• *AOCS Commentary*

The Changing Scene in the Detergent Industry

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THE OLD ADAGE that "nothing is as constant as change" is certainly applicable in the Soap and Detergent Industry. There is constant pressure for new products and innovations to satisfy consumer demands. In addition, scientific and economic conditions are changing, and technological obsolescence is an ever present problem.

The first upheaval in the detergent industry came in the 1930's with the introduction of synthetic detergents. Syndets became economically important both in the United States and Europe only after World War II, when synthetic detergents began to take over the cleaning markets previously dominated by soap. The predominance of detergents over soap was well established during the 1950's. Now, in the sixties, we are again confronted with changes. Some of the petroleum-derived synthetic detergents have come under attack because of their lack of biodegradability. Unsightly foam on rivers, difficulties in sewage plants, and other pollution problems have focused attention on these products. While it is generally recognized that detergents play only a minor part in the overall pollution problem, the chemical and detergent industry is now engaged in an active program aimed at changing present type products to a line of biologically softer materials.

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The most important technical effort now taking place is the industry's development of more biodegradable raw materials. Their prime effort is directed toward changing the highly-branched alkylbenzene sulfonate (ABS) molecule derived from tetrapropylene and benzene to a more biodegradable structure. Over half a billion pounds of ABS are used in the United States annually. It is this material which is blamed primarily for many of the foam and pollution problems. Straight-chain alkylbenzene sulfonates are being developed as substitutes for the highly branched tetrapropylene-based detergent alkylates. These straight-chain alkylbenzene sulfonates have been proven to be readily biodegradable under proper sewage treatment conditions, and utilization of these products will greatly reduce the foam nuisance problems. Soft ABS materials are being produced by a variety of new processes. Several large plants to produce these materials are now under construction, involving the investment of an estimated 50 million dollars.

Looking beyond straight-chain alkylbenzenes, other raw materials are being developed as building blocks for surfactants. The application of the Ziegler process for the manufacture of fatty alcohols by the polymerization of ethylene is an interesting development. These primary alcohols can be ethoxylated to produce biodegradable anionic detergents for use in shampoos and liquid detergents. They differ from alcohols derived from natural fats and oils by having a different relative distribution of molecular weights. This difference allows greater flexibility in designing the hydrophobic end of the detergent chain.

Alpha-olefins are another class of new raw materials offering a potentially inexpensive approach to the synthesis of a large variety of surfactants. *Alpha*-olefins are manufactured either by wax cracking or by Ziegler catalyzed ethylene polymerization. And while *alpha*-olefin technology still is in need of further process development, a good potential exists because of the versatility of these molecules. They can be sulfated to yield alkyl sulfates, or converted to primary or secondary alcohols. *Alpha*-olefins also react readily to form primary alkyl sulfonates, epoxides, amines and many other intermediates in the manufacture of surface-active derivatives. A breakthrough in this area could open up new sources of soft detergents.

Straight-chain paraffins are in a similar position. These materials could become available in large volume, since they are intermediates in many of the processes now being developed for the manufacture of straight-chain alkylbenzenes. Here again, new technologies will have to be developed to allow attachment of a hydrophilic group onto the relatively unreactive paraffin chains to convert them into surface-active molecules. One rather imaginative approach being pilot planted is Enjay Chemical Company's application of gamma radiation to attach a sulfonate group to the chain.

Last, but not least, derivatives of fats and oils are excellent biodegradable surfactants, which have been somewhat neglected in the past, because of economic considerations. In particular, the tallow-derived materials have been ignored for use in detergent formulations by all but one major company. Changes and improvements in technology, coupled with an excess of over one billion pounds of tallow per year, might easily change the picture. Fat-based nonionic surfactants were recently introduced by several companies in this country for use as biodegradable nonionics. In Europe, where legislation requiring more biodegradable detergents will be enacted earlier than anticipated, several firms have announced the building of increased fatty alcohol capacity.

Detergents derived from coco alcohol are already playing an important role in shampoo and cosmetic formulations, and in the future their role is likely to grow more important in the general detergent product market. Thus, the use of tertiary amine oxides in light-duty liquid detergents is a recent example of a move in this direction.

In addition to fatty alcohol derivatives, other potential fat-based starting materials for synthesizing biodegradable surfactants are free acid, the methyl esters and the triglycerides. *Alpha*-sulfo fatty acid derivatives and fat-derived sugar derivatives have been reported useful in this area. In general, the synthetic possibilities of the "fat" molecule containing reactive sites at the double bond, the *alpha*-carbon atom and the carboxyl group are quite extensive. Therefore, it is likely that we will see a wider use of these derivatives in the future.

Many important changes are also taking place in the processes and technologies used by the Soap and Detergent Industry. There is a strong trend towards developing continuous manufacturing operations. A number of new continuous saponification processes are being used throughout the world, based either on the fatty acid or the natural fat route. Several continuous sulfonation and sulfation processes for the manufacture of a variety of detergent raw materials such as alkylbenzene sulfonate, sulfated alcohols, or ethoxylated nonionics have been developed and are being used successfully. Some of these new processes start with elemental sulfur, others use liquid sulfur trioxide, or the more conventional oleum approach. Finally, the move towards straight-chain alkylbenzenes has required the development of a whole series of new processes. These include techniques for the separation of branched and unbranched paraffin chains, chlorination of paraffins, and alkylation of the benzene ring.

It is not astonishing that analytical and physical testing techniques are also changing to cope with these new developments. They are also becoming more sophisticated: application of many new instrumental techniques, such as nuclear magnetic resonance, mass spectroscopy, gas chro-

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matography, or radiochemical analyses are greatly extending the field of knowledge in the detergent area. Biodegradability problems pose their own analytical headaches, requiring determinations of trace amounts of all types of detergents in the presence of many interfering substances. A considerable amount of cooperative research is now in process between various industry laboratories, government laboratories, universities, and technical societies aimed at the development of more sensitive methods and better methodology to follow the biodegradation phenomenon. Automatic analyzers are being used to great advantage in this area.

Correlation of fundamental physical properties with performance characteristics and molecular structures has been a fascinating field of study for many years. Here, too, methods of investigation are changing and becoming more elegant. Progress has been made in utilizing physical-chemical factors, such as critical micelle concentration, solubilization, and surface properties for the measurement and prediction of performance effects. New radiotracer techniques, as well as improved photometric methods are being utilized. One important field of investigation has been the elucidation of problem soils. Greater emphasis has been placed on clay soil, in addition to the more conventional oily carbon soils of the past. Good progress has been made in achieving better correlation between these new laboratory techniques with actual use conditions.

Thus we see the Soap and Detergent Industry, in an era of change and opportunity, rising to the challenge. The American Oil Chemists' Society has long been an important forum for exploring and serving the needs of this industry. Short Courses dealing with Soaps and Detergents have been held in 1952, 1958 and again in 1963. The most recent AOCS Short Course in 1963 on "Advances in Soaps and Detergents," held at the Princeton Inn, came at a very timely moment and served to focus attention on the many changes now occurring. The 1963 Short Course attracted close to 250 registrants from the chemical and detergent industry, many of them actively engaged in this field. One result of the increasing interest in this field of chemistry has been the effort by AOCS to schedule regular detergent sessions at their national meetings since 1961. These have grown steadily in importance and have attracted well-known speakers and good attendance. Even the 1962 Bond Award was won by a paper presented in the detergent session.

In coming years, activities in the soap and detergent area will continue at a high rate. As the pace towards biodegradable detergents quickens, the AOCS will be in an excellent position to focus the interest of the scientific community on these new developments. The 1964 Spring Convention in New Orleans has scheduled a special symposium on biodegradability problems.

Finally, we are in the presence of many changes. Business leaders, legislators, and scientists are cooperating in solving the problems arising from water conservation, pollution, and sewage problems. It is an exciting and challenging time for the detergent and chemical industry—full of technical opportunities.

NRA 30th Annual Convention Highlights Intensive Program

When the National Renderers Association, Inc., held their 30th Annual Convention in Hollywood, Fla., Nov. 2–6, 1963, the program was geared to valuable information for the entire industry—with speakers personalized to meet individual needs.

Research Foundation activities were reported. Expanding foreign markets played an important role via the Common Market, market surveys, and new developments in both East and West. Protecting home markets, meeting competition, the Washington Report, and new processing equipment came in for their share in the program.