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A GENERAL METHOD OF SELECTING FOAM INHIBITORS

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SUMMARY

Most known foam inhibitors and antifoaming agents as found in this investigation and described in the literature are insoluble. A criterion is described here for selecting foam inhibitors from insoluble liquids that form emulsions with the foaming liquid. By determining the surface tensions of the foaming liquid and of the additive saturated with that liquid and the interfacial tension between them, spreading and entering coefficients may be calculated. High positive spreading and entering coefficients are characteristic of a liquid foam inhibitor for the specified foaming liquid. Negative spreading and entering coefficients are characteristic of liquids which will not reduce foaming. Fifty-four experimental cases are cited, for three foaming systems, to which the principle has been applied with high correlation.

A mechanism of foam inhibition is described. Bubble coalescence, rather than bubble rupture at the top of the foam, is emphasized. It is shown that a spread film of a foam inhibitor on the surface of the foaming liquid may actually stabilize bubbles at the surface, although promoting rapid coalescence.

INTRODUCTION

The problem of foam inhibition is one of perennial interest in many commercial processes and arises in numerous and diversified applications. While many substances are known which act as more or less effective foam inhibitors for specific foaming systems, no general principles for selecting such inhibitors have been recognized. This paper describes such a general principle, which should be of practical value.

Generally speaking, foam is excessive and obnoxious only when air or other gas is being continuously introduced into a liquid capable of foaming, by injection under the surface, by agitation, by aspiration through a circulating pump, by occlusion under a stream of liquid impinging on a liquid surface in a tank, and by other similar means. Presumably, the introduction of such gas cannot be avoided, and the best way in which objectionable foaming may be eliminated is to so treat the liquid that gas will pass through it harmlessly, each bubble breaking the moment it reaches the surface.

In certain applications in which liquids are circulating so rapidly, or are so turbulent, that very small gas bubbles are not given opportunity to escape, such bubbles may accumulate in the liquid in a "gas emulsion" which is objectionable. The considerations about to be applied to foam inhibition are also largely applicable to gas emulsion inhibition.

Gas will leave a liquid without forming a foam only if every bubble that reaches the surface ruptures quickly. In an agitated system, or at any liquid surface normally encountered, a large bubble will rupture much more readily than a small one. (See reference 1.) (Whether this is true in the case of bubbles at the surface of a liquid which is clean and protected from all mechanical, thermal, and electrical shocks is uncertain.) It follows that a foam inhibitor <u>may</u> operate by causing the coalescence of colliding bubbles below the liquid surface, the coalescence of bubbles with their neighbors at the surface, or both. A foam inhibitor <u>must</u> act: (1) by causing coalescence of smaller bubbles into larger bubbles at or below the surface, (2) by causing the rupture of individual bubbles at the surface, (3) by destroying the inherent stability of the liquid films, or (4) by causing any or all of these simultaneously.

As used in this paper, the term "foam inhibitor" refers to a substance which prevents foam formation, while the terms "antifoam" or "antifoaming agent" are generic terms embracing all aspects of the destruction, elimination, or prevention of foam.

The present discussion is restricted to insoluble foam inhibitors and the mechanism by which finely divided emulsified droplets of them may cause bubble coalescence or bubble rupture.

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MECHANISM OF FOAM INHIBITION BY EMULSIFIED AGENTS

Mechanism of Bubble Coalescence

Bubble coalescence beneath the surface of a foaming liquid containing an insoluble liquid foam inhibitor is pictured as the result of a triple coincidence — namely, the practically simultaneous collision of two air bubbles with the same small droplet of the dispersed foam inhibitor. The droplet enters both bubbles and spreads upon their inner surfaces. The two air bubbles are momentarily connected by the droplet of liquid, which forms a weak spot in the otherwise stable film of liquid between the bubbles. Unequal surface tensions and possibly the spreading of the liquid in the droplet upon the inner surfaces of the bubbles complete the destruction of the lamella separating the bubbles, and they coalesce. The process is diagrammed in figure 1.

The requirement for a droplet of liquid to cause bubble coalescence in this manner is that it enter the air-liquid interface on contact and may be that it then spread upon the foaming liquid, inside the bubble. A droplet of liquid in contact with an air bubble is pictured in figure 2. If the droplet is to enter the air bubble, a foaming-liquid-and-air interface and a foaming-liquid-and-foam-inhibitor interface will be replaced by a foam-inhibitor-and-air interface.

It may be seen from figure 2 that the surface tension of the foaming liquid σ_F and the interfacial tension between the foaming liquid and the foam inhibitor σ_{DF} favor the formation of the new interface, and the surface tension of the foam inhibitor σ_D opposes it. The direction of these forces is indicated by the vectors in figure 2. The criterion for the liquid droplet to enter the air bubble is therefore that $\sigma_F + \sigma_{DF} > \sigma_D$. The inequality may be expressed as a difference, here designated the entering coefficient, E,

$$E = \sigma_F + \sigma_{DF} - \sigma_D$$

The condition for one liquid to spread upon another clean liquid was derived by Harkins from a similar diagram and the tendency to spread was designated the spreading coefficient (reference 2). If the same symbols are used, the spreading coefficient for the foam inhibitor is S.

$$S = \sigma_F - \sigma_{DF} - \sigma_D$$

The requisite for the foam inhibitor to spread upon the foaming liquid is therefore that

$$\sigma_F > \sigma_{DF} + \sigma_D$$

The difference between E and S is in the sign of the interfacial tension, σ_{DF}. It is seen algebraically that a positive value for S necessitates a positive value for E. A positive value of S indicates that the insoluble liquid will be an effective foam inhibitor when dispersed in the foaming liquid. The surface tensions to be considered in computing S are most conservatively those of the foam inhibitor saturated with all the foaming-mixture components and the foaming mixture saturated with the foam inhibitor. The interfacial tension correspondingly is that between the mutually saturated phases. In practice, conditions may be more favorable to foam inhibition than indicated by the surface tension of the mutually saturated phases, since the fresh surfaces of new bubbles are not instantaneously saturated or fully stabilized. Ross (reference 3) suggests that the surface tension of thin films may be greater than the surface tension in the bulk. In cases where this is true, the spreading and entering coefficients calculated are lower than correspond to the actual condition.

Mechanism of Bubble Rupture

The breakage of a bubble is distinguished from the coalescence of two submerged bubbles, in that when it rises to a free surface and lifts a film of liquid above the surface, that film ruptures so that the air in the bubble escapes and the liquid in the film falls back to the surface. All air passing through a liquid must escape in this fashion. Whether or not a foam is produced depends upon the length of time the film of liquid raised above the surface persists before rupturing. The function of a foam inhibitor which promotes bubble rupture is to decrease the stability of the raised films.

It has been observed, in this investigation and elsewhere, as pointed out later, that film rupture is frequently associated with heterogeneous film composition. The rupture of a film may be likened to the bursting of an inflated rubber ballon when a weak spot is produced in the rubber by touching it with a lighted cigarette or a sharp point. Quite similarly, if a point of lowered surface tension is suddenly produced in a film, the tension of the film, like that of the rubber, pulls it away from that point.

It is concluded that patches of the foam inhibitor, spread on the liquid surface, cause differential surface tensions which render unstable the liquid film raised by a bubble. The origin of patches is presumably the spreading of droplets of the emulsified foam inhibitor which reach the surface.

TEST PROCEDURE

Foam Tests

The foaming systems used (hereinafter designated A, B, and C) were three of those selected by Ross and McBain (reference 3), and the same additives were studied for convenience in comparison. Ross' data on the foam-inhibiting ability of the agents in 1-percent concentration were utilized, where the method of testing foam inhibition was by shaking the liquids in test tubes. Complete inability to form foam was marked E; pronounced loss of ability to form foam was marked M; and no observable effect on the ability to form foam was marked N. All the materials were used without further purification.

Film Tests

Film rupture tests were performed by picking up a film of the foaming solution on a loop of platinum wire 6 millimeters in diameter and touching it with the end of a platinum wire which had been dipped in the agent to be tested. The procedure provides an analogy for the behavior of the agent in the actual foam and permits the observation of a number of interesting phenomena. The information so obtained is difficult to tabulate for extensive comparisons, because of the diversity of effects obtained. The value of the observations is principally in their suggestiveness as to the mechanism of antifoaming action.

The least ambiguous results were obtained when the films ruptured unfailingly and instantaneously. However, with other combinations, the ruptures were not instantaneous, but delayed from a fraction of a second to several seconds, either with or without accompanying visible effects. The spreading of the applied droplet is sometimes visible. The most amazing phenomenon is the formation of "windows" of the applied agent in the film. The droplet pushes the film aside and replaces the center portion with a film of itself, which may be quite thin. Such windows are generally fragile, although several apparently have been capable of an extended lifetime. Also, such a window may form and then dissolve.

To make a simple tabulation, the film rupture tests are graded L for instantaneous rupture, M for delayed but definite rupture, and N for no rupture. The incomplete agreement between the data herein reported and those of Ross is mainly accounted for by the larger diameter loop and consequently thinner films which he used.

Surface and Interfacial Tensions

Surface and interfacial tensions were measured, using a Cenco-du Nuoy tensiometer, with a platinum-iridium ring 4.00 centimeters in circumference, and a radius ratio of 39. Measurements were made at room temperature, the liquids being contained in 4.5-centimeter-diameter crystallizing dishes. The surface tensions were measured on the phases separately, not mutually saturated. The interfacial tensions were made in 5 to 10 minutes, no attempt being made to permit equilibrium to be established. The ring corrections were made by the method of Harkins and Jordan (reference 4). To make corrections, it was necessary to determine the densities of the foaming systems and anti-foaming agents. This was done by weighing 1 cubic centimeter of the liquid delivered from a tuberculin syringe pipette. The surface tensions and densities are reported in table I, where the additives are designated by arabic numerals and the three foaming systems as A, B, and C.

RESULTS AND DISCUSSION

The literature to date has paid little attention to bubble coalescence (see reference 5), but is principally confined to consideration of films at the free-air surface. That a free-air surface and the surface of the inside of a bubble in the same system may have quite different properties was shown by an earlier series of experiments performed at Stanford University on the stability of air bubbles released beneath the surface of lubricating oil on which was spread a thin film of a foam inhibitor (Additive 13 table I). (It should be noted that the visible film, when fully spread, did not cover the entire surface. The extent of the film was traceable by its displacement of a ring of tiny air bubbles floating on the surface, and the displacement did not extend farther than the film which was visible through its interference colors.) Air bubbles on this surface, when in contact, coalesced rapidly, but did not rupture. Bubbles containing as much as 6 cubic centimeters of air were formed by coalescing several small bubbles of measured volume. The largest bubble that could form on the surface of the oil alone contained 0.5 to 0.7 cubic centimeter; several such bubbles could exist side by side, usually rupturing without coalescing. The foam "inhibitor" in this case stabilized bubbles against rupture, although promoting coalescence. A distinction evidently must be made between the mechanism of rupture and coalescence. It has been noticed that excellent foam inhibitors of the type described in this paper may leave a small residue of highly stabilized foam.

In the present investigation, the method used to test foaming was to shake the liquid mixtures in test tubes. Many of the liquids so rapidly lost the air occluded by shaking that nothing which could be called a foam was formed. In these it was not possible to tell whether all sizes of bubbles ruptured or whether coalescence of small bubbles to larger ones preceded rupture. Observations of more enduring foams showed that both processes were occurring simultaneously. Hence, to explain the action of the foam inhibitors, it is necessary to postulate mechanisms both for accelerated bubble coalescence and for accelerated bubble rupture.

To allude again to the experiments described in part in a preceding paragraph, the coherent film of the foam inhibitor spread upon the surface of the oil stabilized air bubbles at the surface, but, if the spread film became

discontinuous through agitation or upon standing, bubble stability was much less than upon a clean surface. It was further observed that the spread film, visible by its interference colors, disappeared from the surface on standing, after which the bubbles were less stable than upon the untreated clean surface. Also, as more air was injected under a coherent, visible, spread film, forming a large stable bubble, a point was reached where the edge of the visible film was raised by the edge of the air bubble; at this point the bubble burst.

Fresh droplets of the inhibitor (Additive 13 table I) touched to the surface of a sample of a cloudy suspension of itself in lubricating oil, which sample had been aged for weeks to insure saturation, spread in films, in the same fashion as on a clean surface. These films showed some tendency to stabilize droplets released under them. On standing, these films disappeared, even though the oil under them was saturated. A peculiar "corrugated" appearance was noted in some of the films, possibly caused by multitudinous lenses beginning to form, which later consolidated into a few.

These experiments are strong evidence that "patches" of a foam inhibitor render raised films unstable, even though coherent films of the same substance may stabilize the films. Also, these experiments show that even though a substance may spread upon a liquid which is saturated with it, the coherent film formed may be unstable and may disappear from the surface. The disappearance of such spread films may be caused by their drawing up into lenses, since the films are evidently many molecules thick. It follows that a film spread on the inside of a bubble is not necessarily permanent.

Correlation of Foam Inhibition with Entering Coefficient

The degree of foam inhibition caused by the added agents in the three foaming solutions is indicated in tables II, III, and IV, in which the agents are arranged in order of decreasing entering coefficients. In the same tables are listed results of the film tests and the spreading coefficients. Other pertinent observations from the film rupture tests are given as annotations on the tables.

It is immediately apparent that the most noticeable correlation between entering coefficient and foam inhibition is that all agents for which the entering coefficient was

negative, or below 0.1, had no foam-inhibiting effect. There were no exceptions; 14 of the 54 cases were in this category. In contrast, 37 of the remaining 40 cases, in which the entering coefficient was positive, were foam inhibitors. The agreement is too good to be fortuitous.

There is obviously no relation in these data between the degree of foam inhibition (i.e., E or M) and the magnitude of the positive entering coefficient. A very good reason for this is found in the surface tensions used to calculate the entering coefficients. In an emulsion in which the phases were mutually saturated, the respective surface tensions of the phases after saturation might be somewhat different from those of the pure substances before coming in contact. Since the range of magnitude of the entering coefficients is only a few dynes, small changes in the respective surface tensions used to compute them could easily cause a rearrangement of the order of the list.

The converse consideration is that the same effect of mutual saturation would affect the foam inhibition. If this were the case, foaming of the emulsion mixture would change on aging. Such a case has been observed, when an effectively inhibited solution regained its foaming ability on standing overnight.

For most of the cases reported, the mutual solubilities were very low; hence there are only a few instances in which change of sign of the entering coefficient, or complete loss of foam-inhibiting ability, could occur. Those cases observed in which the foam inhibitor is appreciably soluble in the foaming solution, and vice versa, are annotated on the tables. Since two of the foaming solutions, and several of the inhibiting agents were quite viscous, certain cases of appreciable solubility may easily have been overlooked. The solubilities were determined by watching the behavior of droplets during the film tests. Because the foaming determinations were done quickly in all cases (less than one-half hour after the emulsion was formed), the situation in each emulsion mixture generally would be expected to correspond qualitatively to the situation for which the respective entering coefficient was computed. The three discrepancies, in which positive entering coefficients correspond to no-foam inhibition, occur in table III, for System B. The System B solutions have the viscosity of water; so a nonequilibrium emulsion system would change comparatively rapidly with time.

For practical application, in which a foaming system is to be rendered permanently nonfoaming, it is apparent that a significant entering coefficient should be calculated from the surface tensions and interfacial tension of the mutually saturated phases. However, because of the considerable difficulty attendant upon making the equilibrium measurements, a study of the nonequilibrium surface and interfacial tensions and the behavior of prospective inhibiting agents upon films should be profitable guides in surveying a foaming problem. It is also significant that freshly formed bubble surfaces are neither instantaneously saturated nor fully stabilized.

There are certain other factors by which the relation between entering coefficient and foam inhibition may be complicated. A very high interfacial tension tends to make a high entering coefficient, and, if the surface tension of the destroyer is low, still permits a positive spreading coefficient. However, high interfacial tensions are associated with poor emulsibility, and it obviously is necessary for the inhibitor to be so finely dispersed that there will be droplets in the vicinity of every bubble or film. The failure of Additive 13 in System B (table III) may be such a case, especially in view of the high film disrupting power shown in the film tests.

Confusing results may be obtained when the inhibitor consists of several components, one or more of which may be soluble in the foaming solution. In such a case, the entering coefficient calculated from the surface tension of the unaltered inhibitor would be completely misleading, although the surface tension of the inhibitor after extraction by the foaming solution would be valid. Such a situation is represented by Additive 12 in System B (table III), Additive 12 being dissolved in a water-miscible organic solvent.

Correlation of Foam Inhibition with Spreading Coefficient

The correlation of spreading coefficient with foam inhibition is similar to that between entering coefficient and foam destroyer, as would be expected from the relation between entering coefficient and spreading coefficient. The figures in table V show the degree of correlation in the two cases.

From the present work it is impossible to decide whether entering coefficient or spreading coefficient is the better criterion for predicting foam inhibitors. Since a positive

spreading coefficient necessitates a positive entering coefficient, but not the converse, positive spreading coefficients will occur less frequently than positive entering coefficients. The question is whether bubble coalescence, by the mechanism postulated, depends upon spreading of the droplet of foam inhibitor upon the interior surface of the bubble, or only upon the droplet entering the bubble surface, where, in the case of positive entering coefficient and negative spreading coefficient, it could stay without spreading.

Correlation of Foam Inhibition with Film Tests

It may be significant that there are fewer film ruptures than successful foam inhibitions, considering again the data of this paper. In the films, equilibrium is approached quickly, due to the rapid solution at surfaces. Using fairly thick films, therefore, of sufficient stability to withstand some shock of adjustment, observations of the tendency of the films to rupture may be more analogous to those in an equilibrium emulsion system. On the other hand, when thinner films are used, the correlation of the film rupturing would be with the foam inhibition of a freshly formed emulsion system. This tendency is illustrated by comparing the film test data of Ross and McBain (reference 3), who used a 10-millimeter loop and obtained almost perfect agreement with foam inhibition, with the present data, where a 6-millimeter loop was used and a smaller number of film ruptures were obtained. Of the 54 cases considered in film tests in both papers, Ross and McBain reported 13 cases as E or M, which are here reported N; 8 cases as E, here M; 1 case as M, here E; 4 cases as N, here M. The last indicate systems in which the equilibrating process was favorable to foam inhibition.

Criteria for a Satisfactory Emulsion-Type Foam Inhibitor

From the foregoing data and discussion, the following requirements are deduced for selecting an emulsion-type foam inhibitor:

1. The surface tension of the agent must be several dynes lower than that of the foaming solution; the lower the better.

2. The solubility of the agent in the foaming solution must be low.

3. The agent must be readily dispersible in the foaming solution, a requirement favored by low interfacial tension.

Theory of Foam Inhibition

The only generalizations regarding inhibition of foaming have been made concerning the effect of insoluble substances. It has long been realized that the relative surface and interfacial tensions concerned must contain a key, but no tangible or easily tested principle has been suggested. Fiske (reference 6), in 1918, remarked, "The presence of undissolved particles of the inhibiting liquid must be regarded as essential... Rupture is accounted for by two opposite forces acting at the periphery of the drop of antifoamer on the film surface: (1) The tension of the uncontaminated part of the soap film itself, directed outward; and (2) the tension of the double surface acting inward." The all-important tension of the inhibitor itself was overlooked. Fiske also described another film test, by which the antifoaming properties of a liquid are tested by touching a drop of it to the surface of a single soap bubble.

Sasaki found that the foam height produced by shaking butanol-water mixture increased with increasing butanol content, but dropped to zero when the water was saturated. Similar results were obtained on addition of butanol to a soap solution. He concluded that the stability of the foam was related to its homogeneity (reference 7). Sasaki also stated that, in heterogeneous systems with limited solubility, the foam stability was low (reference 8).

However, heterogeneity alone is not a sufficient requirement for a non-foaming system, as shown by some of the cases herein reported. Sasaki generalized (reference 9), that in the heterogeneous region (of the phase diagram), foam formation is limited to mixtures in which the volume of the layer with the lower surface tension is greater than the volume of the layer with the higher surface tension. This is consistent qualitatively with the concepts presented in this paper, since, generally speaking, the sign of the entering coefficient is governed by the two surface tensions rather than by the interfacial tension. The writers have been

considering those systems in which the foam inhibitor was present in only 1-percent concentration. Sasaki defines a transition concentration at which the inhibitor would become the foamer, but the former foamer could not be an inhibitor. Cases in which the inhibitor apparently became ineffective, or actually a foamer, when its volume concentration was much less than 50 percent, have been observed.

The possibility of foam inhibition by a soluble agent is not excluded by the demonstration of the foam-inhibiting and breaking properties of the insoluble agents here discussed. Some of the foam-inhibiting agents listed in the present paper are soluble, but it is suspected that their reported efficacy as foam inhibitors might disappear were the mixtures aged. Some suggestions of soluble foam inhibitors are found in the general theoretical researches upon foam stability. An idea has been expressed by Berkman and Egloff (reference 10), that the more widely diversified the types of molecules in the surface layer (implying adsorption from solution), the more stable the foam; therefore, the addition of a second (soluble) surface active substance, further displacing water from the surface and increasing the surface "homogeneity," makes the foam less stable. The same authors add that colloidal solubility does not favor foaming; the formation of large molecular aggregates interferes with the "principle of heterogeneity."

Bartsch (reference 11), studying the foam formation curves for butyric, nonylic, and caproic acids, and octyl, heptyl, and amyl alcohols, found that these capillary-active foam-forming substances lose their foaming ability when a certain fraction of saturation is exceeded. (See also reference 12.) Antifoaming action in a single phase is here indicated. Sodium cholate and saponin were found to lose their foaming ability in supersaturated solutions. Bartsch (reference 11) states that the foaming ability increases when the boundary layer becomes heterogeneous, again referring to adsorption from a multicomponent solution. Thus, heterogeneity of composition of an adsorbed surface layer favors foam stability; whereas phase heterogeneity may oppose it.

CONCLUSIONS

In accordance with the mechanism of foam inhibitors postulated in this report, the following conclusions are presented on insoluble liquid foam inhibitors:

1. The ability of any liquid to act as a foam inhibitor depends on the relative values of the surface tension of the foaming liquid and the inhibitor, as expressed by the spreading coefficient S and the entering coefficient E.

2. High positive values of S and E are indicative of efficient foam inhibitors.

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TABLE I.- DENSITIES, SURFACE TENSIONS, AND INTERFACIAL TENSIONS

Additive No.	Name of additive	Density	Surface tension	Interfacial tensions		
				A	B	C
1	Ethyl oleyl glycol o-phosphate	0.958	31.3	1.2	0.1	0.2
2	Trioctyl tripolyglycol tetrapolyphosphate	1.159	25.9	Sol.	.8	Sol.
3	Glyceryl mono-ricinoleate	1.036	34.6	2.3	1.0	.6
4	2-Amino-2-methyl-1-propanol	.931	32.5	.8	1.0	Sol.
5	Tetraoctyl pyrophosphate	1.004	30.9	2.0	2.2	1.2
7	Carbitol maleate	1.164	36.8	Sol.	.2	Sol.
8	Mono-oleyl dipolyglycol o-phosphate	1.053	29.4	1.6	1.0	.7
9	Diethylene glycol mono-oleate	.954	31.0	1.4	.9	0.6
10	Diglycol dinaphthenate	1.002	32.5	.9	.1	1.5
11	2-Amino-2-ethyl-1, 3-propanediol	1.160	39.7	1.5	.9	1.0
12		1.027	29.5	1.2	.1	.1
13		.976	20.6	7.3	5.0	2.7
15		1.050	33.1	.9	Sol.	1.0
16	Diethylene glycol	1.128	44.5	Sol.	.1	Sol.
17	Ethyl phosphate	1.080	29.5	1.1	.1	.4
18		1.082	34.4	.8	1.5	2.0
19	n-Nonyl alcohol	.789	27.8	.8	1.7	.1
22	n-Butyl phthalate	1.046	32.3	1.8	1.5	1.3
System A:		1.1	36.7			
System B:		1.00	31.6			
System C:		1.13	35.5			

TABLE II.- SYSTEM A: ENTERING COEFFICIENTS, FOAM INHIBITION, FILM TESTS AND SPREADING COEFFICIENTS

Additive No.	Entering coefficient	Foam inhibition	Film test	Spreading coefficient	Notes
13	23.4	M	M	8.8	
2	10.8	E	N	10.8	(1) (2)
19	9.7	M	E	8.1	(3) (2)
8	8.9	E	N	5.7	(1) (2)
12	8.4	E	M	6.0	(4)
17	8.3	M	E	6.1	(2)
5	7.8	E	M	3.8	(2)
9	7.1	E	N	4.3	(1)
1	6.6	E	E	4.2	
22	6.2	E	N	2.6	
10	5.1	E	N	3.3	
4	5.0	M	N	3.4	(4)
15	4.5	M	M	2.7	Slow[2]
3	4.4	E	N	-.2	(1)
18	3.1	E	N	1.5	(1)
7	-.1	N	N	-.1	(1) or (4)
11	-1.5	N	N	-4.5	
16	-7.8	N	N	-7.8	(1) or (4)

[1]Mutually soluble.
[2]Additive forms "windows" in films of foaming solution.
[3]Foaming solution soluble in additive.
[4]Additive soluble in foaming solution.

TABLE III.- SYSTEM B: ENTERING COEFFICIENTS, FOAM INHIBITION, FILM TESTS AND SPREADING COEFFICIENTS

Additive No.	Entering coefficient	Foam inhibition	Film test	Spreading coefficient	Notes
13	16.0	N	E	6.0	
2	6.5	M	M	4.9	(1)
19	4.5	E	E	1.1	
8	3.2	M	N (M)	1.2	(2)
5	2.9	M	M	-1.5	(2)
12	2.2	N	N	2.0	(3) (4)
17	2.2	M	M (N)	2.1	
9	1.5	M	N (M)	-.3	(3) (4)
22	.8	N	M	-2.2	
1	.3	M	M	.2	
4	.1	N	N	-1.9	(5)
10	-.9	N	N	-1.0	(4)
18	-1.3	N	N	-4.3	
15	-1.5	N	N (M)	-1.5	(1)
3	-2.0	N	N	-4.0	(6)
7	-5.1	N	N	-5.4	(5)
11	-7.2	N	N	-9.0	(5)
16	-12.9	N	N	-13.0	(5)

[1]Mutually soluble.
[2]Additive forms "windows" in film of foaming solution.
[3]Foaming solution soluble in additive.
[4]Additive forms fine emulsions readily in foaming solution.
[5]Additive soluble in foaming solution.
[6]Additive spontaneously emulsifies in foaming solution.

TABLE IV.- SYSTEM C: ENTERING COEFFICIENTS, FOAM INHIBITION, FILM TESTS AND SPREADING COEFFICIENTS

Additive No.	Entering coefficient	Foam inhibition	Film test	Spreading coefficient	Notes
13	17.6	M	E	12.2	
2	9.6	M	E	9.6	(1)
19	7.7	M	E	7.6	(1)
8	6.8	E	E	5.4	(2)
17	6.4	M	M	5.6	(1)
12	6.0	E	M	5.9	
5	5.8	E	E	3.4	
9	5.1	E	E	3.9	(1)
10	4.5	E	E	1.5	
22	4.5	E	E	1.9	
1	4.3	E	E	4.0	
15	3.4	M	E	1.4	
18	3.4	E	E	-1.4	(1)
4	3.0	M	E	3.0	(2)
3	1.5	E	E	.3	(1) (3)
7	-1.3	N	N	-1.3	(4) or (2)
11	-3.2	N	N	-5.2	(4)
16	-9.0	N	N	-9.0	(4) or (2)

[1] Foaming solution soluble in additive.
[2] Mutually soluble.
[3] Additive forms "windows" in film of foaming solution.
[4] Additive soluble in foaming solution.

TABLE V.- CORRELATION OF FOAM INHIBITION WITH ENTERING COEFFICIENT AND SPREADING COEFFICIENT

Total Number of Tests		54
Foam Inhibition:	20 E 17 M 17 N	
Number with Negative Entering Coefficient		13
Foam Inhibition:	13 N	
Number with Positive Entering Coefficient		41
Foam Inhibition:	20 E 17 M 4 N	
Number with Negative Spreading Coefficient		19
Foam Inhibition:	15 N 2 M 2 E	
Number with Positive Spreading Coefficient		35
Foam Inhibition:	18 E 15 M 2 N	

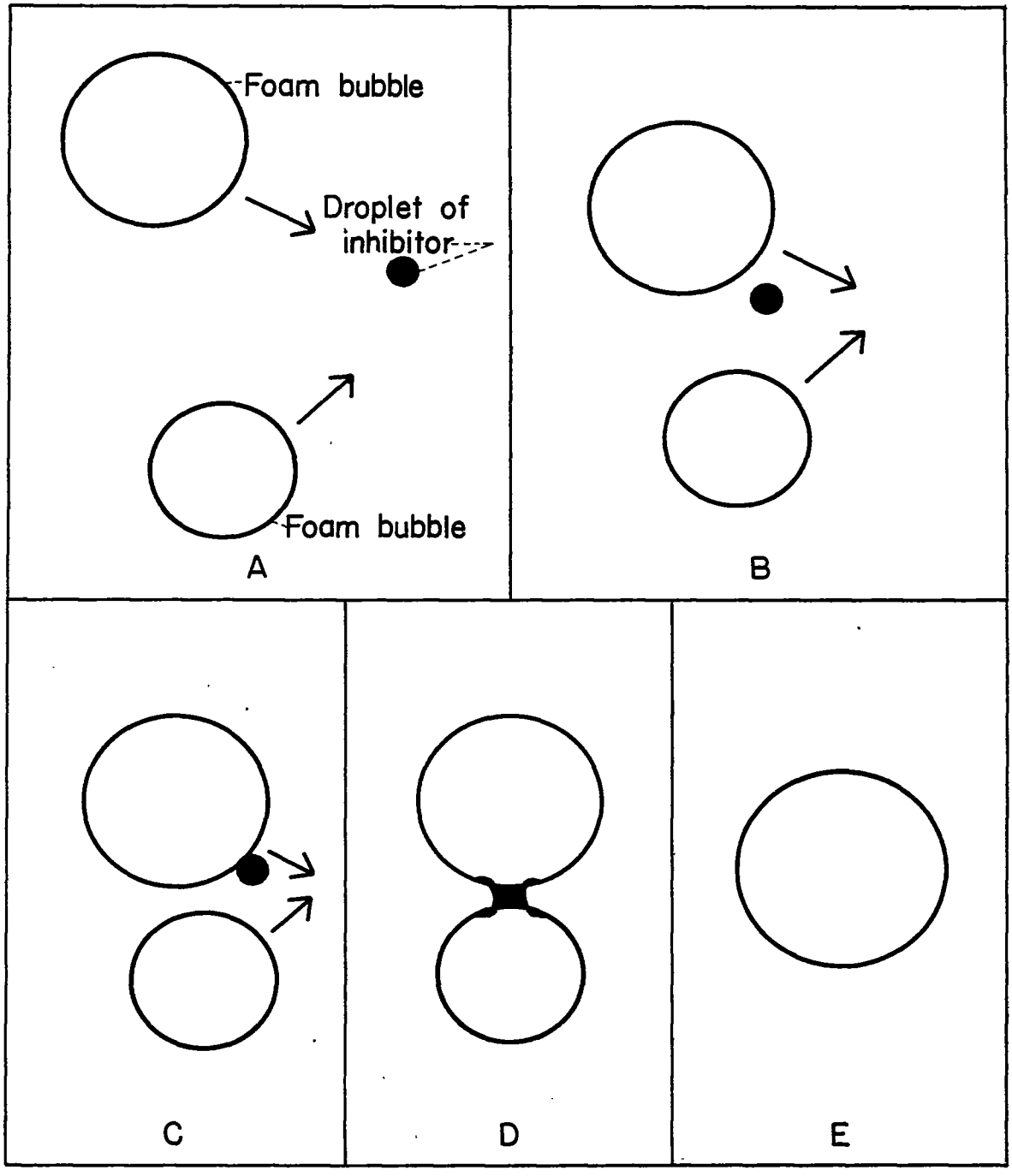

FIGURE 1.- COINCIDENCE OF DROPLET OF FOAM INHIBITOR CAUSING COALESCENCE OF SUBMERGED BUBBLES.

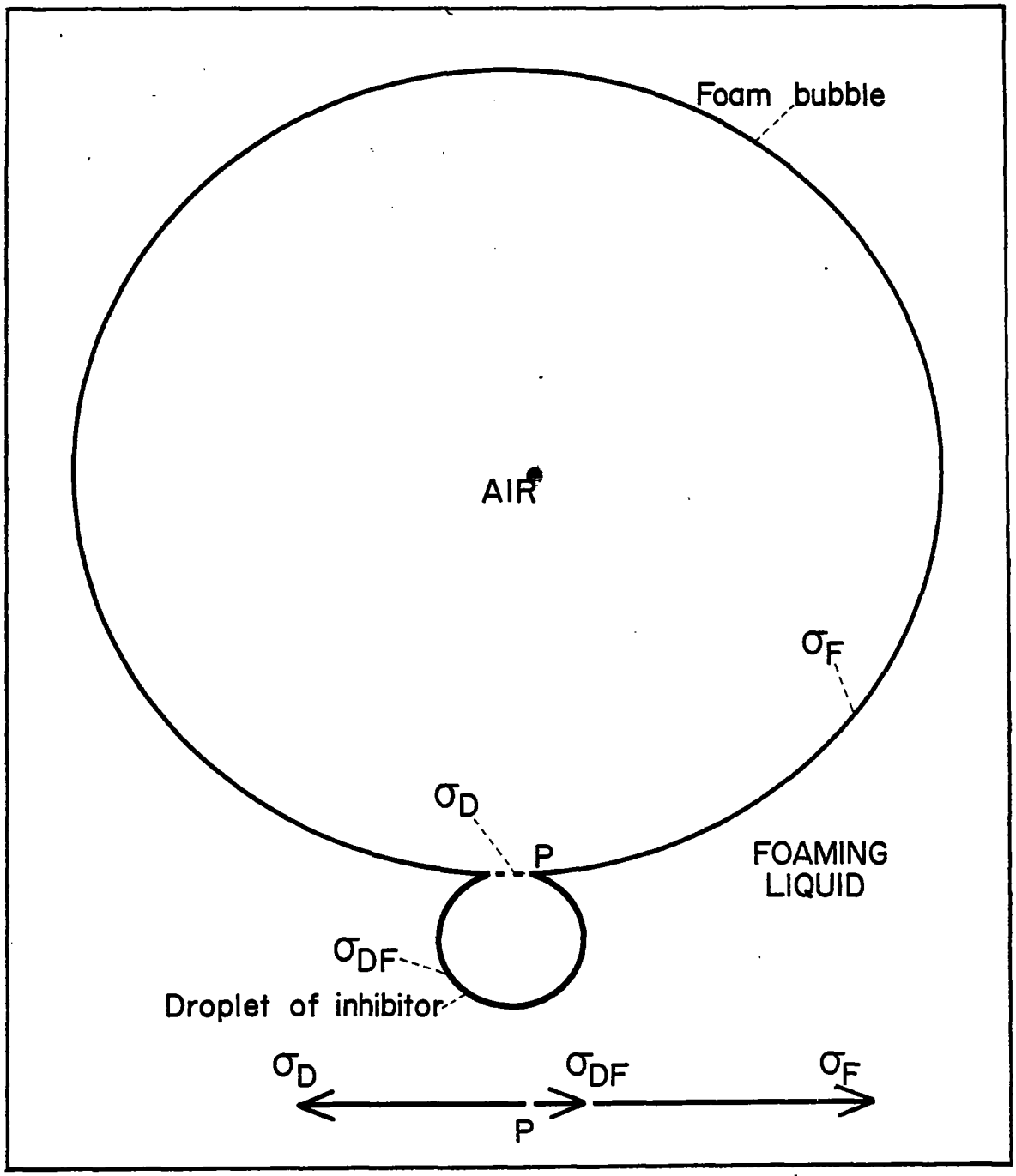

FIGURE 2.- DROPLET OF FOAM INHIBITOR ENTERING SUBMERGED BUBBLE.