An Apparatus for Comparison of Foaming Properties of Soaps and Detergents

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THE EVALUATION of the foaming properties of soaps and detergents is a difficult problem because the volume and quality of the foam produced by any method from a given solution of a soap, detergent or foam-forming material is a function of many complex factors. Thus the shape of the apparatus in which the foam is made, the means by which the foam is formed, the subsequent history of the solution and the destructive forces to which the foam is subjected are all factors that enter into any method for evaluating the foaming properties of a foam forming material.

Several studies of foam comparison have been described in the literature and a short review of these will clarify the present discussion.

C. Stiepel (Seifensieder Ztg. *41,* 347, 1914) proposed what was essentially a shaking method which has been found very subject to the personal equation of the operator.

H. J. Christmann (U.S. Pat. 1,866,296, 1932) bubbled air for a given time, and at a given pressure, through a column of liquid and measured the volume of foam and rate of its collapse. He applied the method to compare the frothing qualities of materials such as cresylic acids for mineral flotation.

C. W. Foulk and J. H. Miller (Ind. and Eng. Chem. *23,* 18, 1931) describe a similar method to that of Christmann for examining unstable foam where the order of magnitude of the foam stability is much lower than is the case in detergent foam.

E. L. Lederer (Seifensieder Ztg. *63,* 331, 1936) and W. Ostwald and A. Siehr (Kolloid. Zeit. 76, 33, 1936) used the same method with soap and other solutions.

J. J. Bikerman (Trans. Far. Soc. *34,* 634, 1938) attempted to establish a unit of foaminess as a physical characteristic. He used materials which give highly unstable foams with the experimental procedure described by Christmann, Foulk and Miller.

S. Ross and G. L. Clark (Wallerstein Laboratories Communications, New York, 1939, *6,* p. 46 also Ind. and Eng. Chem. *32,* 1594, 1940) examined the stability of beer foam by measuring the weight or volume of beer in the collapsed foam. The foam was produced with uncarbonated liquids, by bubbling carbon dioxide gas through the liquid, and with carbonated liquids, by allowing the beer to fall from a height or by merely shaking the beer.

W. C. Preston and A. S. Richardson (J. Phys. Chem. 33, *1142, 1929*) examined *foam power* by a variation of the gas bubbling method. Air was drawn down a hollow shaft of a rotating stirrer and passed out into the solution centrifugally. The volume of liquid retained by the foam was measured and this foam power (per cent of solution retained by the foam) was found to bear no simple relation to surface viscosity or surface tension of the solution of the material examined.

It is to be noted that Christmann, Foulk and Miller, Bikermann, S. Ross and Clark, were concerned with the production and breakdown of unstable foams. Their methods and conclusions do not necessarily apply to such stable foams as are given by soap solutions. A column of bubbles of homogenous or heterogeneous size formed from a soap or detergent solution when protected from disturbances such as pressure or temperature change and evaporation, we have found to have a life period measurable in hours or days. Such foams we have made by bubbling air at constant pressure and rate through a liquid volume contained in the bottom of the column protected by a thermostatic jacket. Under these conditions when the major causes of adventitious disturbance are thus reduced or eliminated, the life period becomes very great. The drainage of such a stable foam bears no direct relation to the collapse or stability of that foam; for this and other reasons, we find it necessary to dissociate phenomena of liquid held or drained by a column of foam from such conceptions as the stability of the foam.

In our examination of various materials we have found it useful to distinguish between capacity to foam and foam stability and it is desirable to isolate these conceptions as far as possible.

Consider a solution that will give a foam possessing absolute stability, then, neglecting small effects due to surface tension and liquid density of the solution, the volume of foam produced is limited only by the supply of air or gas introduced beneath the surface of the liquid. Therefore, we must consider that such solutions are potentially capable of giving a volume of foam approximately equal to the volume of air bubbled through the solution.

When the foam is not absolutely stable, the final volume of the foam will be less than the volume of air introduced by an amount which is a measure of the instability of the foam, assuming that no change in bubble size has occurred. From this it follows that various materials differ in the stability of their foam and not in their capacity to foam. Hence, any method of measuring *foam formation* is actually a method for measuring the stability of a foam towards that particular stress to which it is subjected.* It must be concluded that the term "capacity to form foam" used in a relative or comparative sense is meaningless.

With the exception of the crude handshaking procedure of Stiepel, the methods previously described did not involve sufficiently large stresses to cause any considerable breakdown in very stable foams such as are obtained with soap and detergent solutions.

The test described here is an attempt to provide sufficiently large breakdown stress so that the resulting volume of foam produced is a measure of the relative foam stability of soaps and detergents. In other words, we measure the relative stability of a foam by the effect of an arbitrary standard destructive mechanism acting

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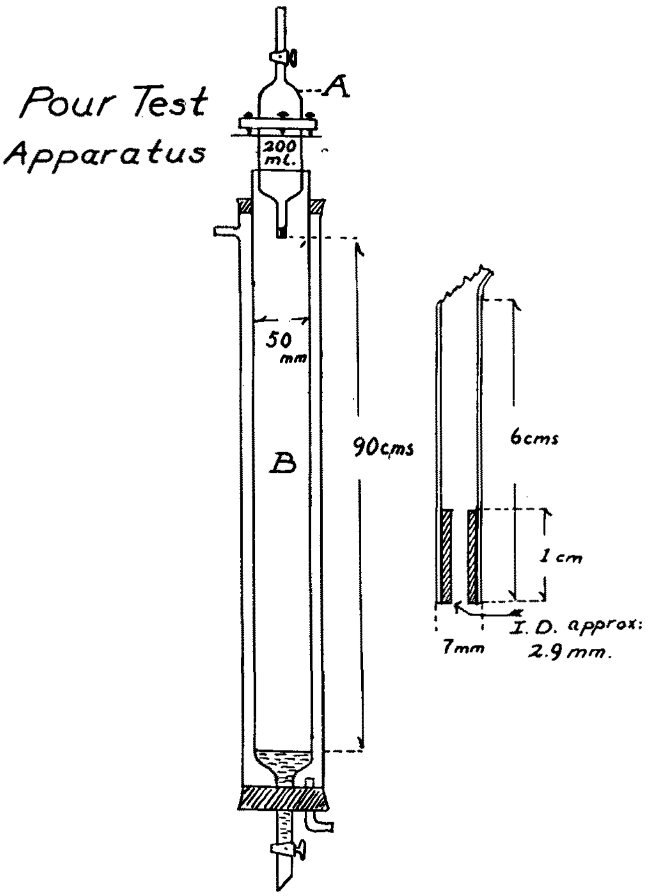
* Foam stability appears to be associated with those materials which will give films possessing a certain limited degree of elasticity (see N. K. Adams, Physics and Chemistry of Surfaces, p. 142, Oxford-Clarendon Press 1938). A stable bubble is one that can maintain slight differences of tension in its different parts so that it will outlast small sudden disturbances. Foam films will break down because of evaporation, mechanical and thermal shocks, and chemical change within the film surface.



upon a foam produced under standard conditions and protected from adventitious destructive forces.

A satisfactory correlation between the physical properties of surface films, solutions and foaming tendencies still remains to be established. Until all the physical phenomena concerning foaming are more completely understood, any method for comparing the foaming qualities of detergents and soaps must necessarily be arbitrary and probably incomplete. In a spirit which recognizes such limitations, we offer the following apparatus and procedure. This method will be seen to possess certain advantages over the methods discussed above. We have found it to have the virtue of simplicity, reproducibility, rapidity and some freedom from errors due to personal equation of the operator. The values obtained with this apparatus we have used empirically to evaluate detergent and soap foam stability, and used for this purpose, we have found it to be superior to any other method known to us.

The apparatus shown in sketch is made to standard dimensions from stock glass. The reservoir or pipette A is filled with the solution to be examined and then placed on the supporting ring at the head of the receiver B which contains 50 m l. of the same solution. The stopcock or reservoir A is opened and as the solution falls, foam is formed in the receiver and is measured in B immediately after the reservoir A is emptied. The orifice of A is so constructed that the turbulence set up causes the stream of solution to break up into droplets just after emerging from the orifice. Foam is produced when these droplets strike the surface of the liquid or foam in the receiver.

This foam test, in common with many other foam tests, produces foam by introduction of air into the solution under examination. The means of production of foam is in this case also an agent of destruction of foam. There is thus obtained a simple standardization of the means of production and destruction since both are a function of the average kinetic energy of the droplets as they impinge on the solution and foam.

Extraneous destructive forces and thermal shock are excluded from the system by circulating liquid of known temperature from a thermostat through the jacket which thus maintains the liquid and air column at uniform temperature. Evaporation is reduced to a minimum by previous wetting of the receiver walls with the solution.

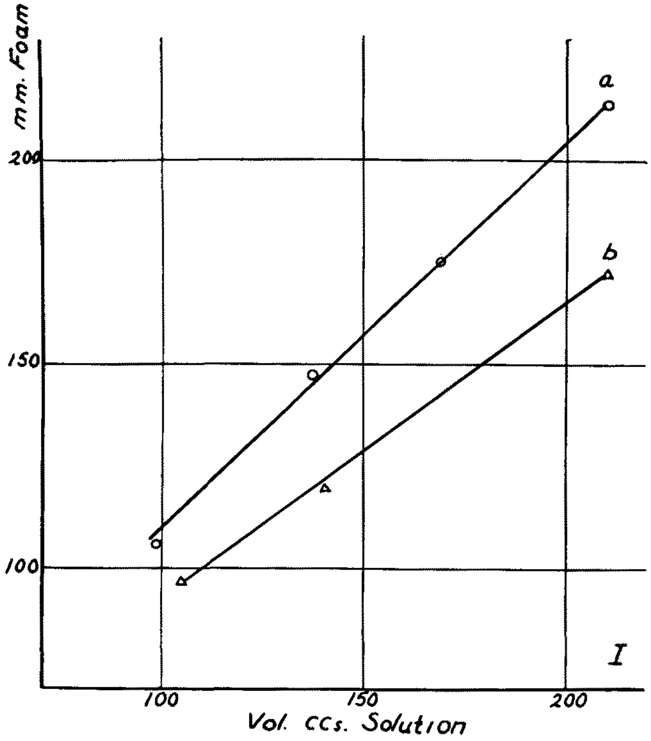
For convenience in measurement, the height of foam is read and taken as proportional to the volume of foam, assuming that the cylinder is uniform in cross-section.

The volume of foam formed is a linear function of the volume of liquid that falls, provided that the height of fall remains approximately constant. This is illustrated in Graph I.

The volume of foam formed is an approximately linear function of the height of fall (See Graph II), subject to the following qualifications: (a) the volume of solution delivered must be constant; (b) the concentration of material in solution must exceed a certain characteristic minimum for that material. It is clear that certain materials will fail to show this linear relationship at any concentration if their foam is insufficiently stable.

Graphs III and IV illustrate the characteristic relationship between concentration and foam production, for several materials, at fixed temperature, volume and height of fall. These last curves demonstrate a most important property of soaps and detergents and serve as an excellent means of comparing various materials.

The depth of solution placed in the bottom of the receiver prior to foam formation has no effect upon the total volume of foam produced, providing that a



Graph I.

Foam production as a function of the volume of solution.
Height of fall 90 cms.
Temperature 25°C.
a. 0.25% synthetic detergent A.
b. 0.05% synthetic detergent B.

minimum of approximately 50 m l. is present, giving a depth of about 5 cm. of solution.

As regards reproducibility, we have found that in cases of solutions of most synthetic detergents where no great variation with age occurs, the maximum difference between results will be of the order of 6 mm. and the average deviation from the mean will be 2 mm. where the foam height is of the order of 200 mm. When applied to built soaps in hard water the spread is of the order of 22 mm. and the average deviation from the mean will be 4 mm. This is probably due to the difficulty of reproducing and aging of such solutions, because it is found that repeated runs on the same solution are in closer agreement than repeated tests on solutions prepared in "parallel" manner. Even with variations of this order the test is still an excellent method for evaluating soaps, soap builders and the like.

The reservoir tip of the pour test apparatus is made from pyrex glass tubing whose outside diameter is close to 7 mm. and length is 6 cms. Another piece of tubing is selected whose outside diameter is such that it fits snugly inside the 7 mm. piece. From this a short 1 cm. section is cut and ground square at both ends. This inner section is placed flush with the extreme tip of the large piece and then the outside of the larger tube is heated to redness at one or two points opposite the middle of the inner section. Then the tip assembly is ready to be joined to the reservoir proper.

We have found that orifices varying in size from 2 to 3 mm. in diameter produced nearly the same amount of foam. However, such variations in orifice size need not occur in constructing the apparatus if reasonable precautions are observed. In standardizing several pieces of apparatus to conform with each other, it was found permissible to alter slightly the solution volume in the reservoir to achieve that end.

In setting up the apparatus we have found it convenient to use a V-shaped wooden stand in which the pour test apparatus rests upon a shelf and is held in position by metal springs. The wooden stand extends the entire length of the apparatus. At the upper end of the wooden portion, a flat annular metal ring is fastened and it is upon this ring that the wooden reservoir holder rests (see diagram). This arrangement is helpful in aligning the reservoir and receiver as well as protecting the apparatus from breakage.

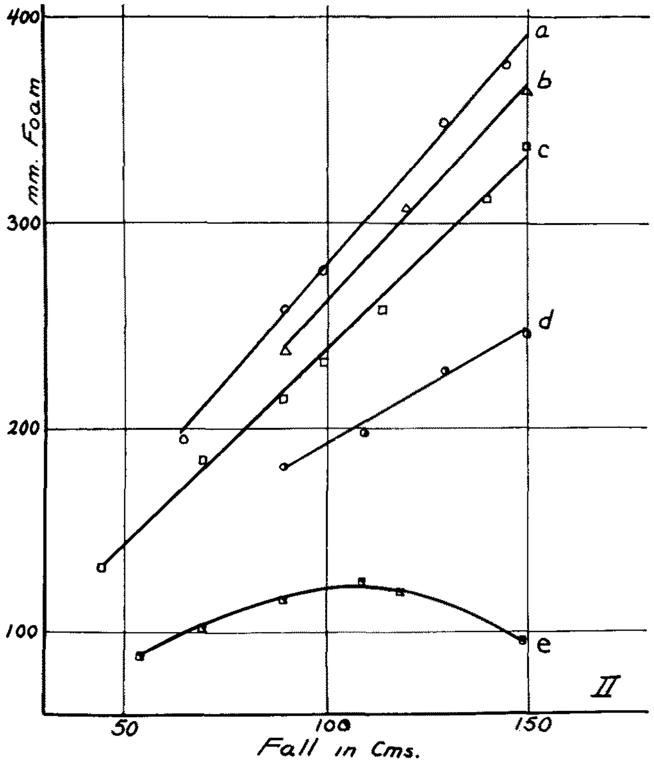
We have found it essential to adhere closely to a uniform procedure in both the operation of the test and the preparation of the solutions in order to obtain reproducible results. In preparing the solutions, care must be exercised, in all cases where the order of mixing and the age of solution can influence the character of the final mixture, to ensure reasonable comparability between different solutions.

Directions for Setting Up and Operating the Pour Foam Test

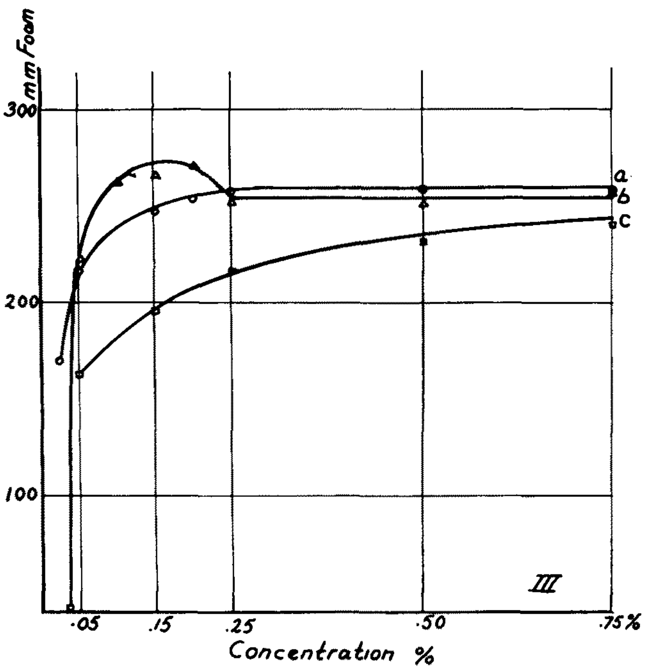
(1) Adjust the receiver so that it is plumb.

(2) Adjust the reservoir by means of the three leveling screws so that a stream of water emerging from the orifice will strike the bottom center of the receiver.

(3) Be sure that both the receiver and reservoir are clean. The final step in the cleansing shall be a thorough rinsing with distilled water. If the glass surfaces are clean, the distilled water should flow over the side walls in an unbroken film, finally



Graph II.
Foam production as a function of the height through which the solutions fall.
Solution volume delivered 210 *ml.*
Temperature 25°*C.*
a. 0.25% *coconut oil soap potassium salt.*
b. 0.25% *olive oil soap sodium salt.*
c. 0.25% *synthetic detergent A.*
d. 0.05% *synthetic detergent B.*
e. 0.05% *synthetic detergent A.*



Graph III.
Foam production as a function of concentration.
Height of fall 90 *cms.*
Temperature 43°*C.*
Solution volume 200 *m l.*
a. Tallow soap sodium salt in distilled water.
b. Olive oil soap sodium salt in distilled water.
c. Synthetic detergent A in distilled water.

draining without the appearance of droplets on the glass.

(4) Close the stopcock of the receiver and by means of a 50 ml. volumetric pipette introduce 50 ml. of the test solution into the receiver. The solution should be run down the side walls of the receiver to avoid foam formation and wet the entire interior of the receiver. Hold the tip of the pipette against the side wall of the receiver and slowly move the tip around the circumference of the tube so that the solution will flow down on all sides.

(5) Fill the reservoir in the manner of filling a volumetric pipette. The reservoirs should be marked at a point which indicates a liquid content of 200 ml.

(6) Place the reservoir in position at the head of the receiver and open the reservoir stopcock.

(7) When all the liquid has run out of the reservoir start stopwatch and take foam height readings immediately, and after 5 minutes. The first reading is our accepted standard, however, additional indications of the relative stability of various foams may be obtained in those cases where breakdown does occur in five minutes.

(8) The readings should be taken as follows: A millimeter scale is placed behind the receiver so that the zero mark is opposite the point in the receiver which would be reached by the total volume of liquid introduced into the receiver. The foam production is measured at the top of the foam column at the highest average height to which the rim of the foam has reached. This height is proportional to the volume of air remaining in the foam. Additional measurements of foam height may be taken at suitable intervals.

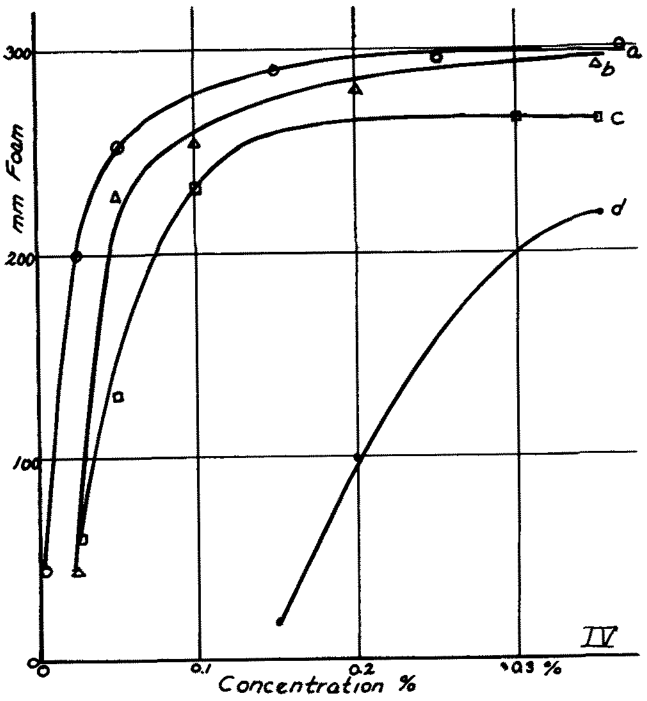
(9) Empty receiver of detergent solution and while the stopcock is open flush down side walls with distilled water until all foam has been swept out of the bottom.

Preparation of Solutions for the Pour Foam Test

Soaps

(1) Distilled water at 110°F.
   a) Weigh out soap sample.
   b) Heat the required volume of water to 110°F.
   c) Add the dry soap to the heated water and at the same time agitate the solution mechanically in such a way as to avoid agglutination of the soap particles. The use of mechanical stirring is preferred.
   d) Continue the stirring until all the soap is dissolved.
   e) Place in water bath at 110°F. until the solution is ten minutes old, starting from the time when the soap was first added.
   f) Run the pour test on the 10 minute old solution.

(2) Hard Water at 110°F.
   a) The artificial hard water such as that prepared from calcium and magnesium salts is diluted to the required degree of hardness in distilled water, and the pH of the solution is adjusted to within the range 9.5 to 10.0 by the addition of NaOH. The pH adjustment is made to avoid soap hydrolysis in the first stages of dissolution.
   (b) Proceed as outlined under No. 1 above.



Graph IV.

Foam production as a function of concentration.
Soaps of commercial fatty acids in distilled water.
Temperature 60°C, Volume 200 ml., Fall 90 cms.
a. Sodium Palmitate.
b. Sodium Stearate.
c. Sodium Myristate.
d. Sodium Laurate.

(3) The addition of builders to soaps.
   a) All solid builders are mixed with the weighed out sample of dry soap and dissolved in the manner described above under Procedure No. 1.

Synthetic Detergents, Etc.

In most cases it will be found unnecessary to observe the precautions described for the preparation of soap solutions. Most of the synthetic detergent materials undergo only slight changes in distilled water and, therefore, it is quite satisfactory to use any procedure which is convenient.

In cases where a reaction is suspected between the detergent and the solvent or other solute, care and control should be exercised over the temperature and age of the solutions.

Summary

1. The measurement of the foaming properties of soaps and detergents is shown to be possible by comparing the ~~relative stability~~ of a foam by measuring the effect of an arbitrary standard destructive mechanism acting upon a volume of foam during production under standard conditions and protected from adventitious destructive forces.

2. A simple apparatus and procedure for carrying out foam tests has been described and the reproducibility of the test evaluated.

3. Previous studies of foam comparison have been reviewed and criticisms offered regarding the procedures and conceptions involved.