TABLE IV

CCD Analysis: Fatty Esters Reduced with $Ni(acac)_3$

Analysis	Percent			
	Stearate	Monoene	Diene	Triene
Methyl linoleate				
Weight	9.0	75.3	15.0	......
trans (as elaidate)	....	38.8	83.1	......
Conjugated	....	......	0.0	......
Conjugatable (alkali)[a]	....	......	45.5	......
Methyl linolenate				
Weight	1.0	15.1	59.8	24.2
trans (as elaidate)	......	32.1	57.4	68.2
Conjugated	......	......	0.0	0.0
Conjugatable (alkali)[b]	......	......	35.3	100.0
Conjugated diene-triene	......	......	......	1.0

[a] Relative to pure methyl linoleate.
[b] Relative to pure methyl linolenate.

Their mechanism may be extended to the hydrogenation of unsaturated fatty esters catalyzed by metal acetylacetonates. The first step may be modified to allow for the absence of the Ziegler catalyst. Since methanol or a suitable protonating or hydride-stabilizing solvent is apparently necessary for the reaction, it may be postulated that one of the acetylacetone ligands is replaced with methanol. This reaction has a precedence with copper acetylacetonate (2). The solvated acetylacetonate would then assume the same role as the alkylated (RMX_{n-1}) intermediate in the initial step. Subsequent reactions in the mechanism would remain the same with the metal acetylacetonate-methanol system. Basic studies are needed to elucidate further the mode of action of this new class of hydrogenation catalysts.

ACKNOWLEDGMENT

Spectral analyzes, Helen M. Peters; and dibasic acid analyses, V. L. Davison.

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Foam Generation Method for Evaluating Biodegradability[1]

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Abstract

Mechanization of a simple laboratory test for foam generation capacity has resulted in a sensitive research tool and a valuable method for investigating biodegradation of surfactants. By standardizing energy input, temperature and other parameters, very acceptably reproducible foam generation capacity and foam decay measurements are obtained.

The method is suitable for organic materials capable of producing foams in aqueous solutions at very low concentrations such as 0.2–30 mg/liter. It is particularly suitable for individual or mixed surfactants and detergent formulations but has broader scope. It is fully adaptable to River Dieaway and Shake Flask Culture biodegradation test procedures and probably to others. The working range of concentrations is substantially that of interest in studies of water pollution by surfactants, and extends well below that for which most physical and chemical methods are suited. The method is broader in application and in information gained than an analytical method alone can be. The two may but do not necessarily yield parallel results. Both examinations are desirable.

Introduction

A LONG BUT MORE DESCRIPTIVE title for this paper would be "Method of Following Surfactant Biodegradation by Foam Generation Capacity and Stability Evaluation." In simple terms, the ancient art of shaking a foamable solution in a graduated cylinder for observation of the foam developed and its decay has been mechanized. After plenty of adverse experience with hand shaking methods, the more important variables have been standardized. The very acceptable degree of reproducibility achieved for diverse surfactant materials has been applied to individual or mixed surfactants or to detergent formulations (but has broader scope in that the foam generation and decay patterns derived characterize not only an individual surfactant but combinations of its decaying remainder, degradation products and other materials present). It shows some promise of becoming one of the few research tools well suited to very low concentrations of surfactants such as 0.2–30 ppm.

Methods of generating foams in reproducible manner have been classified as follows (1):

1. Shaking solutions
2. Beating in air, as by rotating stirrers or moving a perforated disc up and down (2)
3. Bubbling air or other gas through a column of liquid (3,4).
4. Dropping the liquid from a height (5–7).

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[1] Presented at the AOCS Meeting, Houston, April, 1965.

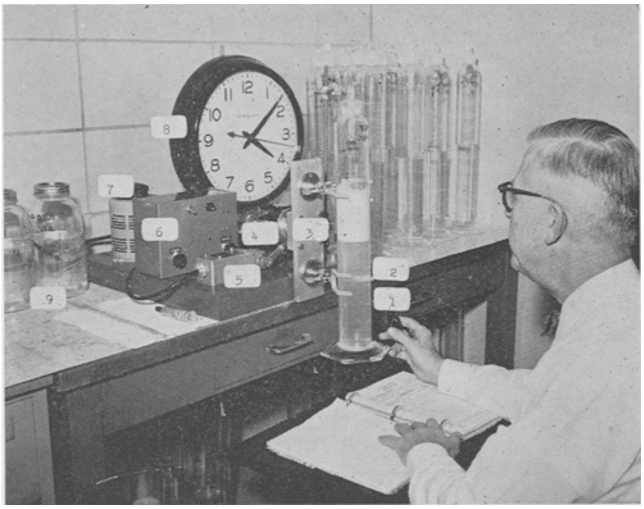

Fig. 1. Foam machine: *1*, swich for starting and stopping machine; *2*, 1,000-Ml calibrated cylinder; *3*, mounting plate for rotating cylinder in vertical plane; *4*, motor drive and speed reducer; *5*, position limit switch; *6*, speed and brake adjustment control box; *7*, variable transformer; *8*, clock with smooth-running sweep hand. Parallel river dieaway tests from which samples may be withdrawn for analytical or other tests are shown as *9*.

Most methods have been developed for solutions at the much higher detergent level concentrations, or for foams exhibiting considerable stability. Some trials of Groups 1, 3 and 4 methods in the below −30 ppm range indicated that better prospects lay in the refinement of Group 1 methods.

The foam test method has been developed and used mainly in River Dieaway type studies on known materials, and adapted to Shake Flask biodegradation tests (8). The method provides considerable information on the desirability of allowing substantial amounts of a particular surfactant to enter a water course or sewage system, subject always to the validity of the biological procedure used, and it is well suited to direct comparisons among materials. The test does not provide a result in terms of "Per Cent of Surfactant Degraded." Such a result very often would be an insufficient measure and statement of biodegradability, a term which continues to defy broadly acceptable definition. The method does show how the capacity of a surfactant to generate foam changes through a period of biodegradation exposure, and how its resistance to collapse and disappearance changes. No methods other than foam tests can exhibit a more direct relationship to the old and continuing practical problem of foaming streams.

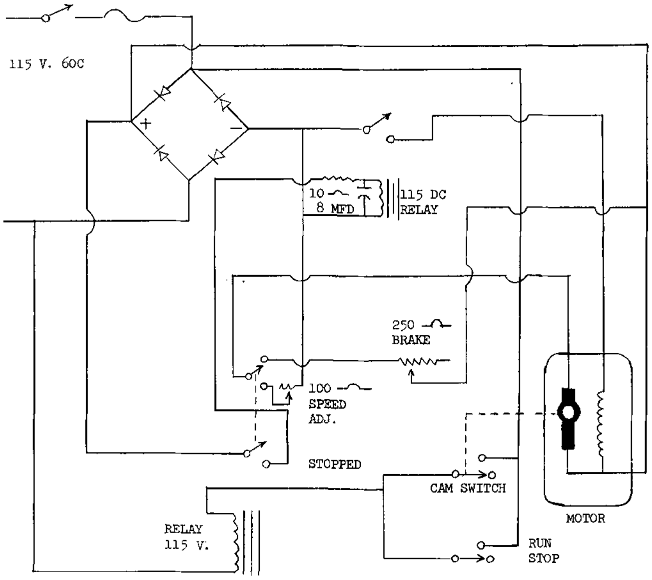

Fig. 2. Wiring for foam test machine.

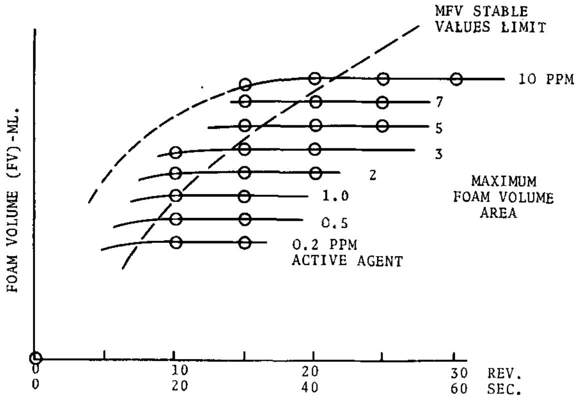

Fig. 3. Determination of required agitation period (idealized).

The Foam Test Machine

The essential features of the foam test machine (see Fig. 1) are a means of accurately mounting a graduated cylinder containing the biodegrading solution to rotate in a vertical plane at controlled speed, and a method of stopping the cylinder by magnetic brake action in erect position suitable for instant reading of foam volumes. Specifications for construction and method of use applied to the River Dieaway Test are detailed in the Appendix. Generally the foam test machine has eight important elements as indicated by the numbers in Figure 1:

An electrical wiring diagram of the Wyandotte Foam Test Machine is shown as Figure 2 (see appendix). On closing the "Run" switch the two relays close rectified power circuits through motor field and armature. Starting the motor closes the cam switch. The cam consists of a large collar mounted on the motor shaft. On opening the "Run" switch rotation continues until the roller cam follower drops into a rounded notch in the collar, opening the relay circuits and closing the magnetic brake circuit to stop the cylinder in erect position. An audible click pro-

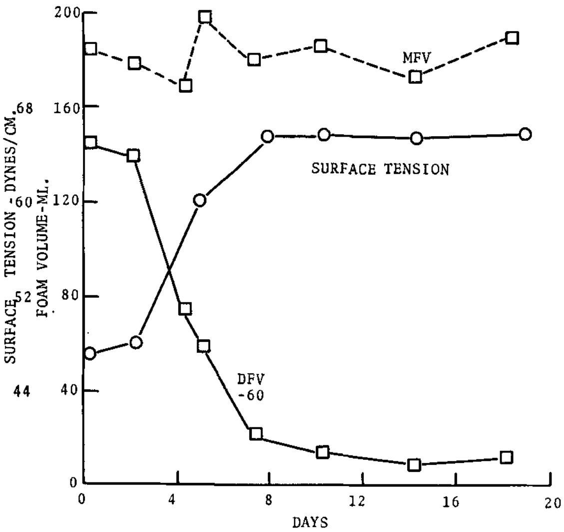

Fig. 4. Biodegradation of an experimental surfactant.

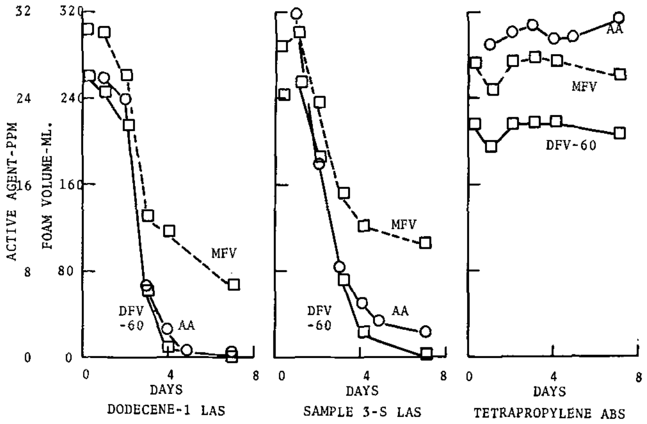

Fig. 5. Biodegradation of alkylbenzene sulfonates (shake flask test method).

duced by the cam may be used as a guide to stopping the machine at a specified time as well as visual observation.

Outline of River Dieaway Foam Test Method

Raw Detroit River water is obtained at the intake to the Wyandotte city water plant. After settling over night, it is decanted and used to prepare surfactant solutions at 7 ppm active agent content. One-liter calibrated glass cylinders are filled accurately to the 600-ml mark and the cylinder centered geometrically at the axis of rotation. A constant speed of 30 rpm is used (one surge per second). The machine is started, and after a suitable period (such initially as 5 min), it is stopped and the *average* upper foam level immediately marked by fingernail while the first discernible foam-solution interface is read. The difference is a "Foam Volume" reading. Successive runs of various lengths determine the minimum time required to attain a maximum foam volume. This may be 1, 2 or 3 min, and sometimes longer. A minimum 20% safety factor is needed. As biodegradation proceeds, running periods usually may be shortened. Figure 3 shows foam volume-running time relations.

When the minimum running time has been established, foam decay readings are begun. Net foam volumes are recorded at 0 (nearly), 15, 30 and 60 sec. Foam is again generated and not less than five successive runs made similarly. If the readings are concordant, averages are taken at each decay interval. These become the initial points of curves showing how foam volumes change as biodegradation proceeds. Foam measurements are repeated as often as needed to define the curves adequately. Different materials show characteristic patterns, and the separate curves reflect different characteristics of individual materials. In practice, it is often sufficient to plot only the initial and the 60-sec curves, but all the data are recorded. The 15- and 30-sec curves, and even others, may be useful at times.

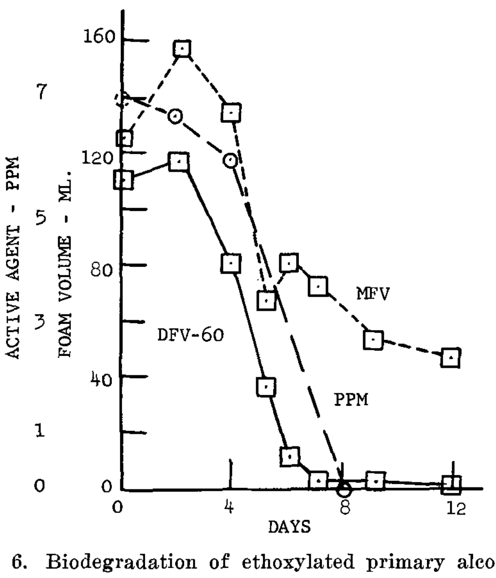

Fig. 6. Biodegradation of ethoxylated primary alcohol.

See appendix for details of this method.

Examples of Foam Test Results

Figure 4 shows the biodegradation characteristics of a moderately high-foaming surfactant. MFV identifies the maximum foam volume curve and DFV-60 identifies the curve showing the volume of foam 60 sec later. These curves show: 1) Little change in the MFV curve during the 18-day test period. 2) Good initial foam stability followed by a rapid decrease of stability. The difference between the curves is a measure of instability. 3) By the eighth day instability has reached a limit and a remnant foam reflects some residue which resists complete degradation. 4) While the substrate river water may show a measurable low MFV, all foam disappears within 2–5 sec. The MFV and DFV-60 curves of Figure 4 therefore reflect real phenomena characteristic of the degrading system.

Concurrent with drop in the DFV-60 curve during the first eight days, surface tension increased rapidly to a limiting value, namely 67 dynes per centimeter and short of the 72 value for water. This seems reasonable in view of the remnant foam observed. This behavior is common to many nonionic types in river dieaway (simple) systems. Full recovery to 72 dynes has been observed, however, in some cases. DFV-60 curves usually reflect primary degradation effects better than MFV curves do. Analyses for undegraded surfactant as well as surface tension behavior usually support this view.

Surfactants showing rapid alteration to yield unstable foams (see Fig. 4) would hardly be expected to develop a practical foam nuisance.

Figure 5 shows the degradation behaviors of three alkylbenzene sulfonates as followed by analyses (9) and foam generation test methods. In this case degradation was carried out by the shake flask method under development by the Soap and Detergent Association. To reduce the surfactant levels from the initial 30 ppm to a level suitable for foam measurement, 100 ml of the degrading solution was diluted to 600 ml using Basal Medium, omitting the yeast extract to avoid foam interference. During a test, the yeast extract soon degrades below an interference level.

The simplest behavior is shown by tetrapropylene alkyl benzene sulfonate (ABS) where little or no degradation is shown either by analytical or foam test within 7 days.

The behaviors of dodecene-1 derived (linear alkyl sulfonate) (LAS) and the 3-S commercial type LAS are similar except that the former degraded a bit more completely and more rapidly, as expected. This is shown by analytical and foam test results as well. The MFV curves also declined although some ability to generate unstable foam remained. Collapse became nearly complete within 60 sec.

The noticeable coincidence of the analytical and DFV-60 results accidentally from choice of scales and is significant only to the extent that it reflects a parallel response. It is more significant that the two methods agree on the periods required for degradation.

Figure 6 shows the degradation characteristics observed for an ethoxylated primary alcohol. Degradation was followed analytically by the potassium mercury iodide turbidity method (10).

Operating Conditions Investigated

The remainder of this paper will discuss some conditions investigated which influenced the choice of operating procedures.

Temperature

Temperature affects the volume of foam generated in various ways (Figs. 7 and 8). These data were obtained by hand-shaking methods (before a machine was built) by one individual shaking 100 ml of solution in 250-ml graduated cylinders for 15 sec, using 35–40 strokes as reproducibly as possible. The average values of five consecutive determinations are plotted in Figure 7 where the size of the circles or hexagons reflects the spread of the data. In some cases a five-centigrade-degree temperature difference introduced foam volume changes greater than the variability of hand shaking. Examples of increase and decrease of foaming capacity and maxima and minima as well, are shown within a ten-degree range. The volume differences and temperature coefficients seem smaller at 6 ppm than 20 ppm active agent.

Figure 8 shows that variation of temperature over a wider range can have a large effect on foam generating capacity of some surfactants. These solutions were warmed slowly from near-freezing to near-room temperatures, then were warmed above 100F and allowed to drift back to room temperature. These data were also obtained by hand shaking. Two concentrations of PLURONIC L62 showed flat minima in the neighborhood of 45F, sharp maxima near 60F, and uninterrupted decline in foam generation capacity above this temperature. TETRONIC 702 showed a similar maximum but no minimum.

Abrupt changes in foam generation capacity must reflect some constitutional change, possibly a solubility limit or attainment of a critical micelle concentration. The more refined measurement of foam generation capacity by machine methods now seems to offer a useful research tool for investigating such properties, quite apart from its use in biodegradation studies.

The practical outcome of the work shown in Figures 7 and 8 was elimination of temperature as a variable by moving degrading systems and foam measurement work into a constant temperature room operated at 23 ± 1C, and further to standardize initial surfactant concentrations at 7 ppm active agent, well below the lowest critical micelle concentration known to the author.

Volume of Solution Used

Figure 9 summarizes considerable work done to see how the capacity to generate foam responded as test solution volume was varied from 300 to 700 ml. Tetrapropylene ABS was used at 7 ppm active agent level. Solutions made up using paper-filtered Detroit River water developed maximum foam volumes within 24 revolutions. The results are well-represented by two almost linear intersecting curves. Solutions made up from the same river water following municipal purification also attained maximum foam volumes within 24 revolutions. The foam behavior was nearly identical at low solution volumes but a single curve showing a flat maximum best represents the results.

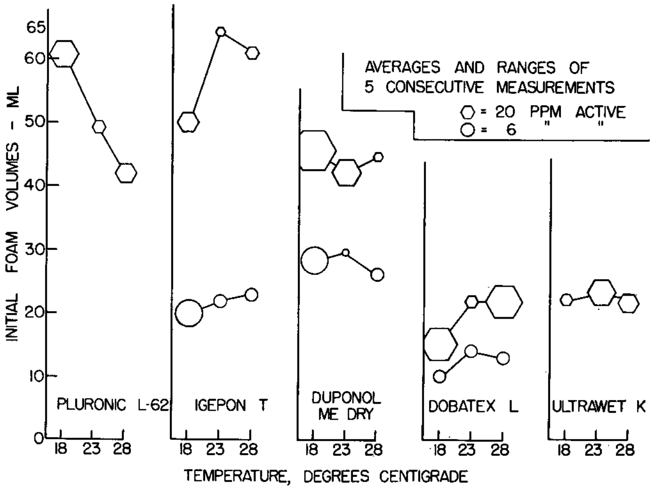

Fig. 7. Dependence of foam volume on temperature.

PLURONIC L62	Wyandotte	Ethylene oxide adduct of polyoxypropylene glycol
PLURONIC F68	Wyandotte	Ethylene oxide adduct of polyoxypropylene glycol
TETRONIC 702	Wyandotte	Ethylene oxide adduct of a polyoxypropylene adduct of ethylene diamine
IGEPON T	General Aniline and Film	Sodium N-methyl-N-oleoyl taurate
DUPONOL ME dry	duPont	Technical sodium lauryl sulfate
ULTRAWET K	Atlantic Refining	Alkylbenzene sodium sulfonate
DOBATEX L	Shell Chemical (British)	Linear alkylbenzene sulfonate (ethyl ether extract 45.2% found)

Earlier work had been done using distilled water where a different behavior was found. Longer periods for stabilization were required—about 40 revolutions. A family of curves (of which two are shown) was developed for different agitation periods. All

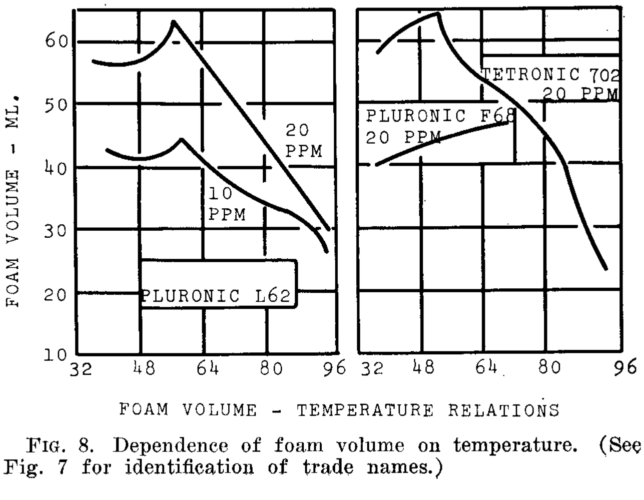

Fig. 8. Dependence of foam volume on temperature. (See Fig. 7 for identification of trade names.)

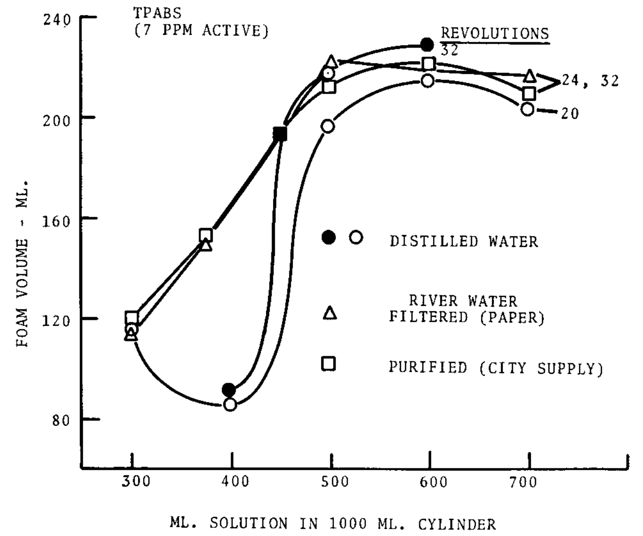

FIG. 9. Effect of solution volume on foam generation.

showed the form exhibited, with a maximum in the vicinity of 600 ml, a minimum near 375 ml and high sensitivity in the 400–500 ml range. It was concluded that the least sensitivity to volume change and water quality occurred at 600 ml, which is very close to half the total capacity of the cylinder. During 2 years of experience no need to change from this standard filling level has appeared.

Cylinder Size

Considerable work was also done with 250 ml cylinders, but insufficient to be conclusive. It appears that the principles of symmetry may not translate directly from 1000-ml to 250-ml cylinders. Behavior patterns differing from those of Figure 9 were observed. The matter deserves further careful study. There are indications that maximum foam volumes could be obtained faster in the smaller cylinders. The cost of cylinders would be less, volumes of solutions required for foam test would be less (important in Shake Flask experiments), and handling and cleaning of glassware would be easier.

Inclination of Cylinder from Vertical

Some experiments were made using a hinge mounting whereby the cylinder could be inclined from vertical position by as much as 30°. Very interesting flow patterns were observed but the energy input was diminished. Maximum foam volumes were lower and a difficulty was introduced in having to adjust the cylinders quickly to vertical position for foam readings. No advantages were found.

Rest Periods

Experience shows that a short rest and decay period is needed between individual foam generation runs. The importance increases from little or none when foams collapse quickly, to considerable importance when foam volumes are high, wet and rather stable. The usual 1-min decay time is enough for the average foam but for very stable wet foams, it may have to be longer. A practical rule is to let decay continue until less than 10 ml of solution is still held up in the foam. Overall time may often be saved by starting with unattended run of 5 min, after which maximum foam volume readings will usually be stable.

APPENDIX

Foam Generation Method for Evaluating Biodegradability

Adapted Specifically to the River Dieaway Type Test
(Revision of April 12, 1965)

1. APPLICATION AND RANGE

The method is suitable for organic materials capable of producing foams in aqueous solutions at very low concentrations such as 0.2–30 mg/liter (Note 1). It is particularly suitable for individual or mixed surfactants and detergent formulations but has broader scope. It is fully adaptable to River Dieaway and Shake Flask Culture biodegradation test procedures and probably to others. The working range of concentration is substantially that of interest in studies of water pollution by surfactants, and extends well below that for which most physical and chemical methods are suited. Although it is highly desirable of course to know the compositions and concentrations of materials undergoing test, it is not essential in the foam method. The results obtained characterize the initial material and reflect the interactions of its declining remainder with decomposition products and any nondegradable constituents if present. The method is therefore broader in application and in information gained than an analytical method alone can be. The two may but do not necessarily yield parallel results. Examinations by still other methods may be desirable.

2. PRINCIPLE

2.1. Foam is mechanically generated periodically under standardized conditions in a calibrated cylinder containing the degrading system. Maximum Dynamic Foam Volumes (MFV) are measured at once as rotation of the system is stopped abruptly in position for reading. Decaying foam volumes are further recorded at fixed intervals up to 60 sec. Curves plotted from volumes determined at these intervals through the degradation period show the characteristics of degrading systems qualitatively and comparatively.

3. EQUIPMENT

See photograph (Fig. 1) and wiring diagram (Fig. 2).

3.1. Remote Operating Switch.

3.2. Supply of 1000 ml Corning No. 2982 glass-stoppered, single graduated cylinders with standard taper solid stoppers. Mark the geometrical midpoint of each individual cylinder permanently. Kimble No. 20039 cylinders are satisfactory equivalents. Soft copper wire, 18 or 20 gauge, may be used to wire stoppers in place, or glass lugs may be welded to the cylinders and rubber bands used to hold the stoppers in place (as illustrated).

3.3. Mounting plate and clamping system for rotation in vertical plane of the 1000 ml cylinder.

3.4. Bodine Electric Speed Reducer Motor, Type N5H-12RG. 115 v d-c, 0.36 amp, 1725 rpm. Output (normal) 29 rpm. Run at 30 rpm by voltage control.

3.5. Micro Precision Limit Switch (Cat. 1 ML, Ser. No. 3). A notch cut in disc on shaft activates switch and makes audible click.

3.6. Control Box. Speed control to achieve reliable 30 rpm, on-off switch, fuse, and electromagnetic brake adjustment to achieve stop accurately in vertical position. See wiring diagram.

3.7. Variable transformer to correct line voltage variations (which affect speed).

3.8. Clock with smooth-running sweep-second hand, directly visible.

3.9. Controllable stream of filtered (dust-free and oil-free air (3.1./min a minimum flow rate).

3.10. Beckman Laboratory Oxygen Analyzer, Model 777, or convenient means of DO determination.

4. PROCEDURE

4.1. *River Water Supply*

4.1.1. Obtain a 3-day supply of raw river water from a local source selected to be as free as possible from variations in flow and quality (Notes 2, 3). Record the time and water temperature at the point of collection.

4.1.2. On arrival of river water at laboratory, test it as received for foam production by hand shaking, using 600 ml in a 1000 ml cylinder (3.2) or if any question remains, by running the machine as directed for surfactant solutions (4.3.2.4). Reject any water which produces foam which fails to collapse to the liquid surface within 5 sec after stopping rotation.

4.1.3. If the water passes the foam test (4.1.2), measure pH and dissolved oxygen (Note 4). Adjust the DO value (if it differs by more than ±1.5 ppm from the theoretical saturation value at dieaway test temperature) by vigorous aeration as long as necessary (Note 5). Allow the adjusted water to settle over night, then siphon or decant as much of the supernatant as required for tests to be started within two days. Discard any remainder unused within 48 hr (Note 6).

4.2. *Surfactant Stock Solutions*

4.2.1. Prepare stock solutions, each to contain 1 g active agent per liter (1000 mg/liter or substantially 1000 ppm). Dissolve test material containing 1.000 ± 0.0005 g active agent in about 500 ml sterilized or freshly boiled distilled water in a 1000 ml volumetric flask (Note 7). Then adjust temperature to 20C and bring to the mark.

4.2.2. If low solubility of the agent results in a non-homogeneous solution (examine closely for lenses, films, suspended droplets, etc.) prepare the solution at 0.100 g/liter, and use this whether homogeneous or not, but with care to withdraw representative samples.

4.3. *Biodegradation Test*

4.3.1. *Test Solutions*

Prepare solutions containing 7 mg/liter (7 ppm) active agent for test by transferring 4.2 ml of stock solution (4.2.1.) or 42 ml 4.2.2.) to a thoroughly clean graduated cylinder (3.2). Use separate graduated pipettes for each test material. Add settled river water (4.1.3) to bring total volume to 600 ml.

If degradation of the foaming agent is to be followed by other methods, duplicate solutions containing 7 ppm active agent must be prepared simultaneously, and stored and treated in precisely the same manner as those examined by foam degradation procedure, except that withdrawal of samples will be permitted. Include also a water blank (no surfactant).

It is recommended that all samples be stored in a constant temperature room at 23C where foam measurements can be made. The temperature history should at least be recorded by 7-day charts.

4.3.2. *Foam Measurements*

4.3.2.1. *Cylinder Alignment:* Place the cylinder with test solution on the machine, adjusting the geometric center of the tube at the axis of rotation. Start the machine and allow a few minutes to warm up and come to constant speed (within 30 ± 1 rpm). Make temporary adjustments, if necessary. Then start and stop the machine a few times, (under load) and adjust the magnetic brake action, if necessary, so that the cylinder stops in true vertical position.

4.3.2.2. *Reading Initial Foam Volumes:* Read foam volumes instantly (1–3 sec) as the machine stops with the cylinder in vertical position. Read both upper and lower foam boundaries. The difference is a dynamic Foam Volume reading (FV) (Note 8).

4.3.2.3. *Maximum Foam Volume Readings (MFV):* These are the limiting FV values that would be obtained if the machine were to run indefinitely (Note 9). To find out how long runs must go, make exploratory runs for each new test solution of 5, 3, 2 and 1 minute duration (in that order) to obtain an approximate time.

To establish minimum MFV running time reliably, make consecutive runs at each of several suitably chosen running times. Allow a foam drainage time of one minute between runs, or recovery of the solution volume to 590 ml at least, whichever takes longer. If the range of 5 successive measurements exceeds 7% of their average, extend the number of runs (Note 10). These data should be recorded (Note 11).

4.3.2.4. *Decaying Foam Volume Reading (DFV)* (Note 12): While obtaining MFV data under 4.3.2.3. also determine and record net foam volumes remaining after 15, 30 and 60 sec of foam decay (DFV-15, DFV-30 and DFV-60 readings). Obtain the results of consecutive runs (up to 7) until 5 consecutive runs show substantially consistent results, free from trends, i.e. volume ranges not exceeding about 10% of the average values at each decay period (Note 13).

4.3.2.5. *Foam Measurement Schedule:* Repeat MFV and DFV determinations at periods which will suitably define the form of the biodegradation curves (Note 14).

4.3.3. *Control Materials:* In connection with each run made, one or more controls should be included, at present left to the option of each laboratory.

4.3.4. *Aeration:* To insure against the development of anaerobic conditions, open each cylinder on each seventh day and blow filtered, oil-free air into it for several minutes.

5. APPLICATION OF METHOD TO SHAKE FLASK BIODEGRADATION TESTS

The equipment and methods of Sections (3) and (4.3.2.) may be applied to Shake Flask

Methods under recent study by the Research Subcommittee on Biodegradability of the Soap and Detergent Asociation, as follows:

During the degradation period withdraw 100 (or 140 ml) samples of the inoculated surfactant solution. Transfer to a clean foam generation cylinder and fill to the 600 ml mark with Basal Medium Solution (omitting yeast extract). Adjust to proper temperature and run the foam test promptly. Run an initial and occasional blank test (inoculated Basal Medium without surfactant). A moderate volume of very unstable foam subject to almost total immediate collapse may be expected (DFV-15 approaching zero). The dilution is required to bring the original 30 ppm active agent level down to usable range, 5 or 7 ppm, according to the dilutions suggested.

Notes

1. The higher concentrations are unsuitable for many materials, sometimes because of long periods required to develop maximum dynamic foam values, and sometimes due to slow degradation from high concentrations. For most surfactants the preferred starting level is 7 ppm.
2. Limit retention and use of a supply to three days.
3. Some recognizable causes of variability are merging flows of tributary streams, merging flows of entering storm or sanitary sewers, churning up bottoms by pleasure and commercial craft, churning by ice breakup or storm conditions. Withdrawal from midstream usually is far preferable to shoreline sampling. The intake feed to a public water supply facility is likely to be the best source. Our water supply is obtained at the intake from the Detroit River to the City of Wyandotte Water Treatment Plant.
4. The determinations under 4.1.2 and 4.1.3 are recommended to spot and control unusual conditions. It is usually desirable to build up background on seasonal and other factors contributing to variability of the water supply.
   Samples may also be plated to obtain bacteria counts. Preferred bacteria counts should be within the range 10^4–10^5/ml of river water, as determined by APHA Standard Methods. We prefer to accelerate growth, however, by incubating 48 hr at 35C rather than 3 days at 20–21C; we usually obtain comparable counts. Counts are sometimes low and colonies hard to count by the standard procedure. We have had no trouble staying within the 10^4–10^5 range either way and no longer take counts regularly.
5. Cold waters are frequently supersaturated with DO in relation to test temperatures. Heavily polluted waters may be undersaturated and are to be avoided, mainly because of probable wide variability and competing oxygen demand.
6. It is assumed that biological activity will remain about constant for 48 hr.
7. Sterile distilled water and aseptic techniques permit stock solutions to have a considerable useful life, even for readily degraded materials, probably 2 weeks or more. Some distilled and deionized water supplies are bacterially contaminated. If the stock solutions can be used promptly and discarded, contamination is immaterial and tap water may be used. While ABS solutions might safely be heat sterilized after being made up, this practice is not favored, especially for nonionics, unknowns, mixed surfactants or formulations.
8. If the upper foam surface is irregular, make a snap judgment of the total volume. Since decay may be very rapid it is convenient to make and hold this level by a finger nail while locating the lower boundary. If the lower boundary is momentarily obscure, observe the first break that can be identified. If the boundary moves downward momentarily, take the lowest value. The boundary position shifts rapidly.
9. The first reading measures (as nearly as possible) the expanded volume of the system resulting from foam production under dynamic conditions of the test. It will not be the required stable and Maximum Foam Volume (MFV) unless the machine has run long enough to develop equality between rate of bubble generation and collapse. Figure 3 illustrates (schematically) how FV values increase with length of run usually to well-defined limits (MFV values). The MFV Stable Values Curve shows the minimum lengths of run needed at various concentrations, and that the time increases with concentration. The periods illustrated are short and representative only of very low foaming systems. Strong foamers generally require longer periods such as 45, 60 or even 90 revolutions at 7 ppm so that it becomes impractical to increase concentrations too far.
10. The first one or two runs in a series are more frequently high, low or erratic than later ones. Proceed in such cases until 5 successive runs agree within the 7% limit. If not achieved in 7 runs, accept the average of 7 runs, provided no trends are discernible, rejecting the results from run 1 or runs 1 and 2 if out of line. For very low, very high or very unstable foams, the 7% standard may be relaxed to 10%, or a little more in exceptional cases.
    When the minimum time to achieve MFV values for freshly made solutions has been properly set, it is rarely necessary to lengthen it, and usually it may be shortened as degradation progresses.
11. These data are best recorded right on the data sheet used to collect degradation data.
12. Experience has shown the value of foam decay data. Usually there is a short ''collapse'' period of rapid drainage, followed by a much longer and more orderly ''decay'' period which finally terminates in ''foam break,'' exposing free liquid surface. In one carefully investigated case the ''collapse'' and ''decay'' periods were very well represented by intersecting straight lines. It is not yet known whether this is a general phenomenon and physically significant. As degradation proceeds foam characteristcs change, generally becoming increasingly unstable, i.e., much of the foam decay may occur within 15 sec. If foam break occurs within 60 sec, break times also are recorded as a characteristic of the system.
13. *Suggestions on Reading Decaying Foam Volumes*
    A. *Foam Hang-up on Walls*
    Rarely significant. Make estimated allowance.
    B. *Caviation (Coalescence to Large Bubbles and Voids)*
    Common and significant. Be prepared to make a quick estimated allowance for void volume.
    C. *Foam Break to Liquid Surface*
    Common and very significant. It occurs at a critical observation period where degradation

is approaching completion. Residual foam volumes are still to be estimated and recorded. Estimation now has to be made on the basis of void surface, and height and contour of the foam. An aid to doing this quickly may be prepared on a card to be mounted in direct view of the operator. The card may show diagrams and an easily readable table of volumes corresponding to observed wall heights at 20% intervals of exposed liquid surface.

14. Obtaining foam data at 0-, 15-, 30- and 60-sec intervals is demanding but quite possible. In examining new compounds, parts at least of all the data have been found useful. The different curves reveal different characteristics of a degrading system. DFV-60 data have generally shown the closest parallelism in form of decay curve to surface tension behavior or acceptable analyses, working largely in nonionic areas. Were a single determination to be left out DFV-15 or DFV-30 usually would sacrifice least. If only two determinations were to be made one proposal would obtain DFV-5 and DFV-30 data. This saves some time but provides no assurance that the foam had first attained maximum volume before decay started. MFV and DFV-5 readings are about equally difficult to obtain.

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Straight-Chain Alkylbenzenes: Structure and Performance Property Relations

III. Light-Duty Dishwashing Formulations[1]

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Abstract

A relationship between mixtures of straight-chain alkylbenzene sulfonates and their performances in light-duty dishwashing formulations has been established through studies of many pure isomers and isomer mixtures in both liquid and powder systems. The foam performance characteristics are shown to be directly related to carbon chain length, phenyl position, and water hardness in a readily calculable manner. Solubility studies on pure isomers are also reported.

Introduction

EARLIER REPORTS (1,2) from these laboratories established the relationship between the structure of straight-chain alkylbenzene sulfonates (LAS) and their performance in *heavy-duty* detergent systems. The performance characteristics of detergency and foam stability were shown to be directly related to carbon-chain length distribution and phenyl position. Appropriate formulae were given to determine the foam performance of mixed LAS systems. The optimum performers in heavy-duty systems were shown to be the internal (5, 6 and 7 phenyl) isomers of the C_{12}, C_{13} and C_{14} carbon-chain lengths. A partial study on light-duty powder system performance was also presented.

The powder system performance relationships were established in formulations where the alkylbenzene sulfonate was the sole organic active ingredient. This is not the case in a typical biodegradable light-duty liquid formulation utilizing alkylbenzene sulfonate, alcohol ether sulfate and fatty alkylolamide. In such a ternary system the determination of structural effects is much more complex. Maximum performance for this type of system was first developed in studies using a standard alkylbenzene sulfonate while varying the ether sulfate and alkylolamide. For the work described here, only the alkylbenzene sulfonate structure was varied; the ether sulfate and alkylolamide components were constant. There are no reports in the literature on the LAS structural relationships (both phenyl position and carbon-chain length) involved in the performance of light-duty liquid systems; this report will bear on that subject. Alcohol ether sulfate structural relationships have been reported (3).

Evaluation Techniques

Light-duty liquid foaming performance was evaluated in the formulation of interest by means of a miniature dishwashing procedure. This procedure was developed in our laboratory to fill two vital needs; reliable data from a small number of tests, and consumption of a minimum quantity of sample. This new method, which is to be described in a future publication, is a modification of a standard manual dishwashing test (4). It involves measuring the number of plates washed to a foam end-point under set conditions when the plates are carefully presoiled with exact amounts of a hydrogenated vegetable oil.

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