Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien

European Committee of Organic Surfactants & their Intermediates

July 2003

ROLE OF SURFACTANTS IN HOUSEHOLD DETERGENTS AND CLEANING PRODUCTS

SUMMARY

Modern household detergents and cleaning products are sophisticated formulations, designed to meet a large number of cleaning problems from cleaning clothes, washing dishes, through to cleaning a variety of surfaces about the home ranging from soft furnishings to floors to toilets. They contain a range of ingredients each of which contribute uniquely and cost-effectively to the overall cleaning profile. A range of chemicals is required to optimally meet consumer needs in a safe and cost-effective manner. Given that products are sophisticated and specifically designed to address complex cleaning tasks, substitution of chemicals, for example individual surfactants, is not straightforward. This is because a product's overall performance is optimised by the interaction of many components and a change of one vital component will require multiple simultaneous changes to other components and a thorough evaluation in order to try to obtain the most cost-effective and effective product.

GENERAL REQUIREMENTS FOR DETERGENT AND CLEANING PRODUCTS

Household detergents and cleaning products should offer an outstanding cleaning performance at an affordable price, allowing a low water and energy usage during the cleaning process and involving as few extra cleaning steps as possible via a process where stains and soils are removed without additional intervention like rubbing, soaking, pretreating or rewashing, in the case of clothes washing.

In addition, existing legislation and the future Detergent Regulation, which is about to go to 2nd reading in the European Parliament imposes requirements on the environmental properties of surfactants. If these criteria are not met, the substance cannot be used in household detergent and cleaning products. If they *are* met there can be no real differentiation between individual surfactant substances and no substitution is needed (nor can any claim of superiority be upheld). All are equally safe for the environment. The levelling process is the sewage works, where effective biodegradation occurs with all currently used consumer surfactants.

Surfactants do differ in various ways - molecular structure, physical and biologically relevant properties - but, due to the legally required high level of biodegradation in sewage treatment, the differences, as far as the environment is concerned, are minimal. ERASM worked with the Dutch Government some years ago to demonstrate the great effectiveness of sewage treatment in degrading all commonly used surfactants.

COMPOSITION OF DETERGENTS AND CLEANING PRODUCTS

Detergents and cleaning products depend upon surfactants for their cleaning. Surfactants are often referred to as the "engine" of the detergent system. They can be present at low levels (<5%) as well as in considerably higher levels (e.g. 20-30%) in concentrated products. They wet the fabrics and soils and so allow the removal of soils and dirt. They suspend a whole range of stains and dirt (particulate, greasy, body soils, cosmetics). However, for laundry and machine dishwashing, other ingredients are also essential such as water softeners (zeolite; phosphate, citrate etc.), bleaching systems (percarbonate, bleach activators), dirt suspension agents (polymers, ..), enzymes, chelating agents, perfumes, etcetera. For other types of cleaners, other formulation ingredients are required such as solvents etc.

PARAMETERS AFFECTING CLEANING PERFORMANCE AND SURFACTANCY/DETERGENCY PROPERTIES

The efficiency of a detergent's cleaning is affected by:

- Water hardness – surfactants are precipitated by water hardness ions
- Type and levels of soils and stains(e.g. water-soluble or insoluble; tea, coffee, wine, blood, clay etc..)
- Fabric type (cotton, polycotton, polyester, nylon, wool, silk, etc…
- Type of surfaces (dishes, floors, etc…)
- Type and efficiency of washing machines (top loader; front loader)
- Wash temperature; the number and length of wash cycles.

It is also essential to consider factors such as the interaction, compatibility and synergy of the various ingredients used in detergents, e.g. interactions between anionic and nonionic surfactants, between surfactants and builders, enzymes or the bleaching system, etc...

In addition, the 'processability' of the individual raw materials during the manufacturing process is key (easiness to transport, store, handle,…) and this for the production for each of the forms of detergents, such as granular, liquid and tablet products. Finally, the formulated detergent and cleaning products must also have an outstanding stability profile (e.g. stabilization of enzyme or bleach system).

IMPORTANT SURFACTANT CHARACTERISTICS

Today, a broad choice of surfactants is commercially available. Some are used as 'mainframe' surfactants, others as co-surfactants, known also as "specialty surfactants" (smaller usage and higher price versus mainframe surfactants). Co-surfactants are typically blended at low levels with mainframe surfactants for synergistic effects.

In general, there are several reasons why a broad range of surfactants is needed.

- The surface activity of surfactants (and thus cleaning power) increases with longer alkyl chainlengths. However, this results in decreased solubility and possible loss of the surfactant via precipitation in hard and cold water. Shorter chain surfactants have superior solubility but reduced surface activity, and thus reduced cleaning performance. Insolubility and precipitation effects can be overcome in many cases by formulating with extra detergent ingredients such as builders or the introduction of co-surfactants and/or polymers.
- The surfactant system must be effective in the range of cleaning conditions described above such as a range of water hardness and soil/stains conditions,… and this for various types of product forms (liquid, tablet, granular).
- There is also a need to adapt to changing consumer habits. For example, long chain linear $C_{16/18}$-alcohol sulfates were widely used around 1960/70, but other alcohol sulphates (for example with shorter chainlength) or other surfactant types were introduced when wash habits moved from boil wash temperatures to cooler temperatures and when other changes in the detergent composition occurred (e.g. changes in use of water hardness builders).
- Surfactants can be derived from petrochemical feedstocks, as well as from oleochemical feedstocks, or from a mixture of both (surfactant alcohol from oleochemical; ethylene oxide from petrochemical). In all cases, they will exceed stringent environmental and health criteria. The cost and availability of oleochemical and petrochemical materials can change regularly since these markets are associated with the global food/fat market, and the petroleum/energy market, respectively. However, for some oleochemically derived nonionics like APG, the cost and performance profile do not make them overly attractive and certainly not a viable replacement for LAS.

EASE OF SUBSTITUTION

There are numerous examples that demonstrate that each surfactant class and type has a specific profile, with strengths under certain application conditions, but also limitations or shortcomings under other conditions. Some examples are described here.

Linear Alkylbenzene Sulphonate (LAS) cannot simply be substituted by alcohol sulphates (AS) in detergents: for laundry detergents, alkyl sulphates (AS) can produce more sudsing during the wash process and require specific suds suppressor systems. Besides sudsing, there are also solubility

considerations that have to be taken into account: alkyl sulphates (AS) with chainlengths predominantly in the 12-14 C-range (derived from coconut oil, palm kernel oil or petrochemically produced) could produce too much sudsing, while alcohol sulphates (AS) with chainlenghts predominantly in the 16-18 C-range (palm oil derived) can lead to insolubility issues. In liquid detergents, more solvent would be required to stabilize alcohol sulphates (AS) (versus LAS). In addition, the processing of AS in laundry detergents can be more demanding than LAS since it is more prone to hydrolysis.
Whilst it is also known that alcohol ethoxy sulphates (AES) are more suitable for cutting grease and are less hardness sensitive than LAS, these properties are most important for hand dishwashing applications. This points to the fact that a range of surfactants are required to meet consumer needs in an optimal fashion, and that reduction in choice of surfactants, provided environmental and human safety are assured, is not either proportionate or beneficial.
In laundry detergents, performance is optimised by the use of a mixture of anionic and nonionic surfactants. Formulations with only anionic surfactants or only nonionic surfactants result in inferior cleaning performances and suffer from other limitations. The use of mixtures of anionic and nonionic surfactants in detergent formulators helps to achieve an optimum cleaning performance, through optimised surfactant 'packing' at the fabric interface, better anti-redeposition properties, water hardness tolerance through preventing the precipitation of insoluble calcium salts of anionics. Raw material and detergent processing is also improved.
Whilst nonionic surfactants can contribute significantly to the removal of greasy stains, they exhibit poor cleaning performance due to poor 'packing' of the water/fabric interface and in addition, they have a considerably lower ability to suspend particulates in the wash liquor, which is essential to avoid the redeposition of soils from the washing solution onto the fabrics.
Manufacturing powdered detergents with only nonionic surfactants is technologically more difficult, since nonionic surfactant raw materials are typically available in a waxy or liquid form, which is convenient for transport and handling, but not optimal for use as the only surfactant in granular detergents. Anionic surfactants are typically available in a solid form (after the surfactant neutralisation step from their 'acid' version into the Na-salts), and a mixture of anionic and nonionic surfactants are best for an efficient production of granular detergents.

CONCLUSION

The described examples show that there is a need to use mixtures of anionic and nonionic surfactants in detergent formulators in order to achieve an optimum across all important parameters, such as cleaning performance, 'packing' at the fabric interface, anti-redeposition properties, water hardness tolerance, etc...
In terms of economics, there are significant cost differences between commercially available surfactants. For example, LAS is one of the most commonly used ‘workhorse’ surfactants and it is highly cost-effective. Even is 1-for-1 replacement is not possible based on the above arguments, such a theoretical substutition on an equal weight basis by other surfactants can lead to a 10-15% cost increase for the surfactant system.

The challenge to the detergent industry is how to optimize the overall cleaning power to better address the demanding and evolving wash habits and consumer needs, both amongst high income and low income groups in society. Getting the engine of the detergent right, namely the surfactant system, is essential in this context.