Measurement of Foam Consistency

(3. V. SCOTT and W. E. THOMPSON, Colgate-Palmolive-Peer Company, Jersey City, New Jersey

DETERGENT solutions are generally evaluated
with respect to foaming by the volume of foam
generated under specified conditions. The stagenerated under specified conditions. The stability of the foam will be reflected in the initial foam volume and subsequent measurements of the volume as the foam ages. Procedures have been suggested for such measurements $(1, 2)$.

Other methods have been used for evaluating foam characteristics. The stability of monolayers of foam (3), drainage of liquid from single films (4) or from bulk foams (5, 6), air permeability (7) and stability (8) of single bubbles, and surface viscosity of detergent solutions (7) are examples of determinations made by such methods.

A description is given in this paper of a method for relative evaluation of detergents according to the consistency or "body" of their foams. This method is adaptable for routine examination of foams. On occasion it may distinguish between solutions having obviously different foams but which are similar by tests for foam volume and stability. The properties which principally influence the values of foam consistency appear to be surface viscosity, bulk liquid viscosity, bubble size distribution, and foam geometry. A relation of foam consistency and liquid drainage will be indicated. The latter has been shown to be a function of bulk liquid viscosity, surface viscosity, and bubble size (6).

A method for determination of the consistency or "body" of foam was described by G. Mitkevieh in 1949 (9). The foam is produced in a vertical cylindrical vessel provided with a small indentation in the center of its base. The rounded end of a glass rod is placed in this indentation and the rod is held vertically by an upper support. Withdrawal of the support allows the rod to fall against a wall of the vessel. The time of fall is used empirically as a measure of the consistency of the foam.

Experimental

The instruments used in this paper to measure foam consistency are the following:

a) *Mobilometer.* The instrument as modified for foams is a reduced size version of the Gardner Mobilometer (10). A uniform bore glass tube, length 10", internal diameter 0.630", is used in place of the standard metal tube which holds the sample under test. The glass tube is filled by drawing in foam from a quantity prepared in a specified manner (method A below). The tube with the lower end closed is mounted in a special stand. A metal disc, thickness $\frac{1}{8}$, diameter 0.610' fastened at its center to a vertical guide shaft, diameter $\frac{1}{8}$ is then held in place above the foam surface. Appropriate weights are placed on a pan attached to the upper end of the shaft. The disc is allowed to pass down through the foam. The time required for a fall of a certain distance indicated by markings on the guide shaft is taken as an empirical measure of the consistency of the foam.

b) *Foam Consistometer (Figure 1).* This device measures the torque required to cause slow rotation of a rectangular paddle immersed in the foam. A continuously increasing torque may be applied by means of a clock spring which has its inner end attached to the paddle shaft and outer end attached to the circular drive plate. The plate is rotated manually through a gearing arrangement. An indicator needle is attached to the upper end of the paddle shaft and a circular scale divided into 360 de grees is set on the drive plate. The paddle shaft is supported

FIG. 1. Foam Consistometer. A. Indicator needle. B. Dial marked in degrees. C. Coil spring. D. Ball-bearing race. E. Gear for turning dial. F. Paddle.

in place by a pair of ball-bearing races in such a way that it can turn freely. The number of degrees through which the indicator needle is deflected for a motion of approximately 1 r.p.m, of the paddle through the foam is recorded as a measure of the consistency of the foam.

Several models of this instrument have been constructed to meet requirements of foams prepared by different methods. The models differ principally in size of paddle and sensitivity of spring (Table I). The spring was calibrated by attaching a pulley of 2-cm. radius to the paddle shaft. The degrees of deflection are recorded for different weights attached to the free end of a thread wound on the pulley.

c) *Brookfield Viscometer Model HAF.* This is a commercially available instrument (11) which has been adapted for the measurement of foam consistency by the attachment of a shaft bearing a paddle. The instrument has precision features not attained in the specially constructed foam consistometers

above. However the principle of operation is the same. The torque represented by the twisting of a spring is the measured quantity. The instrument operates at any one of four constant speeds (1, 2, 5, l0 r.p.m.). In measurement of foam formed by method b below, 2 r.p.m, is used with a paddle of dimen-sions: height *1.2",* width *1.8".*

Foam Preparation and Measurement. The following methods have been used for preparing foams and measuring consistency :

Method a). Two liters of solution at approximately 112° F. are placed in a rectangular glass container, capacity 10 liters, prewarmed to 112°F. A stirring paddle, height 5", width 3", is just submerged in the solution and rotated at 710 r.p.m.
for three minutes. The foam consistency is then measured as for three minutes. The foam consistency is then measured as a function of foam age, using instrument No. 2 (Table I).

Method b). The detergent solution (500 ce.) is prewarmed to a temperature of 113-114°F, and is placed in a two-quart unsilvered Dewar Flask (12). When the temperature of the system is approximately 110°F, the solution is agitated by means of a paddle (height 3.25", width 2") oscillating through 470 ~ at a rate of 130 complete oscillations per minute. The paddle is centrally located in the flask with about 1.75" protruding above the solution. A micarta cover is provided for the Dewar Flask to reduce heat loss. The system is agitated for 10 minutes. The foam is tested with Instrument No. 4 (Table I).

Method c). Washing machine foams are formed at 110° F by agitating 10 gallons of detergent solution to which 15 small towels have been added. Twenty minutes is allowed, using a standard oscillating type washer (General Electric). The machine is then uncovered and the foam tested, using Instrument No. 3 (Table I) at various locations in the foam. The instrument is mounted on a large miearta board resting on the sides of the tub. The paddle position in the foam is adjusted vertically by a telescopic arrangement built into the shaft. Readings taken within five minutes after stopping the washer are averaged.

Foam Drainage Measurement. Foams are prepared as in method a). Immediately after mixing, a rapidly rising foam-solution interface becomes discernible. With the aid of a cathetometer this level is followed as a function of time. By calibrating the vessel for volume, the liquid left in the foam may be calculated.

Remarks on Instrument Design and Experimental Techniques. In the development of the instruments for measuring foam consistency certain obvious variations were made. Examples of the effects of such variations are as follows:

Effect of Paddle Size. One restriction on the size of the paddle is that it be compatible with the volume of foam generated. Too large a paddle caused motion of the foam at the walls of the containing vessel, at the foam-solution interface, or at the foam-air interface. This results in loss of torque and a lower reading for consistency. If too small a paddle is selected, the amount of foam actually being tested is correspondingly small and because of foam heterogeneity, reproducibility would be lessened.

For Consistometer No. 2 the effects obtained by varying the paddle size are shown in Table II. A 0.5% solution of a commercial detergent was used for generating the foam. The values represent averages of readings taken for foams 5, 10, and 15 minutes old (i.e. after mixing). Thus for this model doubling the height of the paddle had approximately a two-

TABLE II Effect of Paddle Size on Measurements

Paddle Size		Consistency (average)
Height	Width	Scale Reading ^o
inches	inches	
		20
		45
		60
-/0		75
		105
		205

fold effect on the torque while doubling the width had a five-fold effect.

Effect of Paddle Location in Foam. The paddle axis is located centrally in the vessel containing the foam in order to minimize wall effects. The distance the paddle should be placed above the *solution* level may be indicated by data in Table III obtained by using the Brookfield Viseometer as Consistometer and foam prepared as in method b). The value of 0.75" minimizes the effect due to foam turning at the liquid surface and yet allows a good coverage of foam above the paddle.

Effect of Rotational Speed of the Paddle. Systems have been examined, using the Brookfield Viscomcter as Consistometer with a 1.2" x 1.6" paddle at the various speeds provided by this instrument. The data obtained with the foams prepared as in method b) are shown in Figure 2. For the foam of low con-

Fro. 2. Foam consistency. Effect of rotational speed. Brookfield Model HAF, rectangular paddle. Preparation of foam: Method b) Experimental.

sistency, the resistance to motion of the paddle seems practically independent of the turning rate and for the foams of high consistency a slight increase of resistance is obtained with increase in turning rate. These foams have also been examined with a more sensitive model of the Brookfield (Model LV), using spindle (No. 3) supplied with the instrument. Results are shown in Figure 3. The foams of different consistency each show increasing resistance to motion of the spindle with increase in speed.

Effect of Time of Mixing. Using method b) the time of mixing was varied to give the data in Table IV. Two 0.25% *solutions* of specially prepared detergent mixtures were used at a temperature of 110° F. On the basis of these results a 10-minute mixing period was selected.

Reproducibility. The reproducibility of the consistency measurement was tested, using duplicate and triplicate determinations for various detergents. The mean deviation from the

FIG-. 3. Foam consistency. Effect of rotational speed. Brookfield Model LV, Spindle No. 3. Preparation of foam: Method b) Experimental.

averages was 15 units for Consistometer No. 4 and 8 units for the Brookfield instrument. For low consistency values this represents mean deviations of 8 and 4%, respectively.

Results and Discussion

Foams from solutions of various detergents in distilled water were measured as a function of the age of foam. The plotted data appear in Figure 4. The shapes of the curves obtained fall into either of two categories depending on whether the particular system is of high or low consistency. For foams of high consistency the curve rises rapidly at first and then more slowly. Foams of low consistency on the other hand produce curves which rise even more rapidly at

FIG. 4. Foam consistency vs. foam age. Method a) Experimental. Distilled water solutions.

first but then pass through a maximum and start to fall toward an apparent lower limit. Visual observations indicate that the decline after the maximum may not be simply ascribed to foam coalescence or collapse.

It was anticipated that foam consistency would show correlation with the amount of bulk liquid remaining in the foam. Foams were prepared, and liquid drainage followed as a function of the age of the foam. The data for systems corresponding to those in Figure 4 is depicted in Figure 5. From a comparison of the two graphs it is apparent that the time for more rapid drainage of the foam corresponds closely to the time of rapid rise in consistency value. Systems of high consistency show a slower drainage rate in the first several minutes of foam age tban do those of low consistency. After the initial aging period the systems retaining more liquid in the foams show higher consistency values.

Fro. .5. Foam drainage vs. foam age. Distilled water solutions. Volume of foam--5 to 6 liters.

Referring to Figure 4 it may be observed that foams termed as "high consistency" actually have lower consistency values during the initial period of aging. The amount of bulk liquid retained at this stage is probably sufficient to make these foams more fluid. The liquid drainage rates have been indicated (6) as inversely dependent on surface viscosity. As bulk liquid is removed by further drainage, it is believed that the consistency values become more directly dependent on the surface viscosity and the high values are obtained for foams of high surface viscosity. The effects of differences in bubble size and bulk liquid viscosity among the various systems have not as yet been determined.

The difference between soap and soap containing builder in Figure 4 led to experiments in which the foam consistency of soap solutions was tested for salt effect (Figure 6). Sodium chloride was added in varying amounts to the soap solution. This reduces the foam consistency considerably and alters the shape of the curve. The lower consistency values in Figure 4 at higher concentrations of detergents may also be partly explained as due to the increased concentration of salts.

FIG. 6. Foam consistency vs. foam age. Effect of NaC1 addition. Method a) Experimental. 0.35% soap solution in distilled water.

The detergents were further examined by including 300 p.p.m, hardness in the solutions. Low consistency curves were obtained for each of the three detergent mixtures (Figure 7). Foams of soap solution in distilled water were examined for temperature effects (Figure 8). A pronounced shift towards lower con-

FIG. 7. Foam consistency vs. foam age. Effect of water Method a) Experimental. Dashed lines: distilled water solutions. Solid lines: solutions containing 300 p.p.m. as CaCO₂.

FIG. 8. Foam consistency vs. foam age. Effect of temperature. Method a) Experimental. 0.25% soap solutions using distilled water.

sistency values was obtained for an increase in temperature of only five degrees Fahrenheit.

To summarize the various effects for the soap solutions, it should be noted that the addition of sodium salts, the addition of hardness, or an increase in temperature may cause the foam consistency to decrease and produce foam age curves characteristic of foams of low consistency.

The foams were examined by the use of the mobilometer described in the experimental section. In this m6bilometer the foam is subjected to greater shearing stress than in the other consistency determinations previously described. Qualitatively similar results $(Figure 9)$ are obtained under these different experimental conditions.

Results from singlc fihu studies (4) and from foam drainage studies (6) iudieated that for certain systems, such as those containing sodium alcohol sulfate,

FIG. 9. Foam consistency vs. foam age. Use of mobilometer. Expcrimental a). Distilled water solutions.

the presence of small amounts of materials, e.g., longchain alcohols, may have pronounced effects on the drainage characteristics of the films or foams. These effects were chiefly attributed to the influence of these materials on surface viscosity of the systems. A. G. Brown and coworkers (7) more recently have described the effect of a high alcohol (dodecanol) on surface viscosity of sodium lauryl sulfate solutions as determined by a rotational surface viseometer.

To test whether there is qualitative agreement with surface viscosity for foam consistency values for solutions such as above, the determinations appearing in Table V have been obtained. The consistency values represent averages of values taken at 5, 10, and 15 minutes of foam age.

The solution of "as received" detergent which has high surface viscosity and low drainage rate gives a high value for foam consistency. Removal of the ether-soluble material reduces the foam consistency to a low value. However addition of a higher fatty alcohol re-establishes the consistency at a high level. From these data it appears that the presence of materials which are known to influence the surface viscosity may have large effects on the consistency of foams. Work with other materials has further demonstrated these effects.

The effeet of various amounts of lorol (alcohols formed by reduction of coconut oil) added to the ether-extracted detergent (Table V) is shown in Figure 10 as a function of foam age. The change in shape of the curves as the systems undergo the transition

FIG. 10. Foam consistency vs. foam age. Effect of lorol addition to distilled water solutions of ether extracted mixed alcohol sulfates. Method b) Experimental.

from low to intermediate to high consistency may be observed.

It has been shown $(4, 6)$ by both film and foam drainage that a transition from slow to fast draining systems may occur over a narrow temperature range. This has been attributed to a rapid decrease in surface viscosity within that range. The temperature effect on foam consistency for a detergent system with and without the addition of cetyl alcohol is shown in Table VI.

The gradual decrease in foam consistency for solution]I in Table VI is attributed to the fact that the material was not ether-extracted. The solution contains components (e.g., fatty acids and esters) which are presumed not effective at 110°F. in producing high surface viscosity but are effective at a lower temperature. Because of the presence of homologues in the ether-soluble components the change in surface viscosity is more gradual. With the system containing cetyl alcohol a large decrease in foam consistency is obtained with a change in temperature from 110° F. to 140° F.

It appears that at least two components in addition to the solvent are required for high consistency foams. One component is the detergent. The second component is a polar organic substance, such as a long chain fatty alcohol or acid. For the soap systems dealt with earlier in this paper (Figure 4) high consistency foams did appear. This is attributed to the presence of the second component due to hydrolysis of the sodium soap. The fatty acids do increase the foam consistency as has been demonstrated by incorporating them into non-hydrolyzable detergents.

The differences in consistency of foams from various commercial detergents agitated in a household washing machine are illustrated by the data in Table VII. The consistency values represent averages of values taken in the first five minutes after stopping the agitator and at various locations within the foam.

The pronounced effect which additional hardness may have on the foam consistency is indicated by the

a Jersey City tap water. Approximate hardness: 50 p.p.m. as CaCO₂.
b Detergent I is based on sodium coconut oil monoglyceride sulfate.

data in Table VII. Depending on the particular detergent system, it may increase or decrease the values.

Summary

Foams from detergent solutions may show large differences in apparent viscosity or consistency. Procedures are given for relative measurement of this property.

A decrease in foam consistency may be obtained with soap solutions upon addition of inorganic salt or of hardness. A critical temperature range exists for consistency of foams from detergent systems. Foams of high consistency may be altered to low consistency by raising the temperature.

The data suggests a relation between foam consistency and the liquid drainage and surface viscosity characteristics of foam systems. High consistency values were obtained for foams having slow drainage rates and high surface viscosity. These characteristics for foams of detergent solutions are attributed to the presence of certain polar organic substances (e.g., saturated fatty alcohols and acids) which are strongly adsorbed at the liquid-air interfaces.

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ABSTRACTS E. S. Lutton, Editor

9 Oils and Fats

R. A. Reiners, Abstractor

The infrared absorption spectra of saturated fatty acids and esters. R. G. Sinclair, A. F. McKay and R. N. Jones (Queen's Univ., Ottawa). *J. Am. Chem. Soc. 74,* 2570-75(1952). The infrared absorption spectra of saturated fatty acids and methyl esters of varying chain length have been measured. In solution, most of the absorption bands are broad; the spectra are qualitatively independent of the chain length but the relative intensity of the methylene rocking vibration at 720 cm. increases progressively as the chain is lengthened. In the crystalline state the spectra show much more structure than in solution and significant qualitative differences occur on alteration of chain length. The spectra also differ for polymorphic varieties of the same acid, a factor which complicates the use of such spectra in analysis. The principal absorption bands are assigned to the vibrations of specific molecular groups.

Band progressions in the infrared spectra of fatty acids and related compounds. R. N. Jones, A. F. MeKay and R. G. Sinclair (Queen's Univ.). *J. Am. Chem. Soc. 74,* 2575-78 (1952). A progression of absorption bands of uniform spacing and intensity is observed between 1180 and 1350 cm.⁻¹ in the spectra of fatty acids in the solid state. The changes induced in these bands by alteration in the chain length, the introduction of substituents and the replacement of the terminal carboxylic acid by other groups has been investigated. It is suggested that the bands arise from interactions among the rocking and/or twisting vibrations of the methylene groups.

The infrared absorption spectra of unsaturated fatty acids and esters. R. G. Sinclair, A. F. McKay, G. S. Myers and R. N. Jones (Queen's Univ., Ottawa). *J. Am. Chem. Soc.* 74, 2578-85 (1952). The infrared absorption spectra of several unsaturated fatty acids, methyl esters and brominated derivatives have been determined at room temperature and when cooled with liquid nitrogen. The absorption bands characteristic of the unsaturated linkages are described and discussed. A spectrographic metbod is proposed for the determination of the degree of unsaturation of mixtures of *cis-unsaturated* acids, based on the measurement of the optical densities of the absorption bands at 3020 and 2920 cm. $^{-1}$. The spectra of liquid films or solutions of stearic, oleic, linoleie and linolenic acids do not differ sufficiently to permit the spectrographic analysis of the individual acids in complex mixtures. However, cooled solid films of binary mixtures of oleic and linoleic acids show large and progressive changes with concentration, especially between 680

and 750 cm.⁻¹ and the quantitative analysis of pairs of the above unsaturated acids from solid fibn measurements would appear to be feasible.

Infrared spectra of branched long-chain fatty acids. N.K. Freeman (Univ. California). *J. Am. Chem. Soe.* 74, 2523-29 (1952). The infrared absorption spectra of *27* branched longchain fatty acids have been studied in an attempt to correlate them with types of chain branching. Branching within five carbon atoms of the carboxyl group, and particularly on the a-carbon, can be recognized. Indications may be seen for ethyl and propyl groups, and for two methyl groups on the same carbon atom. Of the latter type, the isopropyl group is distinguishable. The number of branches (terminal methyl groups) can be determined. The provisional character of this kind of infrared spectral evidence in general must be borne in mind, and specific limitations have been pointed out.

Unimolecular films. III. Mixed films of fatty acids and paraffin. R. Matsuura (Kyusyu Unix'., Hukuoka, Japan). *Mere. Faculty Sci., Ky~ar Univ. Ser. C Chem.* 1, No. 2, 69-79 (1949). The pressure-area and area-composition curves of fihns of paraffin-stearic acid and paraffin-myristic acid mixtures on water were determined. *(Chem. Abs. 46,* 4885)

Orientation of fatty acid and soap films on metal surfaces. J. W. Menter and D. Tabor (Univ. Cambridge, Engl.). *Proc. Roy. Soc.* (London) A204, 514-24(1951). The orientation and strueture of films of laurie, myristic, palmitic, stearic, and oetaeosanoic acids and certain of their heavy metal soaps on surfaces of Pt, Ag, Cu, Cd, Zn, and mild steel were studied by electron diffraction. Films were applied by retraction of molten drops and by rubbing at room temperature. The effect of surface temperature on orientation was studied. For all fihns there was a eharacteristie temperature at which disorientation occurred. For acids on nonreactive metals the transition occurred near the melting point. On reactive metals, Zn and Cd, disorientation occurred near the *softening* point of the corresponding soap, suggesting soap formation. Soap films were found to disorient near their softening point. Film transition temperatures as shown by electron diffraction were correlated with the transition temperatures as shown by the coefficient of friction and found to be in fair agreement. *(Chem. Abs.* 46, 4875)

Structure of thin films of aliphatic esters and alcohols on metals. J. V. Sanders and D. Tabor (Univ. Cambridge, Engl.). *l"roc. Roy. Soc.* (London) A204, 525-33(1951). The structure and orientation of thin fihns of octadecyl and melissyl alcohol, methyl and ethyl stearate, and melissyl melissate in thin crystal layers and as films on Pt, Cu, Cd, Zn, and mild steel were studied by electron diffraction. The orthorhombic structures of