J. of Korean Oil Chemists' Soc., Vol. 12. No. 2, Nov., 1995. 1~ 4

〈總 說〉



Trends in the Development of Surfactants

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Today, many kinds of surfactants are being manufactured. Many were developed with performance properties and economic benefits in mind. Recently, because of social changes including alternations in life-style and common awareness to the environmental problems, additional considerations during development activity have become essential. Products for both industrial and domestic use now must have high functionality, satisfactory cost performance, and compatibility with the environment. In addition, surfactants for domestic use, especially those for personal care, need biological compatibility, good touch on application, and refreshing feeling after use.

Several attempts to make such products have been successful, in terms of down-sizing of products, exclusion of phosphates from the formulation(replacement by zeolites), introduction of enzyme technology, etc.

Besides the factors mentioned above, the ideas of "life-cycle inventory" and "product liability" also are becoming important, resulting a trend somewhat preferable to oleochemical sources over petrochemical ones. (In Japan, "Law of Product Liability" have put in force in the last uly 1).

With these as background, I will discuss sev-

eral topics regarding new surface active substances being formulated in commercial products for domestic use.

During these fifty years, the detergent industry went through several steps; its appearance, popularization with wide use of electric washing machine, exclusion of phosphate to avoid eutrophication, the first down-sizing, and the second down-sizing step to give the "20g type" products, today.

The reinforcement of washing ability in the latter steps were reflected in the reduction of the standard usage at one time per 30L washing solution; from 40g to 25g and lastly to 20g in weight, and more remarkably, the amount in volume was reduced from 133mL, then to 31mL, and now to 24mL. This improvement was realized as results of developments of new surfactants, formulation, and processing technology. Power-up in enzyme components brought by the application of "biotechnology" also have to be evaluated.

While in these years, the society around us, are largely changed. Sense in citizen-life, is also changed with their life style, reflecting eager desire for cleanliness, and pursuits for convenience. These trends are represented, for example, in the prevailed habit of "every morning shampooing" in teen-agers and preference for liquid products.

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Thus the objectives in the development activity are, in addition to the usual items, such as performance properties and economical benefits, now have to contain new factors; high functionality, biological compatibility, and fitness with the environment, etc.

As a result of increased consideration on both the environment and the safety of goods, raw materials tend to shift from petrochemicals to oleochemicals, At the same time, the form of products is shifting from solid/powder type to compact or liquid one.

Importance of fatty alcohol is greatly increasing, because of large supply of palm and palm kernel oils, and newly developed catalyzer such as Cu-Zn and Cu-Si(fixed-bed), and Cu-Fe (fluidized bed); they are replacing the old Cu-cromite catalyst.

Tertiary amines, a indispensable material for cationics, are now produced through new route via fatty alcohol.

Thus, fatty alcohol is becoming one of keystone in detergent industry, the world production of the alcohol have increased by 1.6 times in the recent 5 years.

Alcohol ethoxylate, the most important daughter of fatty alcohol, is changing her pose. Many new catalyzers have appeared as a consequence of researches, initially seeking for elimination of unreacted alcohol from the ethoxylate products.2) The new material, produced by use of these new catalyzers, called narrow range ethoxylate, has marked difference from conventional ethoxylate, in EO distribution.3 Aqueous solution of the narrow range adducts forms more clear solution at low temperature and suddenly crowds by temperature rising, at slightly higher temperature in comparison with that of conventional ethoxylates with comparable EO content. Change in the transparency of the former is very sharp, while that of the latter is familiar phenomenon that occurs in the range of temperature by several degrees. The narrow range adduct foams higher, and the foam formed diminishes sooner than in the case of the conventional ethoxylate. Thus, the former is easier in rinse when applied in detergent formulation.

Alkyl ethoxylate reacts with chloroacetic acid giving ether carboxylate. It is "soft to skin" and stable to bleaching agents, in addition, there is a synergism with other surfactants. As a result, these favorable properties appears in the formulations with other surfactants. Thus, it is formulated as a component in various detergents.

Ethercarboxylates EC RO(CH₂CH₂O)_nCH₂COONa

RO(CH₂CH₂O)_nH CICH₂COONa/NaOH

RO(CH₂CH₂O)_nCH₂COONa

R=H(CH₂)_m-,

m=4-10(Relatively poor in surface activity, used as an additive)

or 10-18(Good in surface activity)

Anionic Character < n < Nonionic Character

Scheme. 1

Alkyl polyglucosides, APG, are manufactured commercially through one of the two ways;

- (1) Hydrolysis of starch and alkylation with fatty alcohol of the hydrolyzate.
- (2) Starch is reacted with butanol and then trans-glycosylated by fatty alcohol.

Typical structures are show below.

They are excellent in foaming ability and stability. But the foam is diminished rapidly by dilution. They show good detergency especially toward oily soil. Advantage of biodegradability and low skin-irritation, must be mentioned along with the merit of biomass in origin. They are used in detergent formulations.

Among alkyl phosphates, monoalkyl ester, MAS, is preferred in commercial production.

While the maximum foaming is observed in

Scheme. 2

Dissociation Equilibrium of MAP

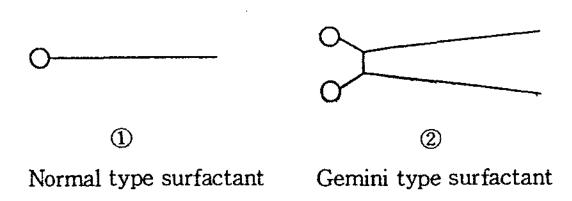
$$\begin{array}{c|c} C_{12}H_{25}O - P - OH & NaOH & C_{12}H_{25}O - P - ON \\ \hline OH & OH & OH \\ \hline C12-MAP & C12-MAP - 1Na \\ pK1 = 2.45 & pk2 = 5.60 \\ (pH = 6.8) & \\ \hline \hline & NaOH & ONa \\ \hline & -NaOH & ONa \\ \hline & C12-MAP - 2Na \\ pk3 = 7.80 \\ (pH = 11.0) & \\ \hline \end{array}$$

Scheme. 3

slightly alkaline solution, aqueous solution of MAS possesses stability over a wide range of pH. Among common anionics, prominence in "low skin irritation" of MAS is remarkable.

There are many other interesting surfactants to be mentioned, such as sugar amide, acyl glutamate, alkyl ethoxyl sulfosuccinate, and so forth, however, I like to close this discussion citing the last topics of so-called gemini surfactants.

This new class of surface active substance is characterized by the structure, just as two individual surfactants are bridged at the vicinity of each hydrophilic groups ②.



Scheme. 4

This class of compounds is first synthesized and studied by late Professor M. Okahara and his co-workers. Their extraordinary characteristics are reviewed workers. Their extraordinary characteristics are reviewed by Professor Rosen,40 and are being foot-lighted. On these surfactants, an excellent review have also published in this Journal.50 Recently, synthetic methods and the properties of this class of compounds are summarized by one of the original authors. 6) Mr. Kim, 7) in the group led by Prof. I. Ikeda of Osaka University, skillfully synthesizes the cationic counterparts of the above mentioned class of compounds, through a single step starting from tertiary amines and epichlorohydrine. The products also have excellent characteristics. Especially, because of the simplicity of synthetic route, it seemed to me that these new cationic "geminis" are more potential to practical applications.

This paper is mainly based on the oral presentation at the Annual Meeting of Korean Oil Chemist's Society, held in Seoul, Oct. 16(1994).

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