



Naval Fuels & Lubricants

Cross Functional Team

Research Report

BASIC PHYSICS OF FOAM STABILITY AND COLLAPSE

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EXECUTIVE SUMMARY

The MIL-PRF-23699 specification has contained a foaming requirement since its inception in 1966. Recent batch acceptance tests on qualified oils (2008-present) have failed to meet the unique MIL-PRF-23669F foam stability requirement which has increased the focus on the test results and validity. In order to understand the factors that contribute to foam stability a literature review was conducted on the structure of foam as well as prevalent mechanisms of foam stability and collapse. Foaming is a broad subject across various industries and materials. The literature search serves to consolidate the information from numerous sources to provide a basic foundation for the physics of foam stability and collapse.

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LIST OF ACRONYMS/ABBREVIATIONS

AFRL/PR Air Force Research Laboratory, Propulsion Directorate
ASTM American Society for Testing and Materials
DLA Defense Logistics Agency
USNUnited States Navy

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BASIC PHYSICS OF FOAM STABILITY AND COLLAPSE

1.0 BACKGROUND

1.1 The foaming test for crankcase oils was developed in the mid forties and issued by ASTM in 1946 as D892¹⁰. The earliest revision of the method (with current online resources available) was document Method No. 321.1.1 in VV-L-791d (revised: 1948) as “Foaming Characteristics in Crankcase Oils”. In the 1965 revision of FED-STD-791A, the foaming test (Method #3211.3) was omitted because it was identical to the ASTM D892 method. Since that time, D892 has been revised multiple times to the current revision of D892-06e1. Since the inception of the method, the basic premise of the test has remained the same throughout this period: introduce air into an oil volume of ~200 mL through a porous medium submerged in the oil. The test results are foam volume stability and tendency. Additional notes and measuring devices have been incorporated with each revision to help minimize variability.

1.2 Work on developing a new foam test for aviation purposes has been stagnant since the 1970’s. Recent studies have focused on improving the repeatability & reproducibility of the current method (through round robins) and not developing a new test method. Within the current method there are several allowed method variations that could potentially increase the variability in the test results. Allowable test variations include, but not limited to: application of mixing with a blender (Option A), diffuser type, diffuser pore size, and exit air device measurement.

1.3 As it pertains to the Navy, there have been several recent DLA batch acceptance tests (2008-present) on qualified oils that pass foam tendency, but do not pass foam stability i.e. long collapse times. These oils have millions of operational flight hours without foaming incidents. To further complicate the situation is the collapse definition in the USN oil specifications. The collapse definition according to footnote # 4 in MIL-PRF-23699F is the following: “Complete foam collapse is that point at which no more than a single row of bubbles remain around the cylinder wall contains segments having two or more layers of bubbles and the difference in height of the foam in the ring is not greater than 10 milliliters (ml), complete foam collapse is the point at which a break occurs in the ring of bubbles without subsequent reforming of the ring” within 1 minute of the cessation of air flow. The definition of collapse in the ASTM D892 method is less stringent with a collapse time requirement of 10 minutes and the definition of collapse is “when the bubble layer fails to completely cover the oil surface and a patch or eye of clear fluid is visible.” However, the basis of the footnote #4 is unknown and first appeared in 1966 of MIL-PRF-23699-A.

2.0 OBJECTIVE

2.1 The objective of this research is to present the following topics about foams.

2.1.1 Physics of foams

2.1.1.1 Structure

2.1.1.2 Stability

2.1.1.3 Rupture

2.1.2 Antifoamer Requirements

The goal is to review the basics of foam formation and collapse.

2.2 The mechanism of collapsing foam and stability is in micro-scale, or what is happening between the bubble boundaries as well as the adjacent bubbles. This nanometer to millimeter scale region will be the focus of the foaming physics research presented in this paper. The break-down structure of foam scale is shown in the figure 2.1 below.

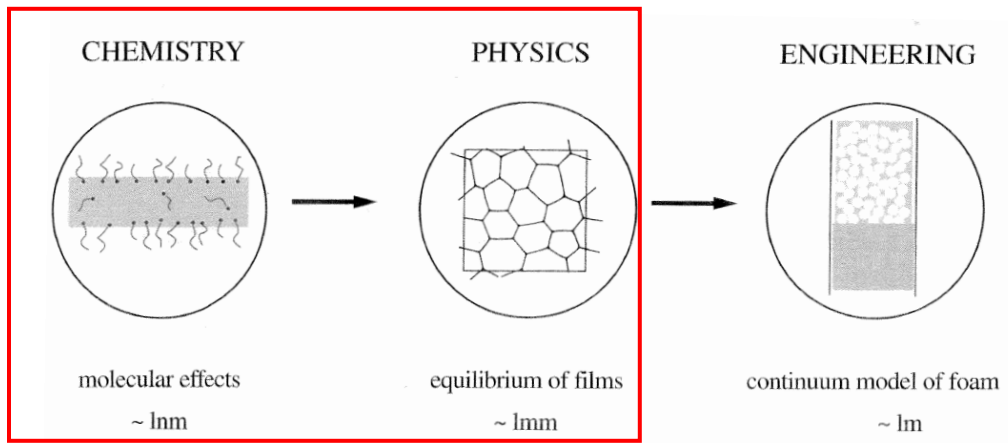


Figure 2.1: Break-down structure of foams³

3.0 FOAM STRUCTURE

3.1 Foam is defined as a two-phase system in which gas cells are enclosed by liquid. The liquid films junctions with 3 or more bubbles are plateau borders and the face of the film between 2 bubbles are lamellae. Where 4 plateau borders meet is called a vertex (refer to figure 3.1).

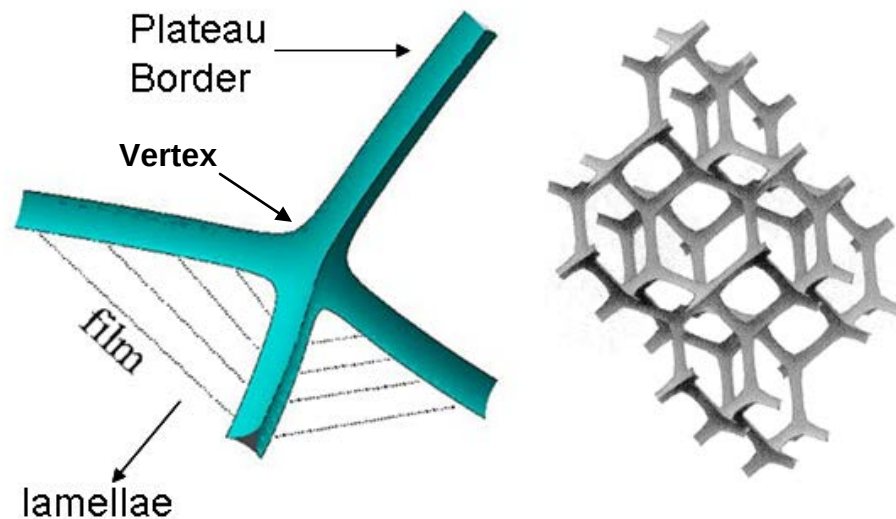


Figure 3.1: Foam structure diagram^{3,5}

The shape of the foam bubbles is dependent on the volume of liquid or gas within the foam. The amount of gas in the foam (volume fraction) is generally between 50% to 97% and bubbles will deform each other when the volume fraction is above 75%¹. Progression from a wet foam to a dry foam is depicted by a change in bubble shape as displayed in Figure 3.2 and 3.3 below. As the liquid drains out, the bubbles coalesce and the foam becomes more polyhedral along the plateau borders. The polyhedral shape of the foam is based on fluid draining from the bubble walls to vertex as shown in Figure 3.4. Pressure differences between the bubble walls and vertex drive the fluid flow direction. The radius of curvature of the bubbles along the walls creates the pressure differential.

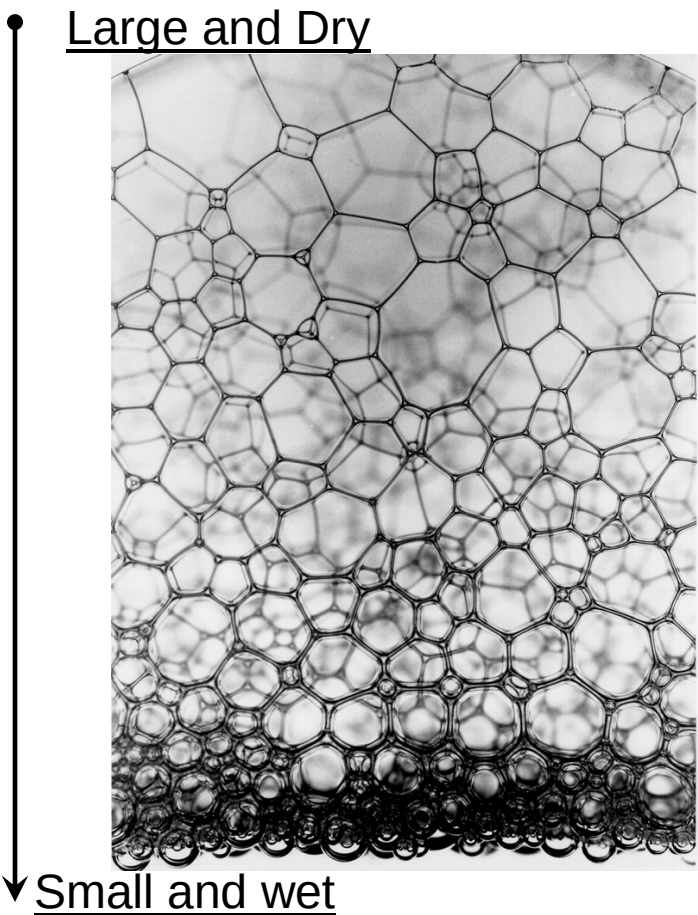


Figure 3.2: Bubble shape based on volume fraction ⁴

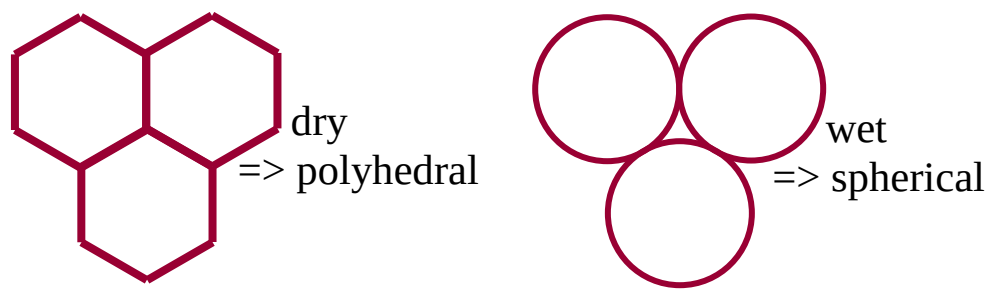


Figure 3.3: Expanded bubble shape based on volume fraction ⁵

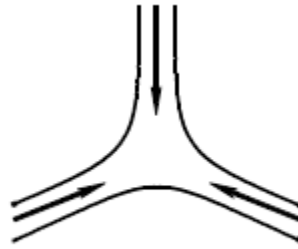


Figure 3.4: Drainage effect of liquid within bubble walls⁷

4.0 FOAM STABILITY

4.1 Forces acting on the bubble

The two counteracting forces, neglecting gravity, acting on the bubble are surface tension (σ) and the excess pressure ($\Delta P = P_i - P_o$). Excess pressure is the difference between inside the bubble (P_i) and outside the bubble (P_o). The relationship between the surface tension and excess pressure in a single bubble is described in Figure 4.1 below and is known as the “Law of Laplace and Young for a single soap bubble”.

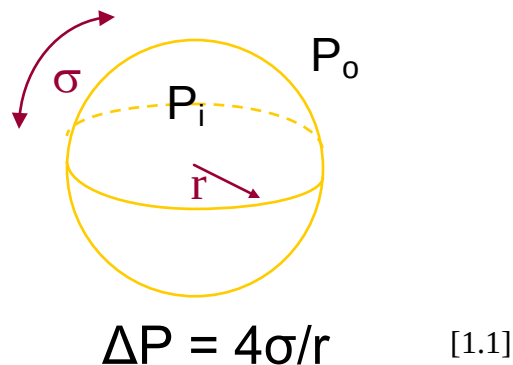


Figure 4.1: Law of Laplace and Young for a single soap bubble

The formula is derived by balancing the forces between the surface film and the excess pressure. Surface tension drives to minimize the surface area of the bubble however the excess pressure counteracts it and an equilibrium bubble size is reached.³

$$\begin{aligned}\Delta P dV &= 2\sigma dA & [1.2] \\ V &= \frac{4}{3}\pi R^3 \\ dV &= 4\pi R^2 dR \\ A &= 4\pi R^2 \\ dA &= 8\pi R dR\end{aligned}$$

Take derivatives of sphere volume and area then insert resultants into the energy balance [1.2]^{3,11}

$$\Delta P [4\pi R^2 dR] = 2\sigma [8\pi R dR] \quad [1.3]$$

Equation [1.3] will reduce to equation [1.1]

4.2 Stabilizing mechanisms of bubbles

Although the goal of the research is to understand how to reduce foam formation in oils; there is more fundamental understanding of how surfactants stabilize foams. The stability of a bubble or foam depends on multiple components that effect surface energy.⁶

4.2.1 Film elasticity (Gibbs and Marangoni effects)

Film elasticity is a stabilizing mechanism that allows the film to figuratively self-heal. Imagine an air-water-air film as depicted in Figure 4.2 below. Within the liquid are surfactants that have hydrophilic and hydrophobic ends. The surfactants arrange at the interfaces depending on their affinity for water. If an applied force or stress creates a thin spot on the bubble surface there will be an increase in surface area and tension. With an increase in surface area the concentration of surfactant at the interface is decreased as well. These gradients will initiate the process of the surfactants to transfer toward the thinned spot. As the surfactants transfer to the area of lower concentration they will bring along the underlying layers of liquid⁶. The resultant fluid flow restores/repairs the thinned spot.

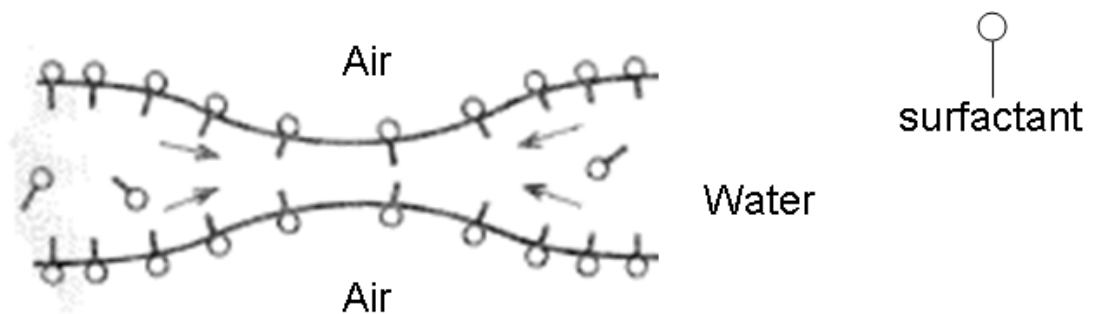


Figure 4.2: Surfactant transport due to film stress¹

The self-healing process is only possible if a surfactant is present therefore pure liquids will not foam⁸. The concentration of the solute in solution can also affect the film elasticity. At low concentration the solute has a limited role and may not stabilize the foam due to marginal increase in film elasticity. On the other hand, at extremely high concentrations the diffusion rate can be so rapid that stabilizing mechanisms could be eliminated². Therefore, a

maximum elasticity is achieved before CMC (Critical Micelle Concentration) as shown in Figure 4.3.

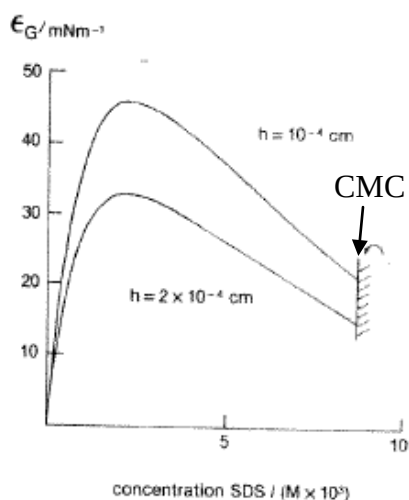


Figure 4.3: Elasticity versus solute concentration²

Concentrations above CMC do not contribute to additional surfactants at the surface, as a result film elasticity is unaffected. The additional surfactants contribute to increased formation of micelles in the bulk solution³. By definition, micelles are an aggregate of surfactant molecules dispersed within the solution, refer to Figure 4.4.

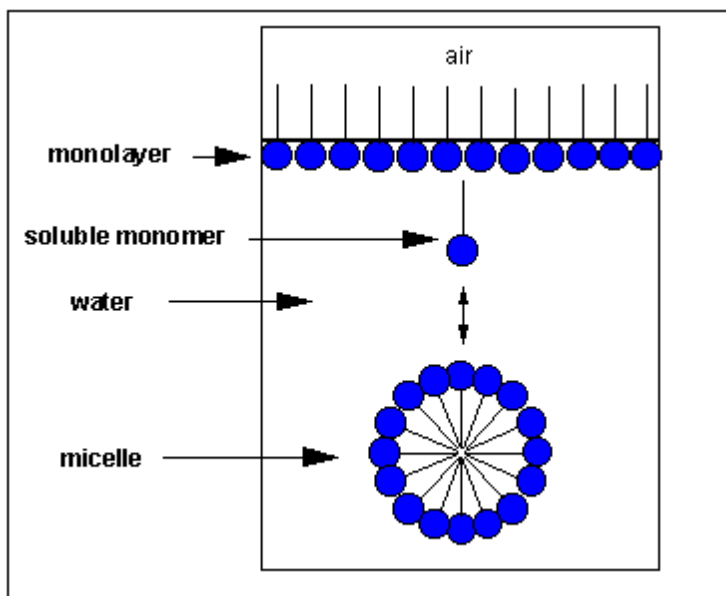


Figure 4.4: Micelle formation¹¹

The theories supporting the film elasticity mechanisms, under different conditions, are Gibbs and Marangoni effects. More detail about each theory can be located on pg 203-207 in reference 8.

4.2.2 Viscous surface layer formation

The presence of adsorbed surfactants at the surface interfaces can increase intermolecular forces with the bulk. As a result, surface layer's viscosity will increase and become more rigid. A common real world example is the froth that is produced for a cappuccino. The proteins in the milk act as a foam stabilizer and produces long-lasting foam after the steaming/frothing process has been completed. Milk is mostly water along with globules of fat and several kind of proteins made of amino acids. During the heating process, the proteins bonds are broken and the molecules unravel. The resultant molecule strengthens the bubble walls and stabilizes the foam as depicted in Figure 4.5 below. The performance of the protein's foam stabilizing ability can be diminished if the milk is heated multiple times because the denaturing of the proteins are not reversible¹³. Therefore, after each time the milk is frothed/foamed, the protein's ability to strengthen the foam is decreased, leading to a progressively less stable foam.

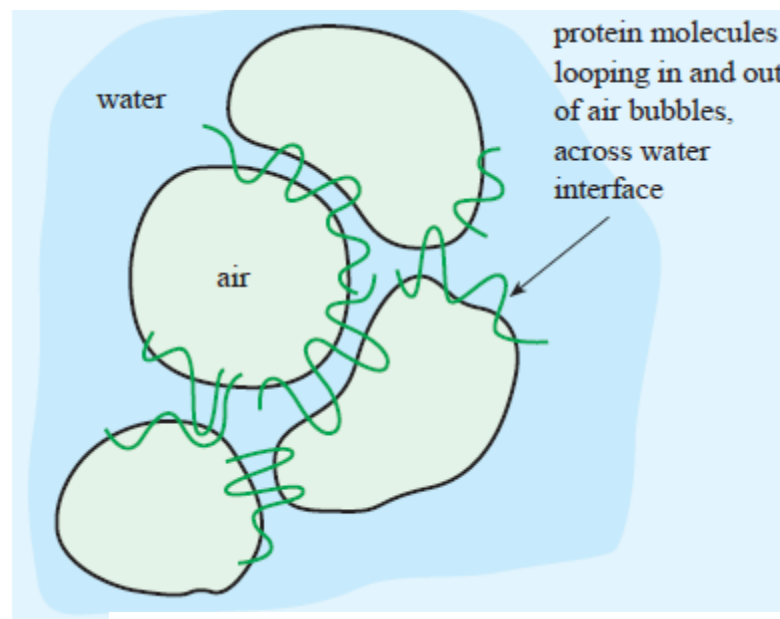


Figure 4.5: Protein stabilizing a foam¹⁴

An additional graphical view of the mechanism is displayed below in figure 4.6. The diagram with no surfactant exhibits a water velocity profile as a response to gravity is constant between both water/air interfaces. There is no reason the water should move in response to the applied gravitational force with a velocity different from that of any adjacent element². However, when a surfactant is present the interfaces are essentially rigid and a parabolic velocity profile will exist. Therefore, the increased viscosity will slow down drainage and collapse. One caveat is if the viscosity is too high then it could reduce the self-healing surface transport mechanism⁸. The viscous forces at the surface interface are

balanced by the tangential force acting in the plane of the surface which is the surface tension gradient from the surface into the liquid/water layer².

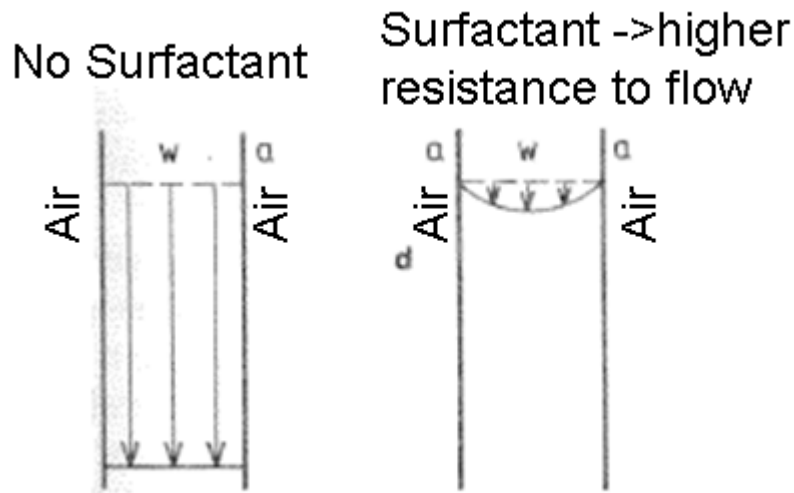


Figure 4.6: Fluid flow in response to gravity ¹

4.2.3 Reduced Gas Diffusion through the Lamellae

Through the application of Laplace's law, bubbles with smaller radii have higher internal pressures (P_i). As bubbles in the foam coalesce, larger bubbles will grow at the expense of smaller bubbles. The higher pressure gas diffuses through the bubble wall into the bubble with a lower internal gas pressure (refer to Figure 4.7).

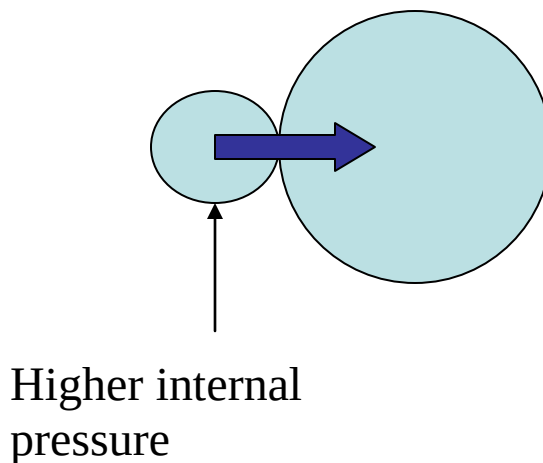


Figure 4.7: Bubble gas diffusion

The rate of gas diffusion (q) is governed by equation [1.4].

$$q = -JA \Delta P \quad [1.4]$$

q =rate of diffusion

J =permeability

A =effective perpendicular area between bubbles

ΔP = bubble gas pressure difference

When a surfactant is present the permeability through the bubble wall can be significantly reduced by closer packing of the surfactant in the film⁸. In general, a lower molecular weight surfactant should be more effective at reducing the permeability due to its ability to pack closer on the film's surface.

4.2.4 Electric double layer repulsion

An ionic surfactant will add stability to the film because of the repulsion of the two film surfaces as the film thinned (refer to Figure 4.8).

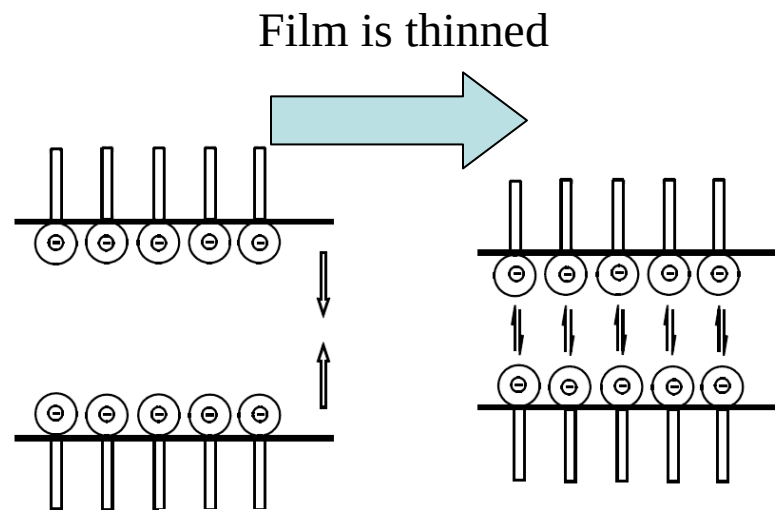


Fig 4.8: Double layer repulsion⁷

However, these electrostatic forces contribute to foam stability only when a film reaches a thickness of 200nm or less. Research has found that an addition of an electrolyte to the solution causes a reduction in the film thickness therefore reducing repulsion forces.⁸

5.0 FOAM RUPTURE

5.1 Requirements to collapse foam

Now that the mechanisms that stabilize foam have been introduced, the goal is to disrupt them. An antifoamer and defoamer are substances that collapse foams but have different mechanisms. An antifoamer prevents foam formation while a defoamer breaks down

existing foam. The research here deals with silicones and they conveniently act as both an antifoamer and a defoamer⁶. Essentially the terminology is used interchangeably and for the remaining of the paper the term antifoam(er) will be used. The requirements below are used to determine if the molecule/substance passes the initial screening of an antifoamer. However, these are generalized requirements and application specific examples may not follow these guidelines.

5.1.1 Entering coefficient

The first requirement is the antifoaming particle must be able to enter the interface (from the aqueous side)⁹. The classical mechanism is governed by equation [1.5] below:

$$E_{a/o} = \sigma_{og} + \sigma_{oa} - \sigma_{ag} > 1 \quad [1.5]$$

o=oil; g=air; a=antifoam

Interfacial tension= σ_{oa}

The simplistic entering requirements associated with this equation provide a rule of thumb when selecting an anti-foamant. Additional considerations about particle size and non-equilibrium conditions that may inhibit entry are beyond the scope of this literature search. A more detailed explanation of the entering mechanism can found in reference [2, 9].

5.1.2 Spreading coefficient

The second requirement after the antifoam particle has entered the interface is its ability to penetrate the oil/air interface. This relationship is linked to the interfacial tensions in equation [1.6] below:

$$S_{a/o} = \sigma_{og} - (\sigma_{oa} + \sigma_{ag}) > 1 \quad [1.6]$$

o=oil; g=air; a=antifoam

Interfacial tension= σ_{ao}

In order for the antifoamer to meet these requirements the new surfaces/interface ($\sigma_{oa} + \sigma_{ag}$) created needs to have a lower surface tension than the original surface (σ_{og}). A graphical representation is shown in Figure 5.1. As the droplet spreads, the surface area of the oil/air interface will decrease and the oil/antifoam and antifoam/air interfaces will increase.

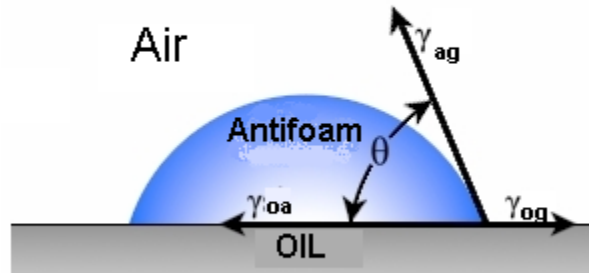


Figure 5.1: Spreading coefficient explained

5.2 Rupture mechanisms

The common rupture mechanisms to collapse foams are: spreading/fluid entrainment and pinch-off/lens formation.

5.2.1 Spreading Fluid Entrainment

The basic principle of this mechanism is to disrupt the surface tension gradients and create a local area of low surface tension. As seen in the Figure 5.2 below, the antifoam creates a localized area of lower surface tension along with an associated surface tension gradient.

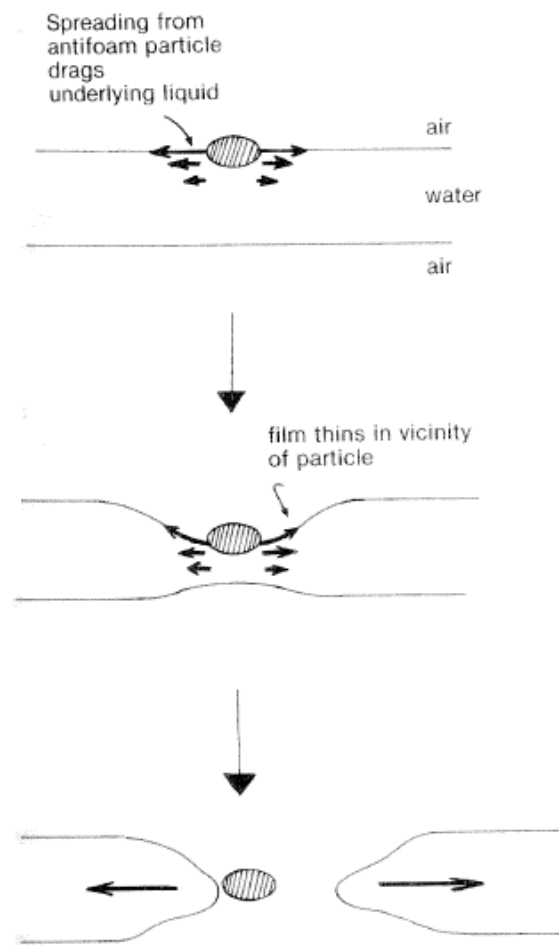


Figure 5.2: General spreading mechanism²

Unlike the self-healing mechanism the surface tension gradient drags fluid away from the particle which induces thinning then eventually ruptures the bubble. One caveat to this general mechanism is the assumption that the particle will rupture the bubble at the thinnest wall region. If the particle entered at a region of the bubble where the wall was thick then this mechanism would stabilize the bubble by driving fluid to regions of thinner bubble walls². Another aspect of the mechanism that must be considered is the penetration depth of the subsurface flow and this depth must be on the order of the foam/bubble film thickness before the spreading layer can influence film thinning⁹. Further complex spreading mechanisms are covered in reference [2] pg 22-30.

5.2.2 Pinch-off/ Lens formation

The antifoam particle bridges the interfaces to form a lens (2-D representation). An existence of capillary pressure at the liquid/antifoam interface will promote fluid flow away from the antifoam particle to a lower pressure region. Eventually the film will sufficiently thin and form a hole, then rupture. This mechanism follows classic dewetting principles and the performance is determined by the contact angle and particle geometry at the 3-phase interface⁹ (refer to Figure 5.3).

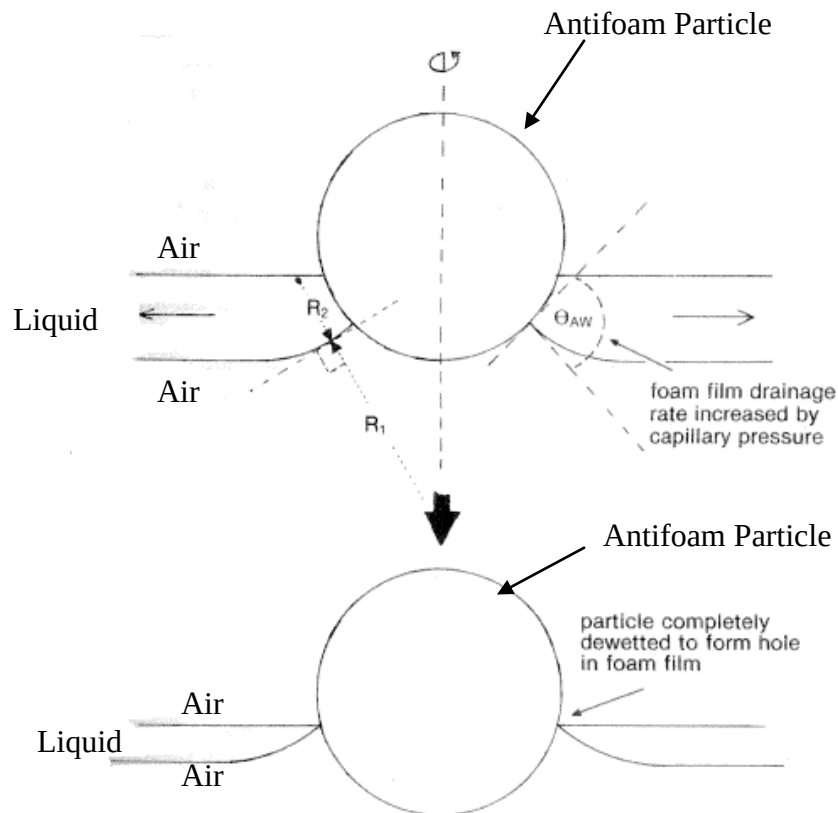


Figure 5.3: Pinching off mechanism ²

5.3 Antifoam Characteristics

Generalizations about an antifoamer are as reported from a Dow Corning reference ⁶.

5.3.1 Insolubility

An antifoamer can become a pro-foamer if the molecule is soluble at low concentrations and has a lower surface tension than the solution. As a result, the surface tension of the solution will reduce and will have a higher propensity to foam.

5.3.1.1 Experimental results by Shearer and Akers showed that the antifoamer must be present as a dispersed phase.

5.3.2 Chemical Inertness

No unwanted side reactions with surface materials that the antifoamer may come in contact with.

5.3.3 High Surface activity (low surface and interfacial tensions)

Required to satisfy entry and spreading coefficient requirements, equations [1.5 + 1.6].

5.3.4 Optimized Droplet Size

If droplets are too big then the antifoam particle will not be able to enter interface. If too small then it will not be able to create a weak spot.

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