A look at LAS and the environment

The following article, summarizing highlights from the International Conference on Linear Alkylbenzene Sulfonates (LAS) in the Environment held in late 1988, was prepared by Adolf L. de Jong of Unilever N.V. with the assistance of Arno Cahn, Associate Editor for JAOCS *News for Surfactants and Detergents. It is based on a talk Dr. de Jong presented on Jan. 28, 1989, at The Soap and Detergent Association's annual convention in Boca Raton, Florida.*

The International Conference on Linear Alkylbenzene Sulfonates (LAS) in the Environment, held Nov. 9–10, 1988, in Aachen, West Germany, was organized by the German Chemical Society (GDCH) in cooperation with the official Standing Committee on Soaps and Detergents (HAD) in West Germany. This committee consists of experts representing the West German government, the Federal Institute for Environmental Protection, regional water research institutions, sewage treatment authorities, universities and industry.

Representatives of the soap and detergent industry, including manufacturers of LAS, helped draft the conference program and select speakers. The conference was modeled on a similar conference held five years ago on cationics in the environment. Approximately 200 environmental experts attended the conference. All European countries were represented, as was the U.S.

The conference program consisted of four sections:

- general introduction and background information on LAS and hazard assessment.
- the environmental fate of LAS.
- environmental effects of LAS.
- summary and conclusions.

The program included a paper by W. Giger of the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG). Earlier publications by Dr. Giger had been critical of the environmental fate of LAS; these prompted the Swiss government to consider imposing substantial restrictions on the use of LAS in detergent products. However, as was announced after the conference, Swiss authorities now see no further reason to pursue this course of action.

The conference summary and conclusions were presented by L. Huber, a member of the Water Research Institute of the State of Bavaria in Munich. He is a highly respected expert on water quality management. The following are some of the key points of his presentation:

General

"The presentations of the International Seminar on LAS in the Environment have fundamentally broadened and deepened the basis for an ecological evaluation of this substance."

Required ecological profiles

"Nowadays, considerable demands such as harmlessness toward aquatic and terrestrial ecosystems must be made. These include:

- a detailed description of the breakdown pathways including metabolites, taking the various homologs and isomers of LAS (present) in water and soil into consideration.
- No Effect Concentration (NOEC) data for the protection of the fundamental functions of aquatic and terrestrial organisms consisting of metabolism, growth and reproduction.
- the behavior of LAS in soil and possible phytotoxic effects and the possible effects on the microbiology of the soil.
- the influence of LAS (and other surfactants) on the multifunctional reaction processes in ecosystems."

Everyone will recognize at once the enormous evolution of this ecological profile since we started biodegradation testing with the Methylene Blue Active Substance (MBAS) method some 30 years ago.

Consumption figures and volumes

The data presented on consumption and application of LAS clearly showed that LAS represents the second most important surfactant after soap, not only in West Germany but also in many other parts of the world.

Analysis

"This symposium has shown a great change taking place within the area of LAS analysis. The MBAS method is being reduced in importance because it is too nonspecific. Replacement by high performance liquid chromatography (HPLC) is unavoidable. HPLC makes it possible to measure LAS at a detection limit of 0.001 mg/l and also allows statements about the distribution of homologs and isomers in effluent, soils and sediments. Gas chromatography (GC) and gas chromatography/mass spectroscopy (GCMS) methods with high specificity will gain even further significance."

The old work horse—the MBAS method—may remain useful for screening purposes. However, the shift from a range of mg/l to micrograms/l in the environmental analysis of LAS has become unavoidable.

Physico-chemical behavior of LAS during sewage treatment

"It has now become possible to assess the physico-chemical process in the removal of LAS during the sewage process. The formation of precipitated Ca-LAS and the sorption process on sewage particles lead to about 35% being withdrawn from the aerobic biological degradation.

In future evaluations of the total elimination of LAS in the sewage process, the respective portions of the physico-chemical and biological processes must be held clearly separate from each other."

One of the consequences, of course, is that some LAS which is removed physico-chemically during primary treatment will be present

in its original chemical composition in sewage sludge.

Biological degradation

"The clarification of the individual steps of metabolism which lead to the biological degradation of LAS is very advanced. The enzyme systems which ensure degradation are practically described in full.

A primary and total degradability of more than 90% is proven by various tests and analytical methods in the laboratory. The evaluation of numerous data has established that more than 95% of LAS is removed in sewage treatment plants. The concentrations in purified sewage water are below 0.2 mg/l and are below the NOEC values for many important aquatic organisms."

Eco-toxicology

"The NOEC values for numerous aquatic organisms of fresh and salt water lie in the area of 0.1–10 ppm. No phylogenetic group appears to be noticeably more sensitive than others. The LC-50 values differ from the NOEC values by unusually low factors of 3–10. The conclusion can be drawn that LAS does not accumulate its toxicity.

The aquatic toxicity of LAS is modified greatly by environmental conditions. In natural surroundings as a rule, there is a distinctly lower potential for harm as there is usually a lower bioavailability. In the same way, the aquatic toxicity of LAS is lowered considerably through the change in the isomer and homolog distribution during biological sewage treatment.

With the common degree of sewage purification in sewage plants functioning in the normal fashion, effluent values of 0.2 mg/l already fall below the NOEC for very many organisms."

The safety margins for LAS in the environment were discussed at length at the conference. These margins are illustrated by a graph taken from A.R. Kimerle's paper (Fig. 1). This compares the environmental exposure concentrations of LAS with the effect concentrations on aquatic organisms. Although there is a comfortable safety margin of two orders of magnitude between the peaks of the exposure curve and those of the effect curve, the graph also indicates a small area of overlap in the two curves. This suggests that conditions could arise in which some species may respond with a toxic effect. We know that in the real environment, these conditions are unlikely to arise. However, it definitely is our task to clarify this point.

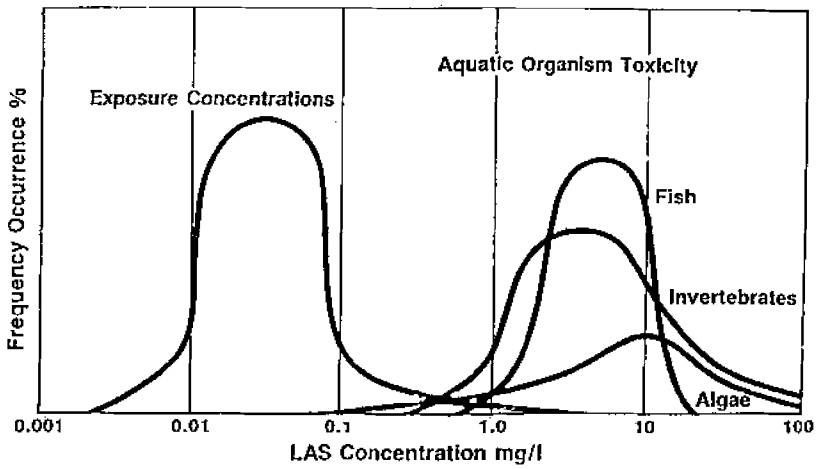

FIG. 1. LAS hazard assessment (from A.R. Kimerle of Monsanto USA).

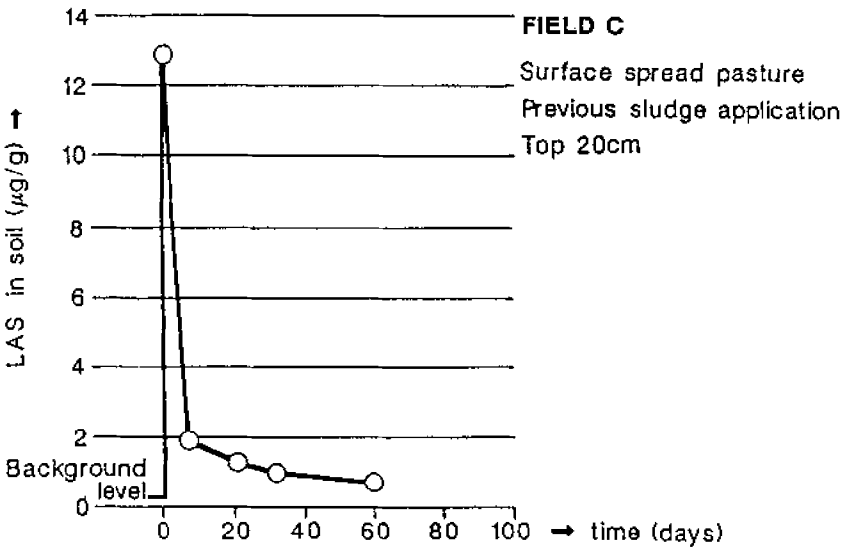

FIG. 2. Disappearance of LAS with time—Field C (from J. Waters of Unilever UK).

Behavior of LAS in the soil

"The load of LAS on sewage sludge is influenced by physico-chemical and biological elimination mechanisms.

The procedure of aerobic sludge stabilization and dry-bed treatment lead to further degradation of LAS.

LAS from sewage sludge is practically completely degraded microbiologically in the aerobic conditions in upper soil layers. The biological half-life times for this are between three to five days. No accumulation processes are expected in the soil.

With an NOEC value of 100 μg in LAS in the soil for agricultural plants and expected levels

of 7-16 μg/g of LAS in the soil, no acute or chronic damage is to be expected in agriculture."

The data presented showing rapid degradation of LAS in soil represent very recent findings. They can best be illustrated by a graph taken from J. Waters' presentation (Fig. 2). However, some questions remain concerning the low residual level of LAS in soil and the potential for LAS uptake by plants. Noting that amounts of LAS remaining in the soil require further study, Dr. Huber posed the following questions:

- What is the chemical structure of LAS degradation products affixed adsorptively to components in topsoil?
- Do accumulation processes result?
- Do agricultural plants take in LAS either intact or degraded?

Behavior of LAS in ground water

Biodegradation processes also lead to the disappearance of LAS. "Half-life periods of 15 days are typical, depending on the degree of adaptation of soil and ground water bacteria."

LAS in surface water

"LAS concentrations in important German surface waters lie on average at less than 0.02 mg/l. They undercut the NOEC values by a factor of 10^{-1}. The MBAS concentrations in important German surface waters have decreased by 92% since 1965.

Because of the need for protection of marine ecosystems, it would seem desirable to realize comparative monitoring programs in marine systems in the future."

Summary

"The results of this seminar, including the documentation produced, show that we are dealing with a basically environmentally compatible substance.

It cannot be perceived that the ecological profile of LAS should force us into substitution. No accumulation is recognizable in the various environmental compartments.

The demand for considerable lower load values in the biological stages of sewage plants will reduce the already extremely low effluent levels of LAS still further. Although more positive, this evaluation does not relieve us of the task of keeping track of the path taken by LAS and its remaining amounts in water and soil."

An announcement after the conference that the Swiss government had dropped its intention to regulate the use of LAS was reassuring—it demonstrated the conference had served a purpose. However, industry may well be advised to address the questions remaining unanswered.

Proceedings of the conference were published in English in the April/May edition of the German journal *Tenside*. Interested persons may request a copy from Keith Booman of The Soap and Detergent Association, 475 Park Ave. S., New York, NY 10016.

Industrial coatings

The market for water-borne industrial coatings in Western Europe reached $650 million in 1987 and is expected to grow an average of 7.4% per year between 1987 and 1992, according to a report entitled "Water-borne Industrial Coatings in Western Europe," completed by CHEMARK.

West Germany, France, Italy and the United Kingdom currently lead in the consumption of water-based coatings, CHEMARK reported. The research and consulting firm credited this dominance principally to the amount of electrocoating and industrial finishing done in those countries.

The report noted that the major challenges for the growth of water-borne industrial coatings include water evaporation and competing technologies.

For more information about the 300-page report, contact The CHEMARK Consulting Group, 9916 Carver Rd., Cincinnati, OH 45242, USA.

The group also has published an updated industry study on the U.S. automotive industry as a market for adhesives and sealants.

Toiletry market

Surfactants and other chemicals used in European personal care products comprised a $1.2 billion market in 1987 and are forecast to surpass $1.7 billion by 1997, according to a new study by Frost and Sullivan Ltd. of London. The report predicted that within eight years, Europeans will spend $26 billion a year on cosmetics and toiletries.

The firm said there will be sustained interest in refined natural products, which are forecast to become more expensive. The most obvious product opportunities appear to be in specialized, gentle-action surfactants, notably amphoterics and some anionics; in specialized emollients and humectants; and in sunscreens.

Overall, there were 683,000 tons of chemical materials purchased in 1987 for use in European cosmetics and toiletries; purchases are forecast to reach a level of 854,500 tons by 1997. The report noted that although the fragrance and flavors category constituted only 1% of the market by weight, it was responsible for 24% of the value in 1987. Surfactants were second in monetary value, accounting for 18% of all dollars invested.

News briefs

Akzo Chemicals Inc. has purchased the benzoyl peroxide paste business of the U.S. Peroxygen Division of **Witco Corp.** in Richmond, California. The equipment and technology is to be moved from California to Akzo Chemicals' plant in Burt, New York. Also, Akzo has agreed to purchase **Filtrol Corp.** from **KaiserTech Ltd.** In other company news, **Henry Steinberger** has joined the detergents/personal care group of Akzo's chemical division and **Timothy Saddow** has been named a sales representative for

the industrial chemicals group. Also, **Kelly Triplett** has been named business manager for the fine and functional chemicals group.

Michael F. Irwin has been elected president of **National Silicates Ltd.**, a Canadian subsidiary of **PQ Corp.** He succeeds **Jack I. Grams**, who has been named corporate vice president and general manager of the Industrial Chemicals Division of PQ Corp.

Nene A. Ackerman has been named marketing manager for specialty surfactants at **Sherex Chemical Co.**

Harold E. Vickers has been named plant manager of the Havre de Grace, Maryland, plant operated by **J.M. Huber Corp.'s Chemicals Division.** Meanwhile, **Satish K. Wason** has been named president of the company's **Chemicals Division.**

Monsanto Chemical Co. has appointed **Martha J. Burmaster** institutional and industrial market supervisor in its detergent and phosphates division.

Union Carbide Corp. has announced that its **Union Carbide do Brasil S.A.** affiliate will double its production capacity for silicone products by relocating production facilities from Cotia, State of Sao Paulo, to a new plant in Itatiba. Completion is expected in late 1989. The new plant will have facilities to produce, blend and finish high-performance products, including silicone surfactants for use in plastics, coatings, agricultural and personal care products.

J.M. Blakeway of Argenteuil, France, gave the **Society of Cosmetic Scientists 1989 Medal Lecture** earlier this year. His lecture was entitled "Directions for Cosmetic Science." Blakeway received the silver medal for his service to the society.

Lonza Inc., the U.S. subsidiary of **Lonza Group** of Basel, Switzerland, has announced plans to intensify its focus on "performance chemicals"—personal care products, plastic additives, water treatment chemicals, microbiocides, preservatives, organic and fine chemical intermediates and advanced materials. The U.S. subsidiary said it is seeking acquisitions as well as new partnerships from among its agricultural chemicals, pharmaceutical and engineering plastics customers. It also is studying the possibility of building a fine chemical plant at Bayport, Texas.

Responding to increasing surfactant demand in the southeast section of the U.S., **Stepan Co.** has announced it is expanding production by constructing a state-of-the-art 130-million-pound continuous sulfonation/sulfation unit at its Winder, Georgia, plant. The Winder plant's previous capacity was 30 million pounds. The expansion is scheduled to be completed in 18 months.

Nirma Chemical Works, a privately owned detergent manufacturer in India, is seeking a license for constructing a 60,000-ton-per-year linear alkylbenzene (LAB) plant. Other projects undertaken by the company include a 60,000-ton-per-year distilled fatty acid plant, a 4,000-ton-per-year glycerine plant, a 100,000-ton-capacity sulfuric acid facility and a project for alpha olefin sulfate production.

Kao Corp. of Japan has announced plans to invest over $110 million in its U.S. operations during 1989, including expansions of the **Andrew Jergens Co.** and **High Point Chemical Corp.** The Japanese producer of household and personal care products has opened headquarters for its U.S. operations in Wilmington, Delaware.