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SUMMARY

A method of measuring foaming volume is described and investigated to establish the critical factors in its operation. Data on foaming volumes and foam stabilities are given for a series of hydrocarbons and for a range of concentrations of aqueous ethylene-glycol solutions.

It is shown that the amount of foam formed depends on the machinery of its production as well as on properties of the liquid; whereas the stability of the foam produced, within specified mechanical limitations, is primarily a function of the liquid.

INTRODUCTION

In a series of recent papers (references 1, 2, and 3) the determination of the stability of foams has been analyzed and shown to depend on a complex of subsidiary effects, each of which influences the measured result in an unpredictable way. The average lifetime of gas in the foam is found to depend on liquid viscosity, limiting foam density¹, bubble size, and foam height; the drainage rate of liquid from the foam depends on bulk and surface viscosities, bubble size, and rate and manner of bubble coalescence. It therefore becomes a question, if the measured stability of a foam can be so freed from the influence of uncontrollable factors as to reflect truly an intrinsic property of the liquid. Attempts to answer this question gradually have increased the number of experimental precautions on methods of measuring foam stabilities, as the complex of subsidiary factors has been revealed. These factors are of two types.

¹Limiting foam density, density of a fully drained foam, is obtained by plotting the changing weight of a foam that is being allowed to drain divided by the corresponding volumes (that is, the mean density from time to time) against the volume of liquid remaining in the foam, and extrapolating to zero volume of liquid. This is the final density at which the last remaining films break, and hence may be regarded as the foam density at which the films become unstable.

Some are themselves intrinsic properties of the liquid, such as bulk viscosity, surface viscosity, the minimum thickness of liquid film before film rupture, liquid density, and so forth. As they are properties permanently associated with the liquid, their influence on the foam stability, while it may be traced, is not an external or fortuitous circumstance but is characteristic of the liquid and should be allowed to operate freely on the foam stability.

There are other factors which affect foam stability but are independent of the liquid itself. It is the recognition of these factors, the isolating of their specific effect on stability, and their control in methods of foam measurement that is the object of the present paper.

It has been pointed out (reference 4) that ease of foam formation, foaming volume, and the stability of the foam that is formed are properties that do not necessarily have any direct relation. Most writers on the subject have confined their attention to the measurement of stability. The limitations of this viewpoint have been referred to recently in a paper by Gray and Stone (reference 5), who emphasize that foam stability measurements should be taken in conjunction with measurements of foam density. It is easily recognized that initial foam densities, as measured by Gray and Stone, also measure amounts of foam formed in cases where the same starting volumes of liquid are used, under their stated conditions where none of the air escapes.

The present paper adduces further evidence to show the relation between foam stability and foam volume and to determine the conditions under which foaminess may be accounted a property only of the liquid, independent of the fortuitous mechanical conditions attendant on its production.

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METHODS

Foam stabilities.- The bubbling method at elevated temperatures, using a porous ball or sintered glass plate, has already been reported (reference 1). The method commonly used at room temperatures with viscous liquids, such as lubricating oils, consists in producing the foam by beating and observing the rate of collapse of a specified initial amount of foam in a graduated cylinder. Both methods already have been described and compared (reference 1).

Foaming volumes.- The average specific gravity of lubricating oils is 0.88; in order to obtain 100 cubic centimeters it is convenient to weigh out 88 grams of oil into the smaller container of a commercial electric mixer with two revolving whips as in an egg beater. This sample is stirred for not less than 3 minutes at the top speed of the instrument. After stirring, the whips are removed and 15 seconds after beating exactly 100 cubic centimeters of the foam is transferred to a graduated cylinder of which the weight already has been determined. The cylinder and its contents are weighed, the difference being the weight of 100 cubic centimeters of foam. As 100 cubic centimeters of oil weighs 88 grams, the weight of 100 cubic centimeters of foam will be less than 88 grams; the difference is due to the loss of oil displaced by the air. This difference in weight can be converted to the corresponding volume of air in the foam by dividing by the specific gravity of the liquid. The result thus obtained is the percentage of air entrapped in the foam and, where all the liquid has been transformed into foam of uniform density, can be manipulated mathematically to measure the amount of foam that can be formed under the conditions of the test.

INVESTIGATION OF THE METHOD USED TO OBSERVE FOAMING VOLUMES

Following the directions specified previously and at a temperature of $25 \pm 1^{\circ}\text{C}$, values for a certain oil, selected as standard, range from 51.1 to 51.7 cubic centimeters of air per 100 cubic centimeters of total oil and foam. Variations in the specifications of the method were studied under the following heads:

- (a) Variation of the length of time of beating
- (b) Variation of the interval elapsed after beating, before pouring
- (c) Variation in the depth of immersion of the blades (i.e., initial volume of sample)
- (d) Variation in the speed of beating
- (e) Variation in the degree of previous aeration of the oil sample

All these tests were performed on the same oil, at temperatures of $25 \pm 1^{\circ}\text{C}$, and the results are given in table I.

Table I reveals the factors important for reproduction of results by this test. With lubricating oil samples of viscosity SAE 60, the foam remains homogeneous after beating at room temperature for a period of greater than 60 seconds; hence slight variations in the time elapsed before pouring it into the measuring cylinder will not affect the result.

Variations in the time of beating at top speed (setting 10) do not affect the final amount of air entrained in the oil; hence an equilibrium can be presumed to be established in the whipping process. At lower speeds of whipping, this equilibrium value or steady state shifts in the direction of the entrainment of more air than at the highest speed. The difference in entrainment at different speeds of whipping is not great but nevertheless shows that the more rapidly moving parts actually break up the foam to a certain extent. Indeed, the direct test in which a more voluminous foam, previously formed by bubbling, was beaten showed that the volume was reduced to the same equilibrium value or steady state.

The degree of immersion of the blades in the sample is a critical factor: the greater the immersion the more air that can be entrapped in the final foam. For this reason, the part of the specification that requires the greatest attention is the weighing out of the amount of sample taken. For the same reason, identical vessels should be used for all the whipping tests to ensure the same degree of immersion of the blades throughout.

This test has been used not only to characterize various existing liquids but also to test the effect of antifoaming agents.

RESULTS

In table II the stabilities of foams formed by the beating method at room temperature are compared with the amount of foam produced under the same conditions for a series of oils. The foam stability is expressed as L_g (average life of the gas in the foam in minutes); the volume percentage of air in the foam is given as an indirect expression of the foaming volume. All the samples are available brands of lubricating oil. Oils 9 and 10 clearly contain agents that prolong the stability of the foam but have no effect on the foaming volume.

Another type of comparison was made using mixtures of water and ethylene glycol. It was found that solutions varied in their foaming properties with different samples of ethylene glycol, which was therefore distilled under reduced pressure as a preliminary measure. When purified, the foaming volume of ethylene glycol in aqueous solutions is always lower than when the material is used directly. Ethylene glycol alone, like all pure liquids, does not foam.

The foaming tests were conducted at 27° C using a bubble-type foam meter (reference 1). Each test was made at an air pressure of 6.25 centimeters of mercury, the air bubbled in through a Cenco gas diffusing stone and the liquid foamed until it reached its maximum height. Both the height of foam and the time of its total collapse were observed. Figure 1

shows the variation of foaming volume with concentration, and figure 2 shows the variation of foam stability (time for total collapse) with concentration. At a concentration of 20-percent ethylene glycol a phenomenon was noted that did not appear at any of the other concentrations. Foaming the same solution repeatedly with only a few minutes interval between each test, resulted in a notable decrease of the amount of foam formed. After three foamings, a steady state is reached. This concentration is close to the optimum for amount and stability of foam and repeated foamings of a 20-percent solution alter the height of the maximum of the curve, as shown in both figures 1 and 2.

When foaming volume tests on these solutions were made by the beating method described, it was discovered that no foam could be formed by beating, not even for the optimum 20-percent ethylene-glycol solution. According to this test, therefore, solutions of ethylene glycol would appear to have no foaming properties; whereas bubbling produces copious foam.

DISCUSSION

Foam Stability

Static methods of measuring foam.— In static methods, foam already formed is allowed to drain and break undisturbed while it is being observed. Units of foam stability, L_g and L_l , have been defined previously (reference 3). These units represent the average life of gas and of liquid in the foam. They are therefore a true measure of the stability of the foam although of course by themselves they tell nothing of the extent to which the measured stability depends on factors external to the foaming liquid.

The mathematical functions by which L_g and L_l are defined are:

$$L_g = \frac{1}{G_0} \int_0^{G_0} t \, dG \quad (1)^1$$

$$L_l = \frac{1}{V_0} \int_0^{V_0} t \, dV \quad (2)^1$$

¹The equations in reference 3 have the limits reversed. They are here correctly printed.

where V and G are the volumes of liquid and gas, respectively, in the foam at time t , and V_0 and G_0 are the corresponding volumes at $t = 0$.

These expressions by themselves provide no information about the nature of the functions. It has been found necessary to supplement them with a mechanical model of a foam in the process of rupture. This model (reference 1) leads to the result that L_g is proportional to three factors: the initial height of the foam, the viscosity of the liquid, and a complex function of the minimum film thickness and bubble size. Of these factors, the last two are largely characteristic properties of the liquid but the first one is wholly an external factor that can vary independently of the liquid. Some experimental verification of this model has been published (reference 1); further verification is provided by an unpublished series of experiments conducted by Mr. W. W. Woods. The collapse of equal heights of the same foam were observed in tubes of different cross-sectional area, and the values of L_g were found to be identical.

The conclusion to be drawn from these results is that the rate of film rupture depends primarily on the cross-sectional area of the exposed foam. This is inherent also in the assumptions on which the foam model was constructed. When foam stability is based on measurements of volume or height, therefore, constant cross-sectional area should be preserved from one method to another.

Considering now that the foam is held always in tubes of the same cross-sectional area, the effect of varying the volume of foam is to be taken into account. According to the foam model of Brady and Ross (reference 1, equation (19)), increasing the volume of foam increases the value of the initial foam height proportionally and L_g varies accordingly; L_g is thus seen to be an extensive property of a foam, varying directly with the amount taken (held always in tubes of constant cross section).

Here it must be recalled that the foam model on which these conclusions are based can be regarded only as a first approximation to a real foam. In the model it is supposed that the rate at which gas is escaping from the foam is constant (dG/dt is constant). But it is only in particular cases that dG/dt is constant for static foams. It happens to be so for some hydrocarbon oils, as can be seen from figures 2 and 3 of the paper by Brady and Ross (reference 1); but figure 4 of the same paper shows an example where dG/dt varies continually during the lifetime of the foam. In the former case, by using the function $L_g/\nu h_0$, where ν is the kinematic viscosity of the liquid and h_0 is the initial foam height, a correlation between different methods and between different determinations by the same method could be obtained independently of the value of G_0 in each experiment. But in other situations the function

$L_g/v h_0$ will not operate, as it does in the particular case of constant dG/dt , to give a foam stability unit independent of the initial amount of foam. Hence comparisons of the same foaming liquid by different foaming methods, or different liquids by the same method, should always be made with the same initial volumes of gas in the foam with the unit L_g used. Such comparisons cannot otherwise be expected to provide information relative solely to the respective foaming properties of the liquid. In this respect, foam stability is like all extensive properties of matter, which must be referred to a constant amount before comparisons can be made between different substances. The beating method described by Brady and Ross (reference 1) takes account of this by beginning always with 500 cubic centimeters of foam, and so is a useful method for direct comparisons of foam stabilities. (See table I.)

The nature of the function L_g by which foam stability is expressed does not readily permit the use of terms such as Specific Foam Stability or Molar Foam Stability, because in the general case no simple relation exists between the stabilities of foam containing 1 mole of gas and half the amount of the same foam. Only when the gas escapes from the foam at a constant rate is the stability in the latter case half of what it is in the former.¹

¹Equation (1) can be written

$$L_g = \frac{1}{G_0} \int_{t=T}^{t=0} m t dt \quad (3)$$

where $m = dG/dt$.

For a constant value of m ,

$$\begin{aligned} L_g &= \frac{m}{G_0} \int_{t=T}^{t=0} t dt \\ &= -\frac{mT^2}{2G_0} \end{aligned}$$

where m is constant, $m = dG/dt = -G_0/T$; therefore

$$L_g = \frac{T}{2}$$

where T is the time required for total collapse of the foam.

The average length of time that gas stays in the foam is expressed by L_g . If the gas is lost at a constant rate, then twice the initial amount of gas will have twice the stability; if the initial amount of gas is the same, then twice the rate of loss of gas will reduce L_g to half its first value.

The difficulty of determining foam stability is further increased by the influence that the mechanical devices for producing foam may have on the characteristics of the foam produced. Cases can readily be found where the stability of the foam depends on the mode of its formation. In certain nonaqueous foams formed by reducing the pressure, the foams initially formed are stable until the films are stretched too far by further evacuation, whereupon they collapse. In foams produced by the bubbling method, when the rate of air flow is allowed to vary outside certain predetermined limits which for some liquids may be very narrow, the air escapes rapidly from the liquid by means of channels plowed forcibly through the foam by the blast or by larger bubbles. Rapid bubbling may also cause coalescence on the porous glass bubbler, leading to such larger bubbles. Any mechanical condition that leads to the production of large bubbles will decrease the value of foam stability. Mechanical arrangements for producing foam must, therefore, first be investigated to ascertain if for a given liquid the foam produced is intrinsically of the same character, especially with respect to size of bubbles, as that produced from the same liquid by other methods before comparison of foam stabilities by different methods can be undertaken. If very fine bubbles are produced by one method (e.g., beating), the bubbles may be allowed to segregate and coalesce to a comparable size before the measurement is begun; but if very large bubbles are produced it is doubtful whether measurements on such a foam will be found to yield any correlation. This, therefore, is the nature of the limitation imposed by the mechanical conditions on comparisons of stabilities of foams produced by different methods or by the same method under different conditions.

The specific manner in which this limitation becomes evident will vary from one method to another and may, in some instances, be relatively obscure. Within the framework of these limitations, however, the stabilities of foams produced by very different mechanical methods have been shown to give values capable of a high degree of correlation (reference 1).

Dynamic methods of measuring foam stability.— In dynamic methods, the foam is observed while it is being formed or replaced. It is a fundamental condition of Bikerman's dynamic foam meter (reference 6) and the dynamic foam meter of Hoffmann and Peters (reference 7) that an equilibrium or steady state between formation and collapse be established, whereby the volume of foam formed depends only on the two rates of formation and collapse. With a constant rate of formation of bubbles of definite size by injection of air the calculation of foam stability is based in the measurement of the volume of foam formed at the steady state.

This is borne out by the present data for ethylene-glycol solutions. In figure 1, the rate of air flow is the same for all the tests. The maximum height of foam is therefore directly proportional to the unit of foam stability. \sum as defined originally by Bikerman (reference 6):

$$\sum = \frac{Vt}{v} = \frac{V}{r} \quad (4)$$

where V is the volume of foam, v is the volume of air injected in time t , and r is the rate of air flow ($r = v/t$).

The parallelism between figures 1 and 2 shows the essential validity of Bickerman's unit as a unit of foam stability provided the rate of bubbling is kept suitably uniform. Although the measurements refer to the amount of foam produced, they bear a general resemblance to direct observations of foam stability, measured by the time for total collapse of the foam. Figure 1 is essentially derived from a dynamic foam-stability method and figure 2 from a static foam-stability method. Other examples of general agreement between the results of static and dynamic foam measurements have been published (reference 1). They are all illustrations of a proportionality between foaming volume and foam stability.

In the bubbling methods, static or dynamic, results should remain reproducible with varying rates of air flow, all other things being equal, only as long as an increase in air flow produces no effect other than a corresponding increase in the rate of bubble formation. As soon as it also causes any change in the bubble size or foam density, the results for foam stability are altered. For many liquids the range in variation in permissible rates of air flow is narrow and rates of flow outside these limits will produce conflicting results. The criticism of the dynamic foam meter by Hazlehurst and Neville (reference 8), on the grounds that different rates of air flow caused the foam stabilities of their solutions to fall in different orders, points out a generic weakness of this instrument, which can be overcome only by a preliminary investigation to discover those rates of air flow that affect only the rate of foam formation without changing the size distribution of the bubbles. Some of this difficulty may be removed by using a series of inlet tubes of known diameter for the injection of air into the liquid, as has been done by Ostwald and Mischke (reference 9).

The measured foam stability depends on a complex of factors, some of them determined by conditions external to the foam and some by innate properties of the liquid or the liquid films. These factors must be investigated for each method to determine their origin, so that those arising from external mechanical conditions can be kept constant and a comparison of foam stabilities made to depend as much as possible on differences existing in the properties of the foaming liquids.

Amount of Foam, or Foaming Volume

It is apparent from table II that the amount of foam produced is not

related to the values obtained for foam stability. Oils with exceptionally great foam stabilities produce, approximately, only the same amount of foam as oils of average stability.

The amount of foam produced is a function of the method by which it is formed. That ethylene-glycol solutions produced no foam on beating, although capable of forming voluminous foam when air is bubbled through them, shows in this extreme case that the conditions imposed by the mechanical method can cause profound variations in their effect. Yet it is logical, on consideration of how a volume of foam is produced, that the amount of foam, or foaming volume, should depend also on the stability of the films at the time the foam is made. Why then do the experimental results (table II) show no relation between foaming volume and foam stability?

If the rate of film rupture, as measured by dG/dt , gets progressively less during the lifetime of a static foam, as is often found to be the case, then the measured value of L_g will not be related to the initial rate of film rupture but to an averaged rate; for by equation (2) the symbol m , designating dG/dt , remains under the integral unless it is constant with variation of time.

But the amount of foam formed, the foaming volume, does not depend on an averaged rate of film rupture considered over the whole lifetime of the foam; it depends only on the rate of film rupture which operates during the formation of the foam. If that rate remains constant thereafter, as it does in those static foams from which the gas escapes linearly with time, then foaming volumes and foam stabilities will be found to have a simple proportionality. Other examples of foams that maintain a constant rate of film rupture are given by all dynamic foams at the stage of equilibrium, but equation (2) refers only to static foams; so the same argument does not apply in all its terms. Nevertheless, by virtue of the constant rate of film rupture during equilibrium of dynamic foams, if the air flow and other mechanical conditions are kept constant, the foaming volume may be read to indicate dynamic foam stability, as suggested by Bikerman (reference 6).

In many static foams, however, the rate of film rupture changes markedly as the foam ages. The rate may be slowed by the accumulation of stabilizing material that falls on the remaining liquid films from all the films that have collapsed above them. Dissolved substances, such as soaps, saponin, or albumens, that make very stable liquid films, characteristically produce foams of this description. The amount of foam and the foam stability here have no simple proportional relation (cf. table II). Once the complete-decay curve of the foam has been determined experimentally the existing relation can be obtained from the data, but it could not have been predicted.

The amount of foam formed depends on certain qualities of the liquid (such as viscosity, density, and stability of freshly formed films) and on the mechanical conditions of its production. For the liquids of table II, the mechanical conditions of foam production were kept constant and the density and the viscosities were also about the same, but the static foam stabilities were vastly different. As the foaming volume was found to be nearly constant and unrelated to the ultimate stability of the foam formed, it may be inferred that the initial rate of film rupture, or the stability of a freshly formed film, is likewise independent of the stability that it will assume on aging and is essentially constant for all the oils whether or not foam stabilizing agents are present. Certain other agents that are found capable of reducing the foaming volume do so by affecting the stability of freshly formed films.

For more complete information on the character of any foam, both the foam stability and the foaming volume must be determined. Since the value of the foaming volume varies with the method used to produce the foam, it is desirable to duplicate or have conditions like those of the practical problem when specifying the laboratory test. A foaming agent or an antifoaming agent can operate to modify either or both of the two characteristics of the foam, stability and amount. It is frequently the case that agents most effective in reducing the amount of a foam to a small residue, also stabilize this residual foam. Other agents reduce or increase the foam stability without altering the amount of foam that is formed.

Stanford University,

Stanford University, California, September 24, 1945.

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Mischke, W.: Investigations on Foaming with Special Reference to Problems of Applied Chemistry. II. Kolloid-Zeitschr., vol. 90, 1940, p. 77.

TABLE I.- VARIATIONS IN SPECIFICATIONS OF BEATING METHOD

Description of treatment	Foaming volume (percent air in foam)	Comment
Treatment as specified in text	51.5	Control
Beaten at full speed (10) for 30 minutes, instead of 3 minutes	51.3	No difference
Foam measured immediately after beating, instead of 15 seconds after	51.1	No difference
Foam measured 60 seconds after beating, instead of 15 seconds after	51.4	No difference
Oil turned to foam by bubbling for 24 hours before testing	51.7	No difference
Taking 76 grams of oil instead of 88 grams	47.9	Lower value
Taking 144 grams of oil instead of 88 grams	54.7	Higher value
Beaten at half speed (5) for 3 minutes instead of full speed (10)	55.2	Higher value
Beaten at low speed (2) for 15 minutes, instead of full speed (10) for 3 minutes	54.6	Higher value

TABLE II.- COMPARISON OF FOAM STABILITY AND
FOAMING VOLUME FOR A SERIES OF OILS

(Foams produced by the beating method at room temperature)		
Oil	Foam stability, Lg (min)	Foaming volume (percent air in foam)
1	18.5	41.9
2	22.3	52.6
3	27.3	49.7
4	31.2	28.7
5	51.5	49.3
6	65.5	52.0
7	79.2	51.3
8	103.6	55.9
9	2056.0	50.6
10	4920.0	45.3

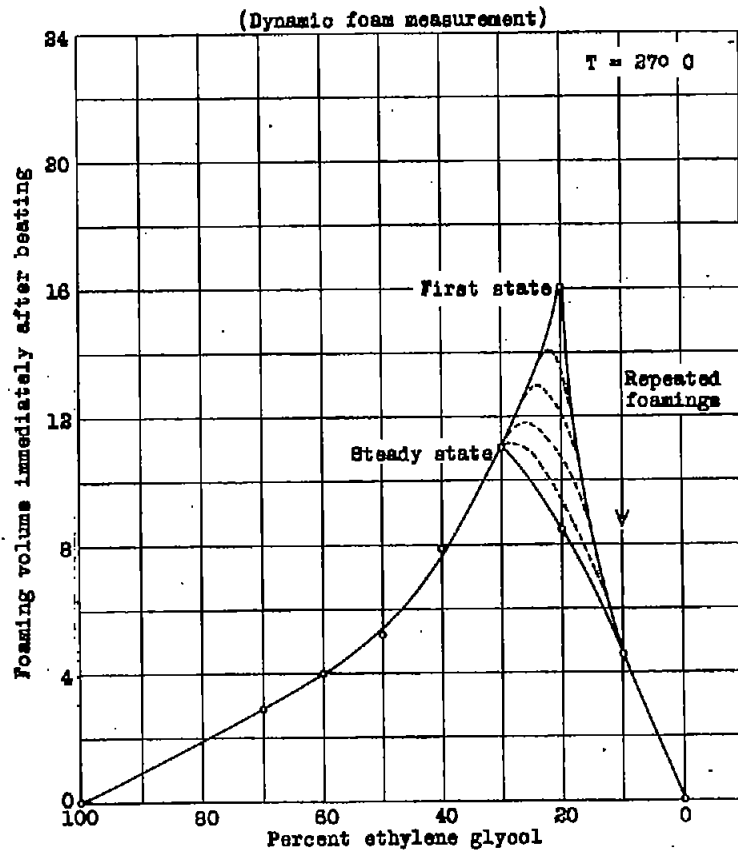


Figure 1.- Variation of foaming volume with concentration of ethylene glycol in water.

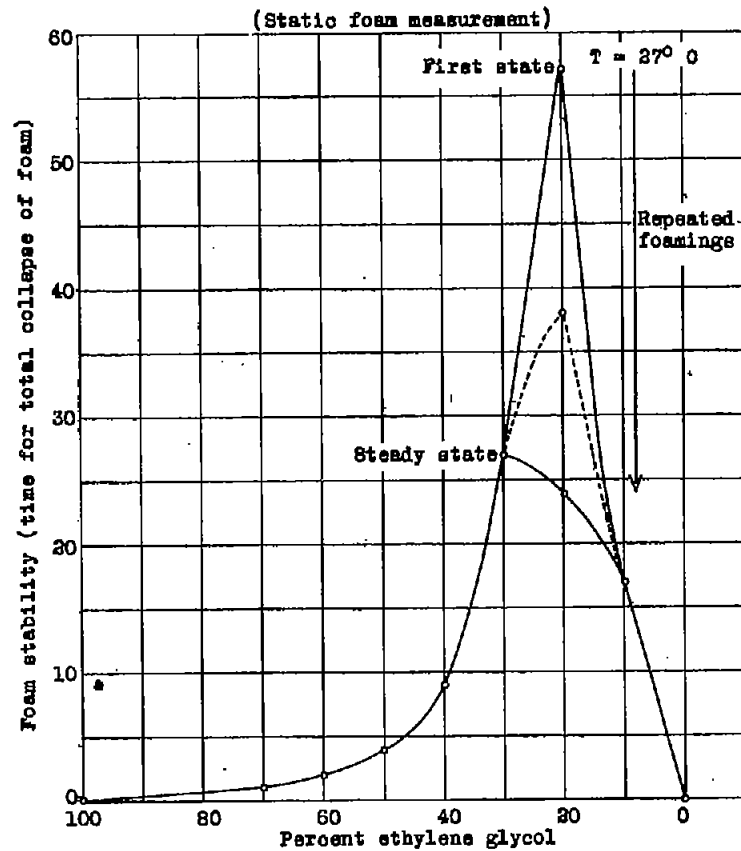


Figure 2.- Variation of foam stability with concentration of ethylene glycol in water.