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RECENT TRENDS OF SURFACTANTS IN THE FABRIC & HOME CARE FIELD

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1. INTRODUCTION

Surfactants remain the most important components for the development of fabric care and home care products. This presentation will overview newly developed surfactants in household products in the past ten years. To start with, there are three major factors influencing changes in marketing focus.

Firstly, consumers' needs and expectations in industrialized countries have recently been more diverse, and the marketing focus is now shifting from perceived needs to more potential ones. People spend less time doing household chores and are less concerned with performance differences in conventional products. The existing technologies already satisfy current consumer expectations. Therefore, the growing consumer concerns for products are how much these new products alleviate household chores and provide new features such as long-lasting fragrance and deodorizing action. Simply put, our industry must be proactive in the development of consumer-needs-oriented technologies.

Secondly, in some countries, mega stores are rapidly dominating and gaining buying power while in other markets, there is an overabundance of stores causing aggressive price wars. These two trends can potentially cause adverse pricing pressure and force manufacturers to adopt cost-effective technologies. In this context, it is important for manufacturers to develop value-added technologies in order to justify premium prices.

Thirdly, environmental awareness is growing worldwide and leading to new regulations on chemical release management and energy and resource saving. In Europe, the proposed Registration, Evaluation and Authorization of Chemicals (REACH) is far stricter than previous regulations. The REACH regulation aims to manage all chemicals, new and old, according to their environmental and human health risk evaluation. Fabric and home care companies around the world can also contribute to energy savings by introducing products that work efficiently even at lower temperatures and with less water. In the United States, for example, new washing machine regulations are bound to reduce the energy consumption per laundry **(1)**.

2. OVERVIEW

The following is an overview of surfactant developments of laundry detergents in Europe, USA and Japan.

Europe

Although there are large differences between various product form segments from country to country, concentrated powders have been in decline whereas the share of liquids has been expanding. One of the notable features of the European market is its success with new product forms, such as tablets and liquid capsules. It is thought that these detergent forms are widely accepted because they are convenient to use with front-loading washing machines.

The trend of lower wash temperatures has given rise to an increase in liquid detergents being consumed. This has also resulted in the development of high solubility powder detergents. Some powders, which are formulated with none of water-insoluble zeolite, have also been available to minimize solubility problems at lower temperatures.

U.S.A.

In the last ten years, liquid detergents in the United States have grown to their almost 70% market share and this volume has triggered changes in surfactants usage. Alkyl ether sulfate (AES) consumption is increasing more rapidly than any other surfactant including LAS.

The trend in the past few years might be due to the federal legislation on low-water-use efficiency standards for residential washing machines. Where Stage 1 of this legislation is taking effect this year and Stage 2 will take effect in 2007 **(1)**, two surfactants, methyl-branched alkyl sulfate (AS) and so-called modified LAS (MLAS), were developed and will meet the demands. Methyl-branched AS was developed to improve detergency and especially to dissolve powder detergents quickly. These methyl-branched surfactants will be discussed later.

Japan

Since the first concentrated powder detergent was launched in 1987 in Japan, concentrated powders have consistently played a leading role, especially for the past 10 years (FIGURE 1).

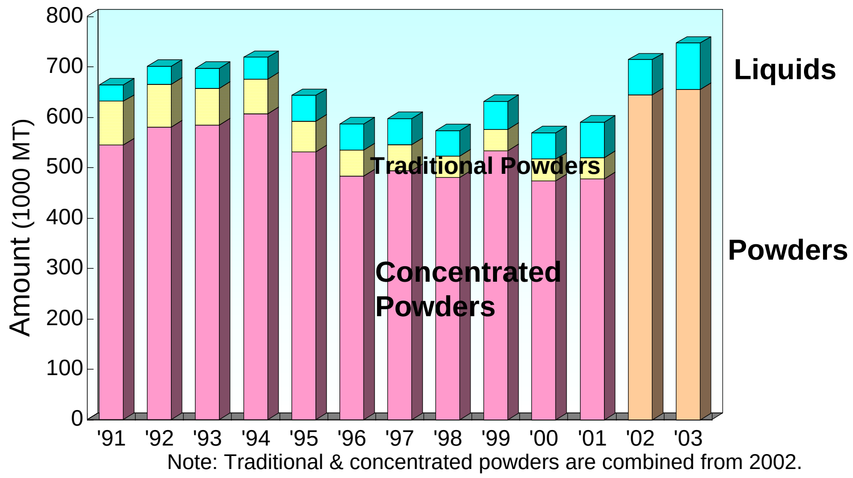

FIGURE 1. Laundry Detergent Trends - Production Volume in Japan **(2)**

There seems to have been almost no change in product form segments but surfactant-wise, a major change occurred around 2001. The new millennium saw a new generation of powder detergents suited to new washing machines developed to save time, water and use low mechanical force for less damage to clothes. This movement resulted in significant changes in the surfactant segments. While the amount of LAS decreased, the amount of alcohol ethoxylate (AE) increased when a new concentrated powder with quick solubility, intended to improve washing performance, was launched. An increased use of methyl ester sulfonate (MES) has been seen in Japan and this surfactant has also been introduced in North America.

3. LAUNDRY DETERGENTS

Two of today's biggest issues facing the laundry detergent industry are the improvement of solubility of powder detergents and detergency at lower temperatures. The solubility of powders is regarded as the driving force behind the trend towards liquid detergents, most notably in the U.S. In 2001 and 2002, two new technological solutions were introduced to improve powder detergent solubility in the Japanese and the U.S. markets.

The first is the development of new manufacturing processes to make quick-dissolving particles infused with higher contents of AE. AE is a nonionic surfactant that easily dissolves and shows good performance in cold water when compared to conventional anionic surfactants. However, AE with good detergency is usually liquid, so it is very difficult to incorporate a large amount of AE into powders. With the new manufacturing processes, the produced detergent particles are highly porous and can retain lots of liquid surfactant without adding any oil-absorbent materials (FIGURE 2) **(3-5)**.

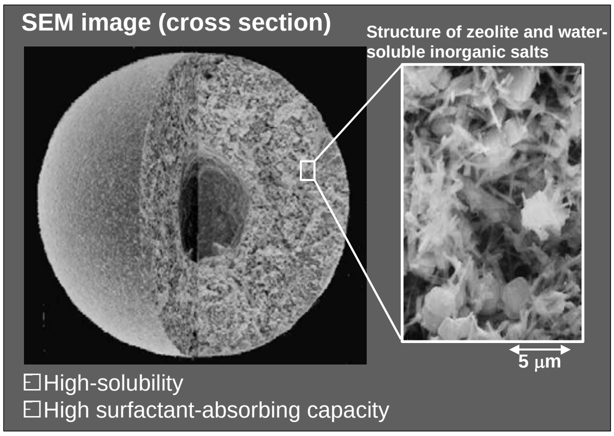

FIGURE 2. High Porous Particle with High AE Retention Ability **(3)**

These fine, uniform particles have a mean size of 280 microns and have no coarse grains like other compact detergent particles. They are all nicely spherical, hollow inside and structured as to contain air within each particle. This lets water immediately penetrate into the particles, which facilitates their collapse thereby realizing higher solubility, a reduction of the total formulation amount of surfactants and superior washing results.

When AE is used as a main surfactant, some builders are necessary to maximize its performance by avoiding the formation of fatty acid scum. Accordingly, AE can work more effectively in powders than in liquid detergents.

The second approach is a chemical modification in the hydrophobic group of conventional anionic surfactants. The branched alkyl chain decreases the Krafft point of anionic surfactants and thus can improve the solubility of detergents containing branched surfactants, and also provide a good washing performance at lower temperatures. In other words, it can solve the problem between high surface activity and solubility, thus allowing the use of relatively longer alkyl chains. In 2002, methyl-branched alkyl sulfates with these longer alkyl chains were introduced in the US **(6-7)**.

Another attempt is the development of MLAS, which was based on the similar concept of branched AS. Usually, for LAS, cmc lowers when the phenyl group gets near the end of the alkyl chain while the Krafft point increases. The introduction of a methyl substitution to an alkyl chain results in the improvement of hard water tolerance and solubility. This substitution allows for the increase of the surface-active 2-phenyl body ratio, which has a relatively high Krafft point **(8)**.

4. LAUNDRY BLEACHES

Today, bleach activators are used in many laundry detergents and bleaches worldwide. The bleach activators can provide excellent bleaching performance without fading colors.

Tetraacetyl ethylene diamine (TAED) has been widely used in Europe. It performs well at high temperatures even though it does not form a peracid very well at lower temperatures. That is the reason why many detergent manufacturers have been competing to develop more effective activators. In Europe, TAED continues to be used because washing temperatures remain high. Nonanoyloxybenzene sulfonate (NOBS) forms a peracid well at lower temperatures. This is why NOBS has been used in the US where washing temperatures are lower than in Europe. In Japan, where it is common practice to use cold tap water, even in winter, NOBS, lauroyloxybenzene sulfonate (LOBS) and decanoyloxybenzoic acid (DOBA) have been employed as well.

There are two interesting technologies for bleaching agents. The first is on metal bleach catalysts, one of which used to be used in laundry detergents and the other is now used in automatic dishwasher detergents in Europe. The second is on molecularly stabilized organic peracids. However, bleach activators will continue to be main ingredients for the foreseeable future.

One of the recent topics in laundry bleach technology is the application of bleach activator to liquid oxygen bleach products. Liquid oxygen bleach with this technology was launched in Japan in 1996. In this product, activator molecules in an aqueous media are stabilized with cationic surfactants by incorporating them in nonionic micelles (FIGURE 3) **(9-10)**. In order to improve bleaching performance, new liquid bleaches formulated with a cationic surfactant which functions not only as a stabilizer but also as a bleach activator, recently appeared on the market.

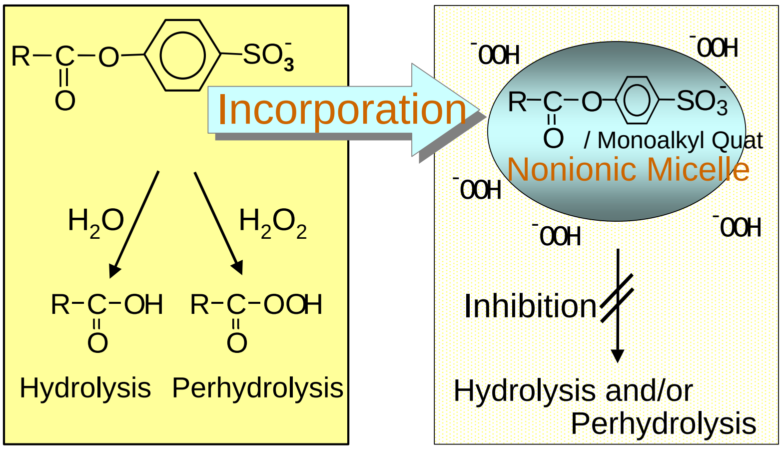

FIGURE 3. Approach to Stabilize Bleach Activators in Liquid Bleaches

Technologies of active oxygen bleaches could be widely applied to products requiring not only bleaching but also disinfecting and/or deodorizing functions. Bleaching technologies will surely be applied to other product categories and help develop future value-added products.

5. FABRIC SOFTENERS

Di(hydrogenated tallow-alkyl) dimethyl ammonium chloride (DHTDMAC) used to be a de-facto standard of softening agents for a long time. DHTDMAC has two long chain alkyl groups and has a similar structure to phospholipids such as lecithin and has the characteristics of forming bi-layer structures in water. There are many types of softening agents, but they essentially all have similar molecular structures.

Significant changes in main ingredients of fabric softeners had not been seen for a long time, but since the latter half of the 1980's, many surfactant manufacturers have actively started to develop new technologies. In 1989, a fabric softener with better water-absorbency was launched in Japan. Then, around 1990, easily biodegradable softening agents were developed and were used in Europe, the United States and Japan.

Dioleyl quaternary ammonium salts deliver good softness without sacrificing water-absorbency. It has been reported that dialkyl dimethyl ammonium salts, whose gel-liquid transition temperature (Tc) is lower than ambient temperature, show good water absorbency and that there is a correlation between the movement of alkyl groups and water-absorbency **(11)**.

The three most common biodegradable fabric softening agents used in the world are: Esterquats of triethanolamine, Esterquats of methyldiethanolamine, and Amide-esteramine of N-(2-hydroxyethyl)-N-methylpropanediamine(Amide-Ester). In each compound, the introduction of one or more ester bond between the long alkyl groups and the heading group effectively accelerates biodegradation by cleaving the ester-bond(s) resulting in smaller fragments.

Recently, one of the most interesting technological developments has been transparent softener formulation. In Canada, a concentrated transparent softener was put on the market more than 10 years ago. The softening agent was an asymmetric dialkyl ammonium salt having both long and shorter alkyl groups in a molecule, and some solvent was indispensable for making it transparent. The technological concept itself was innovative. Other concentrated transparent softeners were put on the market in Europe and the U.S. in 1999. The main components in these transparent softeners were

Esterquats of triethanolamine with oleic acid, and the transparency was achieved by adding solvents and inorganic salts to the products. Another transparent softener put on the market in 2002 in Japan has been using a blend of cationic and anionic surfactants, which have branched alkyl groups. The mixing ratio of the cationic and anionic surfactants can be adjusted to meet the desired HLB to obtain transparency. This technology retains transparency in a wider range of temperatures. Moreover, this surfactant blending technology does not include any unsaturated alkyl groups, so it does not cause any oxidization problems. This technology features smooth-feeling fabrics with high water absorbency.

TABLE 1. Technologies of Clear Concentrated Softeners

Region	Canada	Europe USA Japan	Japan
Softening Agent	Asymmetric Dialkylcation	Unsaturated Esterquats	Anionic/ Cationic Blend

Washer-added liquids used in washing machines and drier-added sheets used in tumble driers remain the only product types available. There have been major changes in the past few years in the liquid fabric softener market and a rapid diversification in the benefits derived from using these softeners. Traditionally, softeners have been used, apart from softening clothes, for the purpose of scenting and reducing static electricity. Recently however, new products with additional functions such as easy ironing, long-lasting fragrance and neutralizing clothing malodors, have been introduced into the marketplace.

6. HARD SURFACE CLEANERS

In the home, undesirable major tough stains such as sebum, dark stains and slime generated by mold and bacteria, and water spots are seen in places where water is frequently used, particularly bathtubs, bathrooms and kitchens. Modifications to the properties of hard surfaces to prevent stain build-up have come on the market in order to maintain surfaces clean. There have been two major methods, hydrophobic and hydrophilic, to achieve surface-property modification.

The former, hydrophobic method has thus far been typically with long chain alkyl cationic surfactants, silicone polymers and fluorinated surfactants. As most of the water does not remain on the surface with this modification, the treatment is effective in preventing the formation of water-spots and the accumulation of stains. It minimizes water on the surface, which slows the growth of germs. Therefore it also enables to prevent stains derived from bacteria.

The latter surface modification, which is a hydrophilic treatment, helps with the easy removal of hydrophobic stains adhering to the surface. Its hydrophilic nature can also help reduce water spots. Some anionic and/or nonionic surfactants can create hydrophilic properties on hard surfaces like porcelain.

7. CONCLUSION

There is a lot of hard work being made to meet consumers’ more diverse expectations for new household products and surfactants will remain key to the development of new products. Understanding surfactant properties such as the effect of molecular structures and synergy effect of surfactant mixtures are indispensable. Also, it is important to look deeply at what the necessary surfactant properties are in order to meet the required product performance.
We need to pay close attention to the growing concern that the development of new chemicals may impact on the environment. One of the most difficult challenges we are now faced with is to achieve a reduction in the consumption of chemicals such as surfactants by introducing effective new technologies.

7. BIBLIOGRAPHY

1. U. S. Department of Energy; Docket No. EE-RM-94-403, Energy Conservation Program for Consumer Products; Clothes Washer Energy Conservation Standards
2. Office of Current Survey for Mining and Manufacturing, Ministry of Economy, Trade and Industry, Japan
3. Yamaguchi, S. et al., Innovative Technologies for Compact Laundry Detergents, New Horizons; Detergents for the New Millennium, October 14-17, 2001, Ft. Mayers, Florida
4. Hasumi, M. et al., Proceedings of 33rd Symposium on Detergency, Japan Oil Chemists' Society, 97 (2001)
5. Tsumadori, M., Chem. Chem. Ind. (the Chemical Society of Japan), 55 (5), 567-569 (2002)
6. Baillely, G. et al., The Changing Paradigm in the Surfactant Hydrophobe Structure, Proceedings of 5th World Conference on Detergents, 115-121 (2003)
7. Battersby, A. S. et al., Effect of Branching on the Biodegradability of Alcohol-based Surfactants, Proceedings of the World Surfactants Congress CESIO 2000, 1397-1407 (2000)
8. Burkett, St. Laurent J. et al., Improved Alkyl Benzene Surfactants: Molecular Design and Solution Physical Chemical Properties, Proceedings of 5th World Surfactants Congress CESIO 2000, 716-722 (2000)
9. Ozaki, K. et al., Proceedings of 30th Symposium on Detergency, Japan Oil Chemists' Society, 193 (1998)
10. Tsumadori, M., J. Oleo. Sci., 50 (5), 367-372 (2001)
11. Yamamura, M. et al., Comun. Jorn. Com. Esp. Deterg., 22, 209-222 (1991)