 9 depicts the rheology of the studied dilutions.
It can be observed that the initial concentrate behaves as a Newtonian fluid (blue plot). Upon the addition of water, more viscous phases with a shear-thinning viscosity profile were

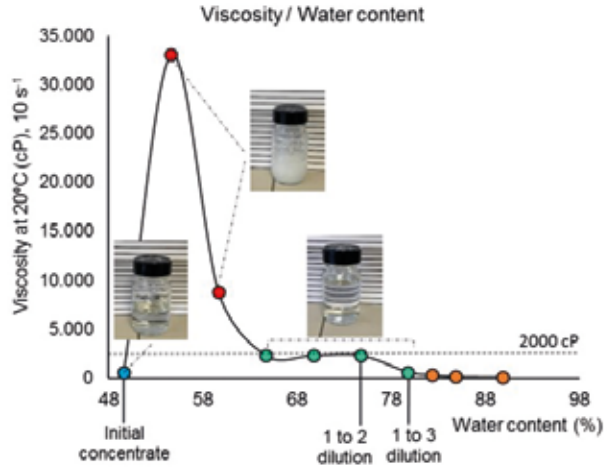


Figure 8. Viscosity as function of the water content in a hand dishwashing dilutable formulation containing (SLES/AO/EMANON XLF), and the appearance of the existing phases. Measurement: Brookfield LV-II at 20ºC.

observed (red plot). However, upon the addition of more water, which would correspond to the 1 to 2 dilution, the crystalline structure changes and the rheological properties as well, behaving as Newtonian fluids again (green plot). This structure seems to be stable until the 1 to 3 dilution. Viscosity significantly decreases with more water addition though, which probably means that the formulation becomes a normal micellar system with spherical aggregates (orange plot).

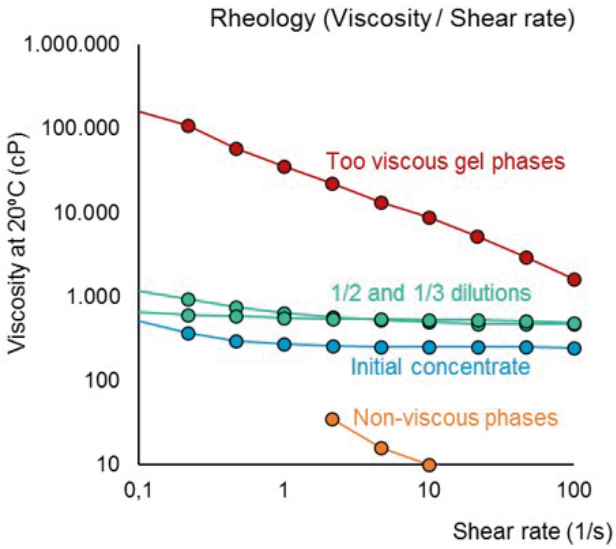


Figure 9. Rheology of different concentrate dilutions. Measurement: Anton Paar Rheometer MCR 302e.

A comparative formulation study has been done with other non-ionic surfactants widely found in hand dishwashing formulations, such as alkyl polyglycosides and polyethoxylated fatty alcohols.

As shown in Figure 10, the glycerine esters family (LEVENOL F-200 and EMANON XLF) is the only non-ionic surfactants

that meets the viscosity/concentration requirements of both surfactant systems (adequate viscosity range established as 200-2000 cP). In addition, formulations with higher viscosities also tend to have no clear appearance, meaning that the surfactant system is not thermodynamically stable, and it will end up separating into different phases.
Both surfactant systems were also studied without including any non-ionic surfactant in the system. This clearly showed the need for using non-ionic surfactants in the mixture, since otherwise it was no possible handle the gel phases that were formed.

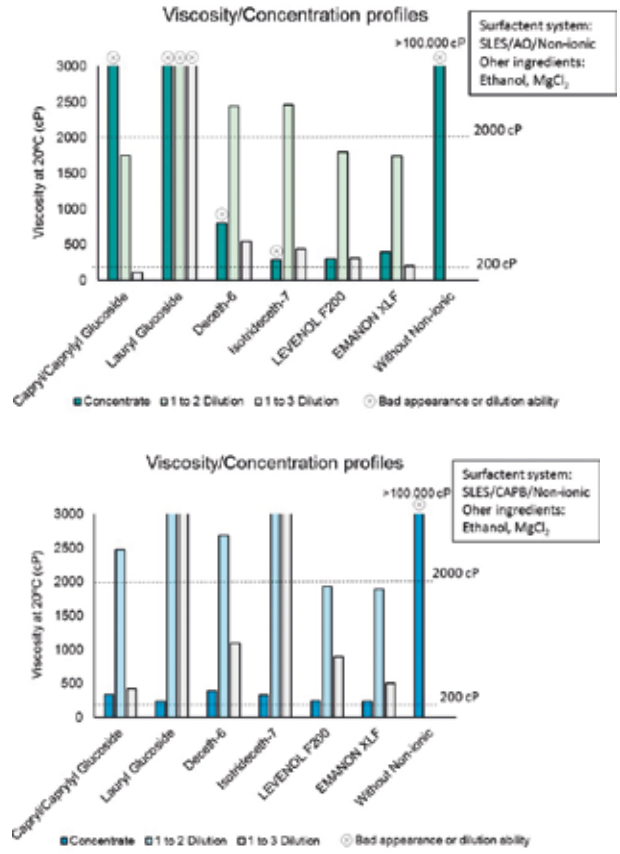


Figure 10. Viscosity/concentration profile of different non-ionic surfactants in the two studied concentrated systems. Measurement: Brookfield LV-II at 20ºC.

Considering the above description, the presence of the glycerine ester surfactants confers adequate rheological properties and clear appearance, not only to the concentrate but also to the 1 to 2 and 1 to 3 diluted solutions. It can be explained due to the resulting phase diagrams of surfactant systems.

Apart from the formulability, non-ionic surfactants can also play an important role in the performance of the formulation. The efficiency of a hand dishwashing product is commonly associated not only to its cleaning ability but also to its foaming ability in the presence of oil. (5) Therefore, both properties have been evaluated.

On the one hand, the cleaning efficiency has been assessed following the IKW Recommendation for the Quality Assessment of the Cleaning Performance of Hand Dishwashing detergents (10). This measure corresponds to the number of dishes, previously soiled with the IKW soil 1 (10) composed of many fat foods, that can be cleaned by using the tested dishwashing detergents at the same dosage. The cleaning efficiency results are expressed in terms of number of a percentage, related to the number of cleaned dishes by the dry matter of the product.

Figure 11 depicts the cleaning performance results for one of the EO glycerine esters, the Glycereth-7 Caprylate/Caprate (EMANON XLF), which presented a suitable appearance and viscosity/concentration profile, contained in both studied surfactant systems, and compared with the market dilutable product and the standard ready to use benchmark. As it can be observed, dilutions 1 to 3 present a very good cleaning efficiency, which means that these compositions are performing very well considering the number of cleaned dishes per active matter.

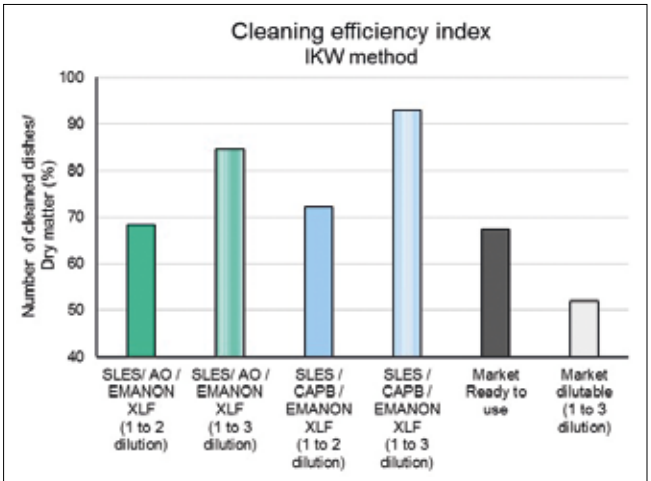


Figure 11. Cleaning performance of hand dishwashing dilutable compositions compared with the ready to use benchmark product (based on SLES, AO, PEO FA) and a market dilutable (based on LAS, SLES, AO, PEO FA).
Evaluation method: IKW recommendation for the Quality Assessment of the Cleaning Performance of Hand Dishwashing detergents (10). Test conditions: Used soil IKW 1, 1 g/L dosage, temperature of 40ºC.

On the other hand, the foaming ability of the detergent solutions has been evaluated with the SITA Foam Tester R-2000, which allows to measure many foam properties, such as the foam volume and stability.
In this method, the foam is generated by mechanical action with a stirring disc, and it consists in the repetition of 50 cycles, each one including the following steps:
Addition of 50 µl of olive oil.
Stirring cycle of 10 seconds at 1500 rpm.
Measurement of the foam volume.

The test is carried out at a temperature of 40ºC. The purpose of the evaluation is to determine the foaming ability of HDW compositions, simulating the real application conditions. Results are expressed as maximum foam volume in Figure 12, where all diluted compositions containing EO glycerine esters show better foaming ability in presence of fats than the standard benchmark and a market dilutable product.

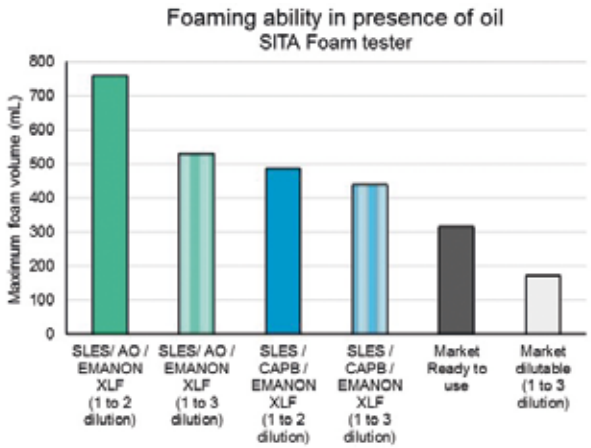


Figure 12. Foaming ability in oily conditions of hand dishwashing dilutable compositions, compared with the ready to use benchmark product (based on SLES, AO, PEO FA) and a market dilutable (based on LAS, SLES, AO, PEO FA).
Measurement: SITA Foam Tester R-2000, 1 g/L product dosage, 400 ppm CaCO3 water hardness, continuous addition of olive oil.

Both evaluations, Figures 11 and 12 corresponding to the cleaning and foaming performance, show that compositions containing EO glycerine esters are equivalent or even more performing than the regularly packaged benchmark, and much better than the dilutable one.

CONCLUSIONS

It has been demonstrated that the following can be achieved choosing the key surfactant products for each application:

- Stable and clear concentrated surfactant systems.
- Proper physicochemical properties as function of the concentration.
- Good functional value with lower active content than standard ready to use formulations.

This will support a good consumer acceptance of innovative waterless products

Ether carboxylates facilitate the formulation of water-soluble tablets which are almost water-free, for the hard surface cleaner category. Stable at extreme pH conditions, they are suitable for bathroom and kitchen cleaner products. The cleaning efficacy that this surfactant-family gives to the dilutable formulation, reaches the performance of ready to use market products.

Ethoxylated glycerol esters are very convenient non-ionic surfactants to be incorporated in dilutable hand dishwashing products. They are suitable for the adequate appearance and viscosity profile they provide in concentrated and diluted forms. Moreover, formulations containing glycerol esters have been shown to achieve a very good performance, which is particularly important for dilutable formats that always contain less surfactant active contents than ready to use formulas.

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