ress, or lack of progress, in abating pollution. Such criteria are to be: 1) based on information now available or readily obtainable; 2) expressed in terms that will be understood by laymen and professionals alike; and 3) expressed in such terms as will have fairly universal acceptance. It will be most interesting to learn what this Committee recommends based on present facts. It will be even more interesting to observe the changes in these recommendations as more facts and better analytical techniques are developed.

Out of all this interest in the matter of water quality standards for water pollution control should come a more enlightened use of the Nation's waters. Once we can clearly understand *why* abatement in necessary, the *how* is more energetically sought, and the *cost* is more palatable.

[Received June 17, 1964—Accepted September 11, 1964]

# Measurement of Biodegradability

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## Introduction

FOR THE PAST TEN YEARS OR SO, it has been common practice to use the nickname "ABS" for tetrapropylene derived alkyl benzene sulfonate. If the same ABS nickname were used now for straight-chain alkyl benzene sulfonate, it would add chaos to the confusion. Since straight-chain alkyl benzene sulfonates are in fact "linear alkylate sulfonates," the Research Committee of the Soap and Detergent Assoc. has adopted the abbreviation "LAS" for the commercial replacement of the present workhorse of the detergent industry "ABS." These technical nicknames will be used in this discussion.

Biodegradability is key to this new development and its measurement is an essential part of the program. In this review of the subject of the "Measurement of Biodegradability," the approach will be that of technical people involved broadly in the water pollution abatement program rather than that of the biochemist who has the extremely important responsibility of developing appropriate methodology.

The discussion will: 1) Define biodegradability; 2) review test procedures with broad brush strokes, including the test which has been adopted in the German Regulations; 3) review some of the research in depth which had established the biodegradability of LAS even before the methods used in such research had been described in publications; 4) discuss biodegradability as one of the characteristics which fits into the picture of over-all detergent performance, and 5) conclude by briefly pointing out the contribution of LAS to the water pollution abatement program.

## Definition of Biodegradability of Surfactants

Biodegradability is the susceptibility of a surfactant to the common processes by which organic matter in waste water is decomposed by bacterial action. A pure chemical is either biodegradable or not, but the rate of breakdown varies among such pure chemicals. In mixtures of pure chemicals, rate of degradation and completeness both must be considered. Degradation, to a point where there is a loss of surface-activity, removes "detergent" properties. Breakdown to carbon dioxide and water represents the theoretical maximum. A realistic goal for the disappearance of surfactants in any given treatment system would be to match, substantially in a quantitative manner, the disappearance of the usual waste organic matter in sewage or surface streams, or natural organic matter in surface streams.

Biodegradability cannot be an absolute value like mol wt, but like the boiling point, it depends on the conditions under which the determination is made. For example, in sterile water there is no degradation of even "completely biodegradable" substances. In a similar manner, in a ground water suitable for drinking purposes, degradation does not occur. Even in some waste treatment systems such as cesspools, septic tanks and primary sewage treatment plants, there is little or no destruction of mildly resistant organic matter, including tetrapropylene benzene sulfonate, although some breakdown of readily degradable substances does occur. In activated sludge treatment, the amount of the destruction of organic matter will vary, as does the disappearance of ABS which probably averages around 50%. In river waters like the Ohio, over a period of 30 days or so, as much as 75% of ABS and better than 95% of LAS is degraded.

## Analytical Procedures for Biodegradability

No matter how you approach the problem, it is not easy to measure biodegradability. Ludzack and Ettinger (1) emphasize that bench scale tests should approach treatment plant conditions as closely as possible. This is particularly true of a method to be used for regulatory purposes, as in Germany. Because of the nature of regulatory processes, a method for this purpose must have extremely good reliability and precision. Also, if the regulatory agency is to do a good job, it must be able to make an adequate number of determinations without too great an expense to the public. For quality control purposes, inexpensive methods should be found from which results are obtained as quickly as possible.

For research purposes, the river die-away procedure is extremely useful and as basic as it sounds. Its use was reported by Hammerton (2) in England, and by Sawyer in this country (3). It has been used extensively as a research tool for the measurement of biodegradability of anionics and non-ionics (4–10).

The details of the river die-away and other methods as used in our laboratories, which have been reported by Weaver (10), are as follows:

*River Die-Away.* A liter of freshly-sampled Ohio River water, seeded to a concn of 20 ppm of the test substance, is added to a new 0.5-gal mason jar equipped with a screw cap. A magnetic bar is placed in the jar and after stirring for one min a sample is drawn off for immediate surfactant analysis. After sampling, the top is screwed tightly on the jar, which is placed under quiescent conditions at normal room

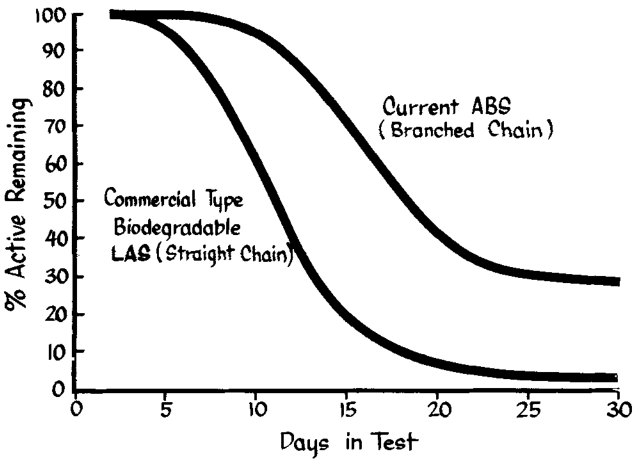


FIG. 1. Rate of degradation of current ABS and new biodegradable LAS in Ohio River water.

temp until the next sampling. Sampling continues periodically for the duration of the test; at its conclusion, the solutions and jars are discarded.

Sampling for analyses by the methylene blue test is carried out as frequently, or infrequently, as is necessary to establish a die-away or disappearance curve. Generally, this will be based on experience. For regular ABS, sampling can be limited to every two or three days.

The advantage of the river die-away test is that it gives both the rate as well as the completeness of disappearance of the test substance. Some of the other tests are limited to measuring the degree of disappearance. The disadvantage, of course, is that while a given river can be used successfully, ever river will not necessarily yield the same results. In Figure 1, which is typical of results obtained by this method (1), LAS is degraded faster than ABS, and 2) whereas ABS produces a residue of ca. 25–30% which is essentially nondegradable, LAS produces practically no nondegradable residue.

A modification of the river die-away technique, which in its simplest form uses raw river water, uses distilled water to which activated sludge is added (11). The authors find that this speeds up the test and increases its effectiveness. The differences between LAS and ABS reported in this test are comparable to those with the river die-away test.

*Batch Activated Sludge.* In the activated sludge batch-type test used in the authors' laboratories, each batch-type unit is fitted out with a coarse dispersion tube for aeration, and is operated daily for both a 6-hr and a 16-hr aeration period. Automatic timers cut off the air supply so as to allow one hr of settling after each aeration period, before withdrawing three liters of supernatant and replacing with new feed. Ten ppm of test surfactant is added in the feed, which is a combination of raw and settled sewage. In these units, as is shown in Figure 2, 50–60% of ABS and better than 90% of LAS is degraded during the 6-hr aeration period. Slightly more is degraded during the 16-hr period. These results are comparable to what has been reported from other laboratories, and, very importantly, from the field.

*Other Tests.* Semi-continuous, and continuous activated sludge laboratory tests also have been used by some investigators. Septic tank and trickling filter test procedures have been reported (10). Also coming into wider use is a more rapid test utilizing a microbial culture, obtained from activated sludge which is grown in a suitable medium. The surfactant under study is then added to this medium and a die-away procedure is followed (12).

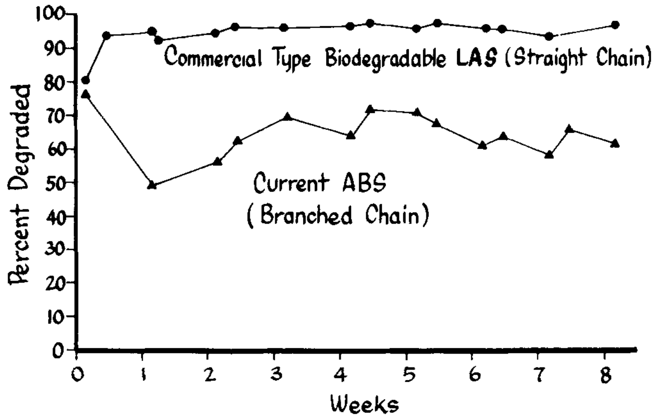


FIG. 2. Degradation of current ABS and new biodegradable LAS in 6-hr batch fed activated sludge test.

*German Test.* The German laboratory test method (13) established by regulations under law is of interest. Products to be suitable for use in Germany after Oct. 1, 1964 are required to be at least 80% "biodegradable" by this method. This is a continuous activated sludge method, and 21 days of successive operation (with somewhat constant degradation values and trouble-free operation) showing an average daily degradation of over 80% are needed to meet the 80% biodegradability requirement. This law is of more than incidental concern to detergent manufacturers in this country because it applies to U.S. brands sold in Germany through PXs and commissaries, and to specification type products sometimes described as "troop issue," purchased by the armed froces and used by them in Germany.

The lab-scale activated sludge sewage treatment unit is fed continuously with a completely synthetic sewage. An interesting aspect of the test is that no bacterial seed is added at the beginning of the test. The operation of the equipment is started, allowing the seed to develop from airborne bacteria which accumulate. While the German test method is capable of measuring the biodegradability of surfactants per se, the regulations apply only to finished product compositions.

The test operates by adding finished product to the synthetic feed at the start of the test, at a concn of 20 ppm on a surfactant basis. The aeration period is three hr. A diagram of the equipment (14) is given in Figure 3. Figure 4 shows typical results obtained for LAS and ABS in this test. Better than 90% of LAS, but less than 20% of ABS, is degraded. The first few days are a preliminary adaptation period during which acclimatization occurs, after which level operations or a steady state is obtained. A 10–20 day preliminary adaptive period has been required, generally. Daily determinations of surfactant into and out of the unit permit daily calculations of percentage removed. If the average of these daily results over a 21 day period give a final single figure of over 80% degradation for the product, it may be sold in Germany. Obviously, this test will require wise judgment on the part of technical people operating the test when results close to the 80% minimum are obtained on a product. While this is true of any regulation, it appears that in a test of this sort more than the usual number of difficult decisions with resulting arguments are to be expected.

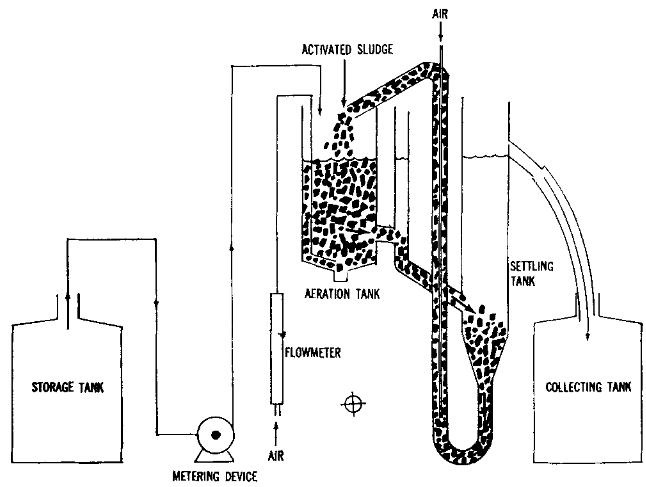

FIG. 3.

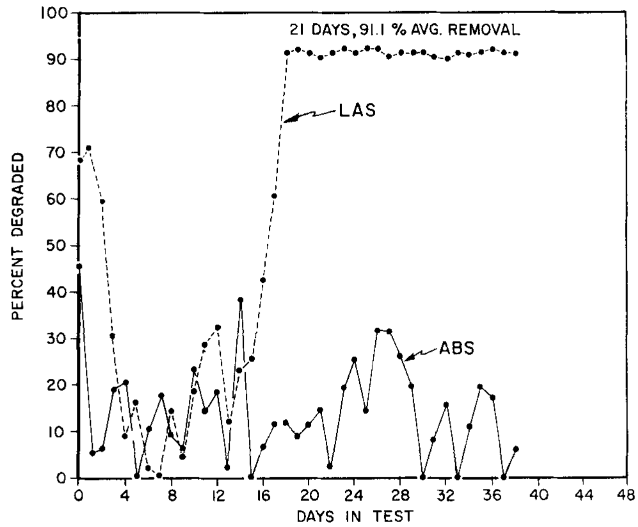

FIG. 4 LAS and ABS biodegradation in German test method.

Also of interest, is the fact that the units in the German equipment are large. The aeration tank has a three-liter capacity, and one liter of synthetic sewage is fed to it every hr. The preparation of 24 liters of feed daily for each test unit as required by the regulations requires manpower, and the expense is considerable. It is especially so if the test, as can easily happen, takes 40 days or so. A single determination by the test, on the basis of conditions in this country, will cost several hundred dollars.

It will be extremely interesting to follow the technical aspects of the experience of the Germans with their test method. It certainly is not at all clear how the German regulatory people can be expected to do an efficient, economical and adequate job of policing brands in grocery stores using the methods which their regulations require.

### LAS Biodegradability Established by Research in Depth

Research knowledge acquired and accumulated over the years, unlike detergents themselves, does not go down the drain. Thus, the knowledge developed around straight-chain materials in the fats and oils and petrochemicals industries was brought to bear on the problem. The early work of Hammerton and also of Sawyer and others, pointed out that straight alkyl chains are more readily biodegradable than branched chains. It is most significant that while straight-chain materials have long been available in quantities suitable for experimental purposes, many such surfactants made from them were completely unsatisfactory for use in washing products. For example, sucrose esters are too hygroscopic for use in granular type detergent products. Until the recent breakthrough with LAS, none of the straight-chain surfactants could be produced commercially except at costs so high as to prohibit their use.

Yet, with straight-chain materials available in the laboratory, a potential solution to the problem was on the horizon. To produce LAS economically and in the larger quantities necessary for testing in finished products required the application of modern technical knowledge. This in itself was a most difficult development problem. Intimately tied up with this program was the research in depth necessary for making "Measurements of Biodegradability" on the new potential raw materials. This research is well documented by Swisher (4,5), Allred et al. (12,15), Sweeney and Foote (6), Fuhrmann et al. (7), Vath (8), Blankenship et al. (9), Weaver (10), Borstlap and Kooijam (11) and others, and the methods used have been spelled out in detail. As a matter of fact the biodegradability literature is beginning to be somewhat repetitive, which is all to the good in this situation for three reasons: 1) The results of research can only be *interpreted* if the details of the methodology are carefully reported; 2) the verification of the biodegradability of LAS by the various methods and by repetition is important; and 3) there is a real need for education in this field, and education requires repetition.

All of the studies referred to considered basic questions such as, "Is the surfactant in question biodegradable?", or, "What is the mechanism of the process of biodegradation?" Thus, these studies are replete with evidence of the much greater biodegradability of LAS compared to ABS.

As previously mentioned, in Britain Hammerton (2) reported that straight-chain ABS was more degradable than branched chain. A few years later the British made a field trial in the area served by the Luton Sewage Works (16) in which a surfactant with greater straight-chain character than ABS showed a definite improvement and pointed to the possibility of further elimination of branching as being worthwhile. For example, the level of methylene blue active substance in the River Lee (17) which increased from about 1 ppm in 1950 to 3–4 ppm in 1958 fell sharply from 4 ppm to 2 ppm during the trial of the test product which replaced ABS.

Present LAS surfactants now being put into commerical use in this country are more biodegradable than the test product used in the Luton experiment and they also exceed the 80% biodegradability limit set as a minimum in the present German regulations.

Also on the international level, the National Institute of Water Research of the South African Council for Scientific and Industrial Research in its annual report for 1961, reported results (18) of a small-scale activated sludge type test in which several straight-chain ABS's gave improved biodegradability over polypropylene-derived ABS materials.

Briefly to touch on septic tanks, a prototype lab scale experiment showed that surfactant residues would be reduced to tolerable levels in a septic tank tile field system when ABS was replaced by LAS

(19). These conclusions are supported by work soon to be published by McGauhey at the University of California.

The latest report to be received is of a field trial completed this year (20) in this country in which the disappearance of ABS and LAS were measured in an efficient sewage treatment operation. Whereas ABS degradation was insufficient to reduce the residues in the plant effluent to a point where foaming did not occur, under the same conditions when LAS replaced the ABS, the sewage plant effluent did not foam.

A hard working and active technical committee of the Soap and Detergent Assoc., composed of experts on detergents and microbiology, is studying the more promising test methods for use in measuring biodegradability. Such studies should yield a greater understanding of the variables encountered and the significance of the values obtained in various methods.

A mechanism to establish or control biodegradability is based on the fact that any pure surface-active agent or any mixture of surface-active agents possesses constant biodegradable characteristics when exposed to identical conditions at different times. Thus, if a commercial mixture is readily reproducible, it will have constant biodegradable characteristics which are measurable, like the boiling point. The chemical characteristics of such mixtures can be the basis for specifications which assure an established degree of biodegradablility in the surfactant mixture. This mechanism is useful to suppliers and purchasers for the purpose of controlling biodegradability of any surface active agent of interest. In the sense that this mechanism controls biodegradability, it also is a means of measuring biodegradability, and is a chemical specification for biodegradability.

Chemical specifications are historically the mechanism by which manufacturers of finished detergent products communicate their needs to raw material suppliers. Even with a substance as widely used as ABS, performance-type specifications are not in use and, thus, it is conceivable that it would not be necessary to have a performance specification for biodegradability.

## Where does Biodegradability of Detergents Fit into the Picture of Over-All Detergent Performance?

Biodegradability has become a new and most important criterion for the products of the detergent industry. Some circles, because of preoccupation with biodegradability, overlook the importance of the traditional properties of detergents which make them useful for their primary purposes of doing a good cleaning job. It is axiomatic that if biodegradability can be included without sacrificing other characteristics, this is the correct approach. It is also axiomatic that a biodegradable material will not be useful to the detergent industry unless it produces finished type products which: a) do a good job of cleaning; b) can be formulated so that they will reach the consumer in a satisfactory condition; and c) are economical. There are hundreds of surface-active agents which have been produced on a laboratory scale, have been well defined chemically, and are potentially available commerically at varying costs, almost always at a higher price than materials now in use. Some of these are biodegradable. Of all the surfactants that are available, only a relatively few are suitable for use in the wide range of types of products the detergent industry offers to the consumer. It might be said in this case that "Many are called but few are chosen."

Although biodegradability is an important factor, the consumer should not be forced to make sacrifices in cleaning effectiveness, because: 1) detergents are only a relatively small part of the total pollution problem; and 2) even the total pollution problem does not currently, and in the next few years is not likely to, affect the great majority of our population. In the metropolitan areas where most of our population is located, the community services of sewage treatment and water treatment combine to protect the population from all aspects of the total water pollution problem. On the other hand, the phases of the problem experienced by the much smaller segment of the population in communities without such services, and the future impact of the total pollution on the population in general cannot be overlooked. As Abel Wolman and others have pointed out on more than one occasion, there is no immediate water crisis and technological solutions are available at a cost wherever they are needed. The detergent industry's contribution of more readily biodegradable detergents is a technical solution to the part of the problem in which it is involved.

## LAS, a Contribution to the Water Pollution Abatement Program

In conclusion, it should be emphasized first that the two goals of biodegradability and effective performance are attainable, and, secondly that the measurement of biodegradability plays an important role in the detergent industry's effort to do its share in cleaning up the nation's water supplies. Unfortunately, the hue and cry about "hard" detergents overemphasizes a minority role and misses the overriding issue of gross pollution. The gross pollution problem will remain even after the detergent industry's conversion is completed. A program to effectively control total pollution will need, in addition to biodegradable detergents, more sewage treatment plants, and improved methods for treating both sewage and water. The success of a program of this nature depends on good understanding of all aspects of pollution and this discussion of the "Measurement of Biodegradability" is offered as a contribution to such understanding.

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[Received May 11, 1964—Accepted September 11, 1964]