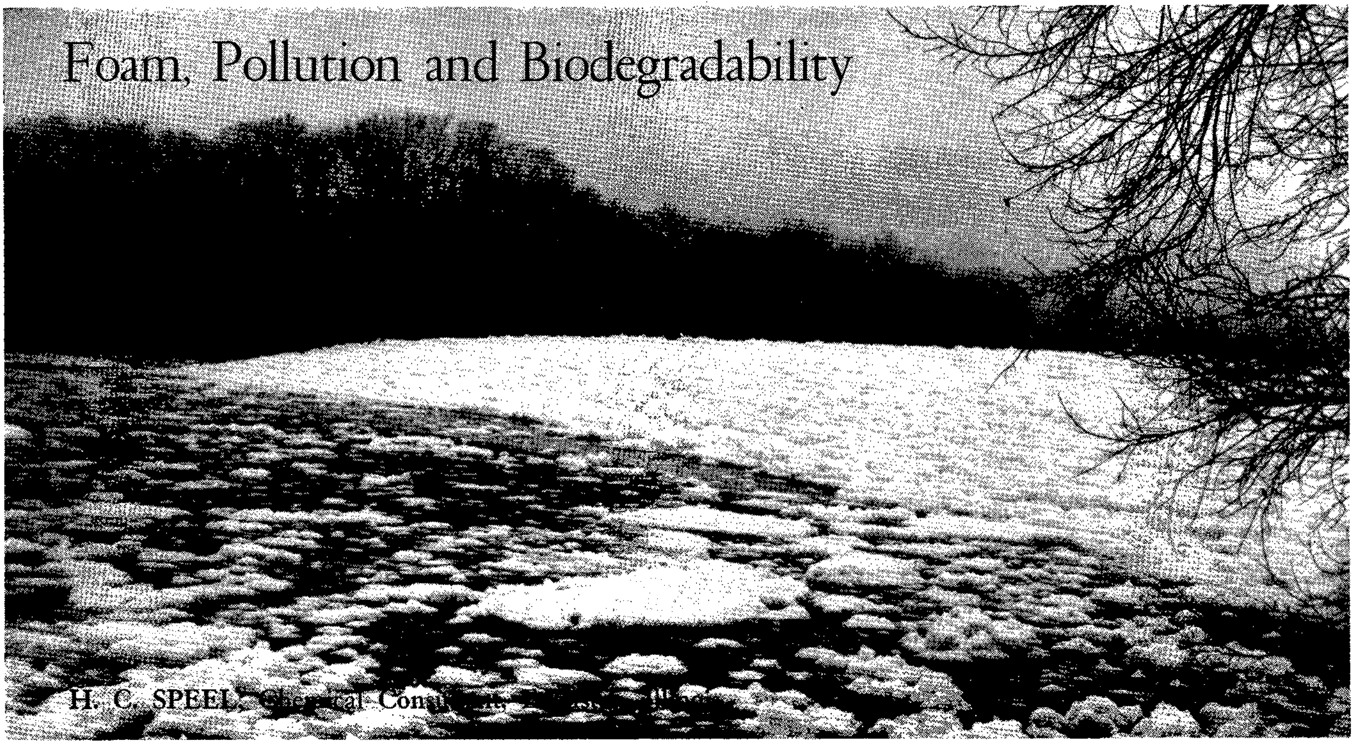
Foam, Pollution and Biodegradability



H. C. SPEEL, Chemical Con[illegible]

ISLANDS OF SUDS flowing down stream, billowing mountains of foam piling up at the foot of a dam, and visions of drinking water with a head of foam are not normal sights. But photographers are finding more and more opportunities to take pictures of such events, particularly in the crowded areas of Europe and in a few sections of our country. The effect of such pictures, with their accompanying newspaper stories, is predictable. The public and its politicians immediately blame it on synthetic detergents.

There is enough truth in this simple conclusion to justify part of the expenditures made during the past 15 years on improvement of sewage treatment and water supplies. The public wants improved products, efficient waste disposal systems, and elimination of all undesirable pollutants and contaminants from their water supplies. Even if the detergent concentration is too low to produce foam in pure water, the probability that it combines with protein wastes and/or other water contaminants to produce persistent foam is undesirable.

The transition from use of soaps based on biodegradable natural fats to petroleum-based synthetic detergents, as exemplified by the alkylbenzene sulfonates, is one of the many examples of modern technical and industrial developments. Similarly, natural fibers are losing ground to synthetic fibers that moths and bacteria will not attack. Synthetic plastics that will not rust or rot away are replacing wood and metals to an increasing extent. Man-made pesticides are being used to upset natural biological systems. These and many other synthetics are contributing to the growing problems of air, water, and ground pollution—particularly when the synthetics are not biodegradable or do not decompose under normal conditions.

Sewage and waste disposal problems are highlighted by such phenomena as the persistence of "detergent suds" and the consequent realization that a rapidly growing population is forcing people in many areas to drink water previously used and reused by others, perhaps with inadequate reprocessing or treatment. Unfortunately, many of today's major foam-producing detergents resist chemical and biological degradation of decomposition ordinarily associated with sewage treatment, river self-purification processes, and ground water travel. Public officials responsible for sewage treatment, water supplies, and public health have long been aware of the broad problems of contamination resulting from waste disposal; various studies have convinced them that where there is foam there is apt to be at least ten times as much other types of contaminants present in the same area.

The foam problem has several aspects. Persistent foam in our rivers, streams, drainage canals, and recreational areas is aesthetically undesirable, regradless of whether or not it is a sign of pollution. Committee hearings at various governmental levels, and legislative actions already underway in many parts of this country and in Europe, indicate that technical, economic, and even medical explanations and arguments carry far less weight than do psychological arguments. The public is sure the problem can be solved without losing the desirable qualities of detergents. Industry agrees, but fears that too rapid, or poorly conceived, legislative action may result in creation of regulatory agencies that will further complicate normal commercial developments.

In this connection it may be noted that Wisconsin's Detergent Study Committee has just issued a report that "refuted the misconception that alkylbenzene sulfonate was a major contaminator" (though it is the major organic detergent found in water supplies). Furthermore, the Committee's Chairman says that proposed antidetergent laws are "an unwarranted emotional approach to the pollution problem" (1). In a sense this is true, but no one can deny the need for greater efforts directed to the removal of all sources of contamination and pollution from our drinking water supplies, whether they cause foam or are invisible to the casual observer.

A Crucial Question

If legislation is to be effective and satisfactory, it must define what is meant by a biodegradable detergent. Degradability can mean susceptibility to complete decomposition to compounds such as carbon dioxide and water, or merely decomposition to a point where the detergent loses its ability to produce foam and act as a surface active agent (surfactant). Biodegradability, in either case, can be defined as susceptibility to destruction by purely biological processes. However, all surfactants are biodegradable, given sufficient time and the right set of conditions. Consequently the law will eventually have to define biodegradability in terms of time, extent, and current practice for water and sewage purification.

Standard laboratory procedures will have to be developed to relate the biodegradability of detergents to the various treatment systems, which range from aeration in streams to septic tank conditions to municipal sewage plants. The test procedures in use today include the method specified by West German law and methods developed by such

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American workers as Hammerton (2), McKinney (3), and Swisher (4). The classical River-Die-Away Test, for example, is based on seeding a sampled river water with a specific concentration of anionic test surfactant, and determining the concentration at intervals by the widely used methylene blue method or a variant thereof. Unfortunately, even though a surfactant may disappear as monitored by methylene blue (or methyl green) during biodegradation tests, this gives no information beyond the fact that it has been altered enough to destroy its surfactancy properties and its response to methylene blue; how far it has progressed toward complete conversion to carbon dioxide, water, sodium sulfate, and microorganisms is left indeterminate.

Alkyl Benzene Sulfonates (ABS)

It is generally agreed that roughly 75% of all household detergents contain some ABS (5). That is why practically all studies (and legislative action) start with an ABS type material. Most of this ABS is produced by condensing propylene (typically the tetrapolymer) with benzene, followed by a distillation cut to yield a reproducible product. The resulting alkylate is then sulfonated to produce a detergent. Every molecule of ABS does not have the same structural arrangement or molecular weight, but it consists of numerous closely related isomers or variants having the same general properties. The alkyl chain, derived from propylene, is branched rather than straight and the benzene is attached at various positions along the chain.

Most investigators are of the opinion that the highly branched isomers of the alkyl chain are responsible for the failure of the ABS molecule to degrade rapidly enough under treatment conditions. Much of the research effort devoted to finding an equally low cost and more degradable detergent has been directed therefore to development of a straight-chain hydrocarbon for use in making a straight-chain alkylbenzene. At least eight American firms are known to be active in research on alpha olefins, either derived from ethylene by a Ziegler-type polymerization route or from paraffin-cracking routes (5). Another source of straight-chain alpha olefins is natural oils and fats, but apparently insufficient research time has been spent on attempts to make them economically, at least for detergent use.

Investigations on the biodegradability of the straight-chain alkylbenzene sulfonates indicate a definite improvement in rate of biodegradability over the rates encountered with branched-chain ABS products. Compounds with strictly linear side chains and those containing one or two methyl branches on the carbon atom attached to the benzene ring are readily biodegradable (3,4). Furthermore, the greater the distance between the sulfonate group and the most remote end of the alkyl chain, the greater the speed with which degradation proceeds. Even so, they do not degrade as rapidly as the straight-chain alkyl sulfates, as indicated in Figure 1.

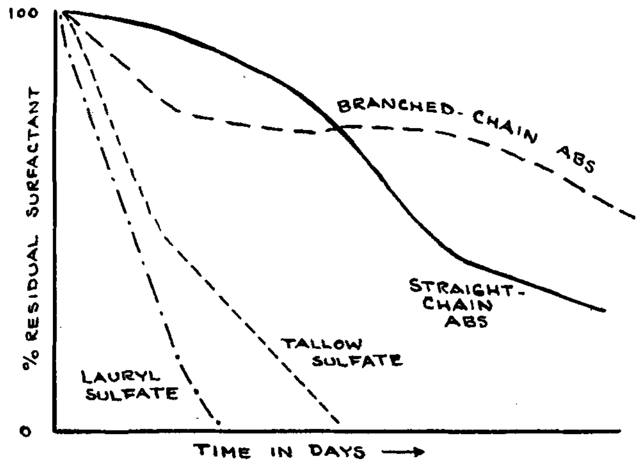


FIG. 1. Schematic river-die-away test for detergent biodegradability.

Alkyl Sulfates

The straight-chain fatty alcohol sulfates, whether derived from natural alcohols, natural fats or oils, or from ethylene by Ziegler-type processes, are generally considered to be completely biodegradable. Sodium lauryl sulfate, for example, disappears in less than three days under River-Die-Away Test conditions that show it takes about ten times as long for a straight-chain alkylbenzene sulfonate, when starting with a concentration of 20 ppm active surfactant. At the same time, tests with a standard branched-chain ABS showed that its concentration was still appreciable at the end of thirty days. Such tests are indicative, but not conclusive for reasons suggested earlier and in various published studies.

A switch from branched-chain ABS detergents to fatty alcohol sulfates, or even to normal soaps, is not necessarily the simplest, cheapest, and most satisfactory answer to elimination of foam from our rivers, streams, and ground waters. Apart from the fact that complete elimination of detergents would eliminate only 5–10% of the organic residue from a sewage treatment plant (leaving more than 90% of the pollution problem unsolved), it is certain that the public will not want to pay more or lose the efficiency it has gained from several decades of detergent research.

Other Detergent Possibilities

The alkylbenzene sulfonates and alkyl sulfates have the largest share of the present market, but do not have it to themselves. The nonionic polyethoxalated alkylphenols and their sulfated and sulfonated derivatives, the various alkanolamides, the alkyl methyltaurides, the tall oil ethoxylates, and other lesser known types find extensive usage in the formulation of both household and industrial detergents and cleansers. The household market alone consumes close to 900 million pounds of 100% active surfactants annually, and ABS consumption amounts for no more than 560 million pounds of that (5). Indeed, this ABS figure may be noticeably smaller if more conservative estimates are employed, and, I believe they should be. In any event, it is obvious that detergent makers consumed about 200 million pounds of surfactants other than ABS and fatty alcohol types.

There is no known acceptable method for determining the biodegradability of nonionics. However, using the BOD and Warburg techniques, Sawyer et al. (6) found that straight-chain polyglycol esters and amides were readily degradable, while the branched-chain alkylphenol derivatives were more resistant. They also found that for a given hydrophobe, lengthening the polyglycol ether hydrophilic group resulted in poorer degradation. Obviously, the outlook for present day, branched-chain, alkylphenols is much the same as for the branched-chain alkylbenzenes. On the other hand, the prospects for ethoxylated fatty alcohols and other straight-chain base nonionics should be brighter.

A privately published report (7) indicates that the ethoxylated lauryl alcohol sulfate is midway between the lauryl and tallow sulfates in its biodegradable characteristics, as measured by a River-Die-Away Test. It is worthy of note that these, like virtually all types of detergents, show the higher molecular weight species degrade somewhat more slowly than the lower molecular weight species.

A factor not often mentioned in conjunction with the problems of finding rapidly degradable detergents is the need to maintain foaming ability as well as detergency under normal conditions of use. The housewife has been encouraged to believe foaming ability is directly related to detergent efficiency, a fallacy but an often used selling point. Detergent compounders have learned how to handle the formulation of high and low foaming products, and undoubtedly will have to reformulate when they can no longer employ the high-foaming branched-chain ABS as a base. It is reasonable to assume that a high-foaming, biodegradable type detergent will have a market advantage, except in certain types of washing machines. Similarly, other physical properties such as emulsifying and soildispersing ability, solubility limitations in the presence of builder salts, hygroscopicity, odor, taste, and toxicity levels will be of great importance in determining which products will be used in biodegradable detergents of the future.

During a recent symposium on detergents it was suggested that there is a tremendous opportunity for specialized detergents and other surfactants that are biodegradable—when the term is legally defined. The dairy industry, for example, offers a real challenge. Sugar esters, now being produced on a small scale for specialized surfactant usages, are still far too costly for household and industrial detergent applications. Synergistic alkyl amine oxides, such as the apparently biodegradable lauryl amine oxide, will certainly find growing markets in liquid detergent products. The future use of hydrotropic agents such as xylene and toluene sulfonates is problematical because their primary reason for major volume usage has been their ability to solubilize the branched-chain alkylbenzene sulfonates in liquid detergent formulations. Alkyl sulfonates, alkane sulfo-amides and their ethylene oxide condensates, prepared from straight-chain olefins or from aliphatic hydrocarbons (the kerosene and white oil fractions of paraffin base petroleums) conceivably could become important again. The list of possibilities appears endless, particularly since no one really knows as yet how stringent the legal requirements for biodegradability may be.

Industrial Surfactants

Most of the attention given to detergent contamination problems has been devoted to household detergent products, though surfactants of all types enter our industrial products and processes and contribute to pollution. Almost every industry uses surfactants in manufacturing or processing operations (8). Since only 50–55% of all surfactants consumed in this country appear as ingredients in formulated household detergents, this problem of waste disposal will affect all industry, not just the producers of household detergents and those industries that dump waste into streams and rivers.

Fortunately for most industrial users there is little need for detergents with high foaming properties. Furthermore, their specialized needs account for a consumption of close to 500 million pounds of surfactants, based on animal and vegetable fats and oils. While such uses have not been consuming anywhere near as much tallow and vegetable oils as did the soapers of a generation ago, they do indicate that petroleum-based synthetics have not been able to take over completely. With evidence mounting up that it is branched chains of alkyl aryl sulfonates and ethers that most strongly resist biodegradation, it becomes even more logical to expand research on the natural fats and oils. Indeed, there is a well-founded rumor that straight-chain olefins can be produced from abundant fatty acids at a cost of about ten cents per pound. This is competitive with estimated eventual costs of petroleum-derived straight-chain olefins.

"There is more than potential detergent markets behind the zooming commercial interest in alpha olefins," according to Stirton of California Chemical Co. He estimates markets of two billion pounds per year are open to penetration, with only 25% of that being in the detergent alkylate field. This threat to many existing products based on fats and oils should not be taken lightly. Similarly, the threat of elimination of detergent alkylate markets for propylene poses a problem to its current producers. That is why this is a time of tremendous opportunities for research and development chemists.

The West German Situation

Legislation enacted in West Germany will require their detergent makers to switch over by October 1, 1964, to products which are at least 80% biodegradable. The test, set up by law, is run in a miniature sewage treating plant—utilizing a simulated, activated sludge system. Its chief drawback is its complexity and size.

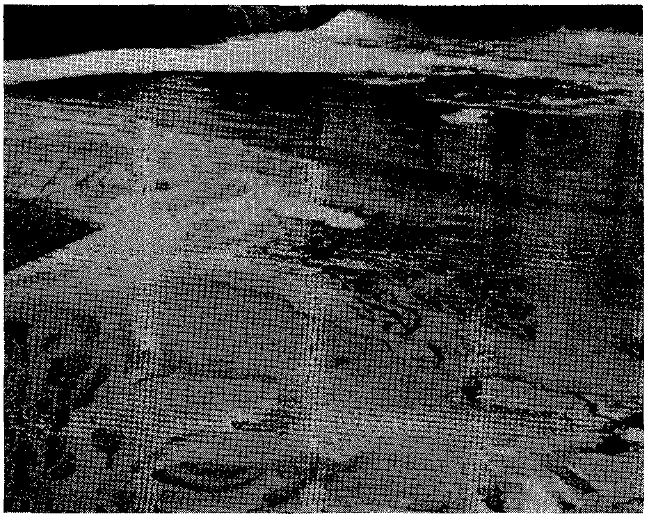
The Germans claim foam is mainly a nuisance and that a far more serious problem is the unseen pollution. There is talk of raising the 80% biodegradability requirement to 100% and adding a nontoxicity requirement. According to one spokesman for an ABS producer, if fatty alcohol prices come down, then fatty alcohol sulfates with their 100% biodegradability might be the detergents of the future (5). The one thing sure is that the race is under way.

This pileup of foam appeared on the Rock River, Ogle County, Illinois, last March. Foam in the detergent-bearing water, generated as the river spilled over the Oregon dam, reached a height of 40 feet above the water.

Results of separate tests for degradation and for toxicity to fish, recently revealed by West German investigators, show that the ten to thirteen carbon isomers of straight-chain ABS sydnets are optimum for both degradation and toxicity. The mid-chain ring position isomers start to degrade later than do the C-2 position isomers (9). Work of this type is also being carried on in the United States (10,11).

Discussion of Test Methods

Direct colorimetric measurements, using a dye capable of forming a detergent-dye salt, are customarily employed for quantitative analysis of anionic surfactants at or below a concentration of 10-20 parts per million. The methylene blue method (12,13) is the best known one, but the methyl green dye technique of Moore and Kolbeson is also used (11,14). Both organic and inorganic compounds interfere with the determination, and positive errors are much more common than negative when determining anionics in contaminated water. Consequently, standard procedure calls



This once pleasant brook a few miles from Kansas City, Missouri, receives waste water that has been processed by a conventional water treatment plant. The foam you see demonstrates the inability of such treatment plants to remove modern detergents. Photo: Courtesy of Midwest Research Institute.

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for use of calibration curves based on reference material.

Mixtures of microorganisms are ordinarily used in studies on biodegradability, these being derived from sources such as river water, activated sludge, sewage, soil or air. The general microbiological makeup of mixtures from these sources seems to be fairly constant, according to Swisher (10). Various environmental conditions are reported in the literature, including both static and dynamic types. The concentration is determined at intervals of perhaps 24 or 48 hours, using the methylene blue test, or a modification thereof. A qualitative estimate of degradation can also be made by observation of changes in such surfactant properties as surface tension or foaming action as the test progresses.

Measurement of the oxygen uptake of the system is also used, because the overall process is oxidative (2,10). However, the technique is limited by the amount of dissolved oxygen which is originally present in the initial sample. This limitation can be avoided by use of the Warburg respirometer, but even so the conclusions may be subject to considerable uncertainty.

Gas chromatography has been very useful in the study of ABS degradation, provided the sulfonate group is first removed (15). The infrared process, though lengthy, is quite specific when applied to raw water samples only, but not to sewage or industrial wastes (12).

Summary

The publicity on water contamination by detergent foams is awakening the public to the growing problems of air, water and soil pollution by all types of waste materials. While detergents account for only 5–10% of total dissolved organic matter after conventional sewage treatment, their foaming tendency highlights their presence. Legislative action therefore seems inevitable.

The branched-chain alkylbenzene sulfonates and the branched-chain alkylphenol polyglycol ethers are generally considered unsatisfactory from the standpoint of biodegradability. Straight-chain alkylbenzene sulfonates are biodegradable, though tests to date indicate the rate of degradation is much slower than that of the fatty alcohol sulfates. In general, the lower molecular weight species of each detergent type produces more foam on agitation, but degrades more rapidly than the higher molecular weight species.

The extensive research work on biodegradables may open new usage potentials for both animal fat and vegetable oil derivatives. It has already led to development of alpha olefins derived from petroleum sources, and unless producers and processors of agricultural fats and oils work equally hard on developing their own derivatives, the petroleum-based raw materials will take over even more than soap's former detergent market. Right now, the natural fats and oils seem to have a built-in advantage of biodegradability to answer the basic problems of detergent suds and stream pollution.

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• New Products

Monsanto Chemical Co., St. Louis, Mo., is now producing its new, highly active Type 11 vanadium catalyst for use in contact sulphuric acid plants. It is available in commercial quantities. This material is reported to be about 30% more active under the overall conditions met within a converter system and about twice as active as the older type catalyst in the final reaction zone where gases are encountered that are predominantly sulphur trioxide.

Science Products Corp., Dover, Del., has developed a heat flux meter ("Q-Gauge"), designed to fill an important need in the chemical processing industries. This gauge is made of the same material as the system being tested, and so perturbations introduced by dissimilar material are eliminated.

Teknika, Inc., Hartford, Conn., is now producing a continuous defoaming machine, the Sontrifuge, which combines centrifugal force with sonic energy to defoam and deaerate up to 500 gal of liquid output per minute.

Beckman Instruments, Inc., Spinco Div., Palo Alto, Calif., has announced a new research instrument, the Spectrochrom™ Analyzer, that automatically separates, analyzes, charts, and collects biological liquids such as proteins, peptides, and nucleic acids. It is designed to provide complex biochemical analyses on a routine basis with little or no operator supervision during runs.

Northo Chemical Co., Painesville, Ohio, has announced the development of a new wax, Norwax 65, which has all the characteristics and appearances of genuine Beeswax—with pleasant odor, tacky, and excellent emulsifying qualities. It is said to be non-toxic, contains no mineral waxes, is made entirely of fatty oils, and is soluble in most organic solvents.

American Balance Corp., New Rochelle, N. Y., now has available a newly engineered single pan balance called "Quik-Chex." In addition to providing nine exclusively advanced design features, Quik-Chex also features rapid and simplified operation, including three-way access in door and sliding panels, hinged cover, and finest quality optical system.

Packard Instrument Co., Inc., LaGrange, Ill., has announced a new line of multi-channel analyzers, marking the company's entry into the important field of nuclear instrumentation for the physical sciences. Analyzers of 400, 1024, and 4096 channels will be manufactured under license from Intertechnique, S.A. (France). Complete analyzer accessories permitting multiple input capabilities, spectrum stripping facilities, and a selection of digital output devices will also be offered.

Mechrolab, Inc., Mountain View, Calif., now has available a new Model 302 Vapor Pressure Osmometer which claims to permit rapid, accurate molecular weight determinations with polyolefins and other low-solubility materials—operating at temperatures up to 130C.

Research Specialties Co., Richmond, Calif., announced the design of a compact Gas Chromatograph (Model 62) for low basic cost, with emphasis on the versatility and flexibility obtained by use of a large variety of accessories. The basic instrument is equipped with a sensitive hydrogen flame ionization detector and permits manual temperature programming. It is also available as a dual flame ionization instrument which automatically compensates for baseline drift, thereby permitting high temperature programming and giving high sensitivity to trace components.