Antifoams

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Synopsis

A general background on the subject of ANTIFOAMS is presented which includes their classification, preparation and testing. Emphasis is given to silicone-based compositions whose introduction in this field some three decades ago led to major changes in antifoaming technology. Fundamental mechanisms involved in the antifoaming process are outlined and a description is given of some of the mechanisms of foam stabilization. Lastly, a new, experimental antifoam, of "transient character," is described and its possible applications are outlined. Its activity in aqueous foaming systems lasts for a limited period; thereafter the full foaming power of the solution is restored.

INTRODUCTION

A foam is an aggregate of bubbles. More precisely, it is a dispersion of gas in a liquid where liquid forms the continuous phase. The phenomenon of foaming is primarily governed by the properties of the interfaces involved and foaming is always accompanied by an increase in the interfacial area of the system and hence its total energy. Thus, in a strict thermodynamic sense, foams are basically unstable and are therefore self-destroying. Their formation requires a net input of energy. The ease of their formation or their stability is, among other factors, determined by the gas/liquid interfacial energy.

Pure liquids do not foam and therefore, for foaming, at least one more component is required. For persistent foams one needs the presence of a surface active ingredient. In most practical systems the foam stabilizing component is either a soluble surfactant, a finely divided solid, or both. While the mechanism of foam stabilization is not well understood, the role of solids, in particular, is least understood. Nevertheless it is well recognized that foams derive their stability by offering resistance to the external as well as internal stresses that can cause foam destruction. For reviews on the subject of foam stabilization see references 1–7.

Depending upon the conditions prevailing in the solutions, a generated foam can span a remarkable range of stabilities, which can vary from milliseconds to almost unlimited duration. In many practical operations foams last long enough to interfere with physical or chemical processing and this has warranted the development of means for

their rapid destruction. Such needs can be visualized for a wide spectrum of systems ranging from waste water treatment, industrial fermentation, textile or paper process- ing, pharmaceutical manufacture, and various filling operations, to domestic machine dishwashing, laundering and cooking. In general, foam control is achieved either by destroying the existing foam, i.e., defoaming, or by preventing the formation of the foam. This is generally accomplished through mechanical, thermal or chemical means. Of these three techniques, chemical means are by far the most efficient for reasons which will be presented in some detail, and are the most widely used. Accordingly, the present paper will deal exclusively with foam prevention or destruction as achieved by chemical means.

We define an antifoam as a chemical compound or mixture of chemical compounds which, when added in small amounts to a foaming system, either reduces or destroys its foaming tendency and so achieves a degree of foam control. Antifoams are, typically, highly surface active compounds having low solubility in the foaming solutions.

A large number of fluids have been used in formulating antifoams, and they include naturally occurring oils and fatty materials, petroleum products and silicone oils. Traditionally, fatty acids and alcohols, and oils and fats have been used as foam inhibitors. These antifoams are able to perform very well for specific systems under particular conditions. Their main limitation is their large variation in performance with slight changes in the physical and chemical conditions prevailing in the foaming system. For example, lard oil and similar products can perform excellently as long as the operating temperatures are close to their melting point. However variation in the operating temperature can have a serious effect on their activity. On the other hand, antifoams based on silicone oil are effective in a large number of systems under a broad range of operating conditions. Their versatility is, in fact, the major reason for their wide acceptance in the field. Accordingly, they will receive chief emphasis in this review.

THEORETICAL TREATMENT OF FOAMING AND ANTIFOAMING

In describing the essentials of this type of foam control, we will put appropriate emphasis on the fundamentals of foaming also. It is important to point out 1) that the fundamentals of both foaming (1–7) and antifoaming (8–20) are incompletely under- stood and 2) that the two phenomena have largely been treated independently with little attempt to understand the one in relation to the other. Our attempt is to treat foaming and antifoaming together so as to obtain an improved understanding of the total phenomenon.

FOAMING

A freshly formed foam passes through several different states before rupture and eventual collpase. During its lifetime, the bubble size and size distribution contin- uously change. The shape of the bubbles correspondingly changes from spherical to pentagonal-dodecahedral in the fully drained state. During drainage, the thickness of the lamellae and the foam density decrease in a rather complex manner. In addition to the force of gravity, films will thin in consequence of the well known capillary suction

force which results from the pressure drop across the curved interface of the bubbles. For lamellae separating bubbles of radius R, the pressure drop, ΔP, is given by the LaPlace equation, $\Delta P = 2\gamma/R$, and this results in suction of the liquid into the Plateau borders of the foam. Thinning will continue until the bubbles rupture, or until an "equilibrium" film thickness is reached when the suction force is balanced by the film's "disjoining pressure" (2) which is made up of the residual forces in the film. We will now consider these in terms of energy, distance (thickness) profiles, writing them in summation as

$$E_{Total} = E_V + E_S + E_E$$

where E_V is the contribution from van der Waals' interaction; E_S is the entropic or steric stabilization energy; and E_E is the electrical or coulombic interactional energy between the neighboring bubbles.

While E_V is generally attractive and promotes film thinning, E_S and E_E generally oppose and retard thinning. Actual estimation of these energies can be made in the following way:

Van der Waals' Energy

E_V is the van der Waals' energy of interaction between two foam bubbles which, in a conventional foam, are surrounded by a layer of adsorbed surfactant molecules. An estimate of this interaction energy can be made using Vold's (21) treatment, according to which

$$E_V = -\tfrac{1}{12}((A_S^{1/2} - A_M^{1/2})^2 H_s + A_S H_P + 2A_S^{1/2}(A_M^{1/2} - A_S^{1/2})H_{PS})$$

In the above equation A_S and A_M are the Hamaker constants of the foam stabilizing surfactant and the surrounding liquid medium, respectively. H_S, H_P and H_{PS} are geometric functions, $H(x,y)$, which are related to the distance of separation and the radius of the bubbles involved such that

$$H(x,y) = y/(x^2+xy+x) + y/(x^2+xy+y+x) + 2\ln\ ((x^2+xy+x)/x^2+xy+x+y)$$

where x is the ratio of the minimum distance of separation between the bubbles and the diameter of the smaller bubble; y is the ratio of bubble diameters, R_1/R_2, chosen for generality to be unequal so that $y \geq 1$, i.e., $R_1 \geq R_2$. Individual values of the H parameters are given by

$$H_S = H(\Delta/2(R_2 + \delta), (R_1 + \delta)/(R_2 + \delta))$$
$$H_P = H((\Delta + 2\delta)/2R_2, R_1/R_2)$$
$$H_{PS} = H((\Delta + \delta)/R_2, (R_1 + \delta)/R_2)$$

where δ and Δ are the thickness of the surfactant film adsorbed on the bubble surface and the thickness of the solution between the bubbles, respectively.

From the above equations it is evident that the van der Waals' interactions will always be attractive as long as $A_M \geq A_S$. However, under conditions where $A_M < A_S$, one can observe repulsive van der Waals' interactions. Thus the actual nature and magnitude of the van der Waals' interactions will be dependent not only on the δ and Δ values, but also on the relative values of A_M and A_S.

Entropic Energy, E_S

E_S is the energy contribution due to the steric interferences which bubbles experience as they approach one another. These contributions are not expected to be significant unless the film thins to a few nanometers thickness. This conclusion is particularly valid for surfactants in which the polar head groups are relatively small. For polymeric foam stabilizers and for nonionic surfactants, in which ethylene oxide or ethylene oxide/propylene oxide chains comprise the head group, the steric contribution is expected to be higher and to operate at longer distances.

Electrical Energy, E_E

E_E represents the energy contribution from coulombic forces. These interactions can be dominant in aqueous solutions of ionic surfactants. The electrical contribution for the case of spherical bubbles in aqueous solution at 25°C can be estimated using the equation of Hogg et al. (22,23).

$$E_E = 8.92 \times 10^{-10} \, G \, \zeta^2 \, [\ln (1 + \exp (-K\Delta)]$$

where ζ is the zeta potential of the bubble/solution interface, G is given by the formula, $1/G = 1/R_1 + 1/R_2$, and K is the Debye-Huckel reciprocal length parameter in cm^{-1} which is related to the total concentration, C, in mole/liter, of uni-univalent electrolyte in the solution by the expression, $K = 0.328 \times 10^{-8} \sqrt{C}$.

The above equation applies for the condition of constant surface potential and nondeformability of the bubbles and assumes that the Gouy-Chapman model of the double layer interactions is applicable. The equation shows how the repulsive coulombic interaction increases as the bubbles come closer together and so opposes the film thinning.

In summary, of the three energy factors involved, the coulombic and the steric energy factors will oppose thinning. The role of the van der Waals' term, E_V, is either to oppose or promote film thinning, depending upon the relative values of the Hamaker constants of the surfactant and the medium. The magnitude and the sign of all these energy factors are a direct function of film thickness, as is demonstrated in Figure 1, drawn on an arbitrary scale. Depending upon the relative values of each factor, two extreme possibilities can be foreseen.

1. The film thinning is favored energetically under all conditions, so that the film will finally rupture causing eventual foam collapse.

2. The film thins to a particular point beyond which further thinning requires crossing an activation energy barrier so that the film achieves a metastable equilibrium thickness. Further film thinning or film rupture requires an additional energy source which is capable of either altering the activation energy barrier or providing enough energy to overcome it.

Corresponding to the above two conditions, two classes of foams are possible, viz., nonpersistent foams and persistent foams, respectively. In nonpersistent foams, film thinning is energetically always favored and the life span of the foam is primarily controlled by the rate of film thinning. On the other hand, in persistent foams, drainage and lamella thinning occur until an "equilibrium" film thickness, h_e, is reached. These foams are relatively stable and their breakdown is the result either of
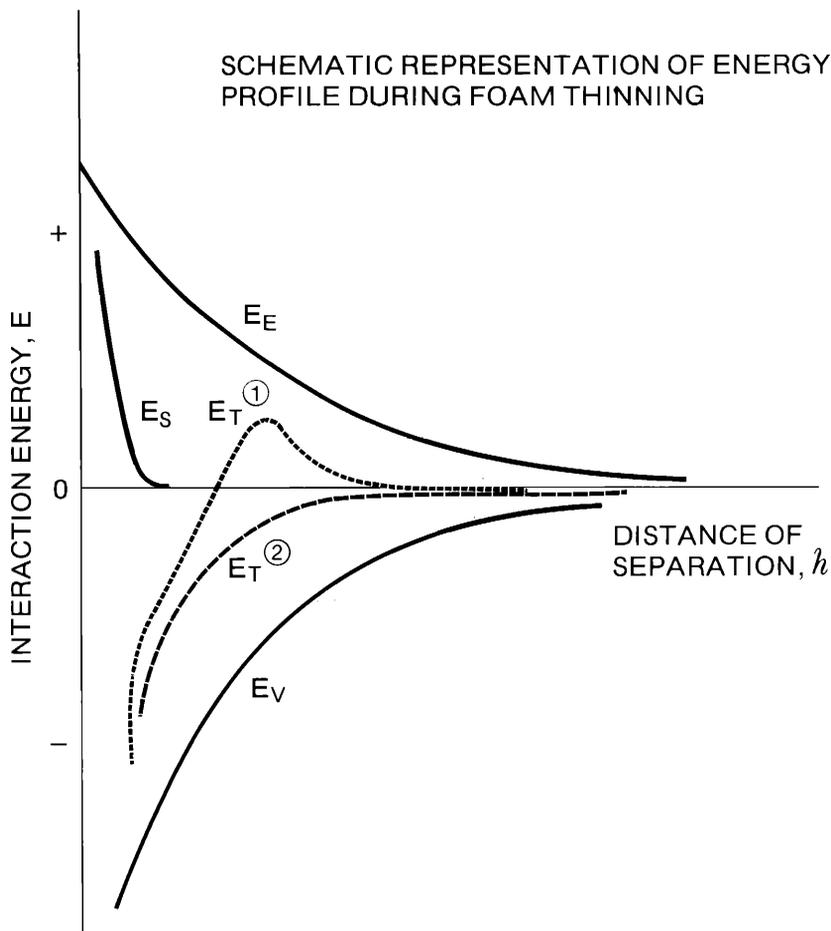
Figure 1. Variation in the interactive energies on approach of two bubbles. Curve 1 shows a net positive energy barrier; Curve 2 does not.

external factors or of local thermal motions which can cause fluctuations in the film thickness to or below the critical rupture thickness, h_r. The actual stability of the foam and the values of h_e and h_r are dependent on (a) the interfacial packing density of the stabilizing surfactant and (b) the nature, size and configuration of its polar group. The rate of film thinning depends directly upon the magnitude of the driving energy and inversely upon the bulk and surface viscosities. In particular, the role of surface viscosity becomes significant when appreciable film thinning has already occurred.

Even nonpersistent foams can demonstrate remarkable stability by virtue of having very slow film drainage characteristics. This is particularly true for foams where the surface and /or bulk exhibit non-Newtonian behavior such that the viscosity increases sharply with a decrease in the shear rate or the drainage rate. Under these conditions, even though film thinning is favored energetically, the slow kinetics of thinning impart appreciable stability to the foam. These types of foam are expected to be encountered with nonionic surfactants or polymers in aqueous solutions or, in general, in nonaqueous media, where electrical repulsive forces play a limited role.

The discussion so far has suggested that there are several conditions under which one can expect to produce foams with indefinite stability. These are, however, seldom encountered because there are, in addition, several factors which can cause local fluctuations in the film thickness, resulting in force imbalances and consequent film rupture. These factors include: (1) evaporation of the liquids, (2) gas diffusion and corresponding changes in the size and size distribution of the bubbles, (3) thermal motions, (4) mechanical disturbances, (5) interactions involving the absorption of sound or electromagnetic radiation and (6) local compositional fluctuations.

Foams derive stability against such local fluctuations by their ability to resist thinning and their ability to heal weak spots. Surface viscosity and surface elasticity are two primary properties which enable a foam to restore itself and resist rupture from local stressing. Gibbs' surface elasticity is defined as:

$$\epsilon = 2d\gamma/d \ln A = -2\Gamma (d\gamma/d\Gamma)$$

where γ is the surface tension of the foaming solution, A is the area per molecule of the surfactant, and Γ its adsorption density, at the interface.

The higher ϵ, the higher the restoring force to a local surface concentration fluctuation and, hence, the higher will be the film stability. Mechanistically, this implies that any external perturbance which either dilates or contracts the surface film, i.e., decreases or increases the surfactant adsorption density, will be opposed by a corresponding change in surface tension thereby minimizing the effect of the perturbance. These aspects have been dealt with in some detail by Mysels (3). However, direct proof is limited owing to experimental difficulties.

A high level of surface viscosity or viscoelasticity represents another factor affecting film stability by its influence on film drainage. A higher surface viscosity implies a lower rate of liquid drainage within the lamellae and the movement of a layer of subsurface solution during the healing of a locally thinned film. Films with viscoelastic properties will, in addition, stabilize foams because film thinning can be practically stopped owing to the high restoring force accompanying a local displacement together with a reduction in drainage rates. The latter is especially significant when the shear stress, due to the drainage, falls below the yield stress of the film.

Scheludko (6) postulated that the film rupture is caused by surface ripples which are generated primarily by thermal motion. He derived an expression for the critical thickness, h_r, which a single film must reach before rupture can occur. Vrij (7), by light scattering experiments, found evidence of such fluctuations and modified Scheludko's equation for h_r, obtaining the expressions

$$h_r = 0.222 \left(\frac{A \, r_o}{f \, \gamma} \right)^{1/4}$$

when $E_V \gg E_H$; and

$$h_r = 0.267 \left(\frac{A^2 \, r_o^2}{f\gamma \, E_H} \right)^{1/7}$$

when $E_H \gg E_V$.

Here r_o is the radius of the single film, A and γ are the Hamaker constant of the film and its surface tension, respectively, and f is a parameter, depending on H and γ, which decreases with thickness.

The above equation yielded satisfactory values of h_r for some foaming systems but there were large discrepancies for other systems, particularly in those where damping of surface ripples was expected to occur through Gibbs–Marangoni elasticity and/or surface viscosity effects. However if rapid adsorption of surfactant from the bulk was possible, the equation again became applicable.

ANTIFOAMING

The phenomenon of antifoaming has been thought of as an interfacial or "spreading" phenomenon in a rather restricted sense. However it generally involves the prior dispersing of the active compound, often a silicone base fluid, into fine droplet form in the foaming system in which antifoaming is desired. For these droplets to be effective, they should possess very low solubility and a positive "spreading coefficient" over the foaming solution (8,14–20). The ultimate process of antifoaming is thus thought to be the displacement of an adsorbed foaming surfactant monolayer by a more surface-active layer which does not support foaming (14–20). This simple view of antifoaming, based on interfacial energies, provides only a partial description of the phenomenon but forms an excellent basis for initial selection of antifoaming compounds. It cannot, however, explain the relative effectiveness of various antifoams in different foaming systems, nor the marked improvement in the antifoaming performance attending the incorporation of small amounts of colloid-size hydrophobic particles in the antifoam, as is now commercial practice (8–10). In other words, much concerning the mechanisms of antifoaming is imperfectly understood. This situation results from the restricted view of antifoaming as essentially an interfacial phenomenon involving the liquid/gas (L/G) interface. Recently, however, we have emphasized (8–10) that the process involves not only spontaneous spreading of antifoam but also the prior step of bringing the antifoam droplet to the bubble surface in a process which can be likened to heterocoagulation. The interfacial forces governing the spreading behavior are all short-range and therefore are not expected to participate in the process unless the droplet and bubble have approached each other to within small (Angstrom) distances. The transport of a droplet to such a distance from the bubble is influenced by other forces in the system such as hydrodynamic, electrical and van der Waals' interactions. The latter interactions can be influenced by the fact that antifoam droplets as well as the foam bubble can adsorb foaming surfactant molecules and acquire a surface charge.

The complex process of antifoaming using silicone oil-based antifoams in aqueous systems evidently involves the following steps: (1) dispersion of antifoam in the foaming solution, (2) transport of antifoam droplet from bulk to the bubble interface (heterocoagulation), (3) entry of the droplet into the gas/liquid interface, (4) spreading and (5) bubble rupture.

Up until recently the details of the second step have never been considered and also the last two steps were considered synonymous inasmuch as spreading of the (appropriate) antifoam was felt automatically to lead to bubble rupture. We now have evidence that even though spreading is necessary for antifoaming, it does not necessarily cause rupture.

Studies on the change in sensitivity of solutions of ionic surfactants to defoaming by standard silicone antifoams, carried out as a function of the concentration of the
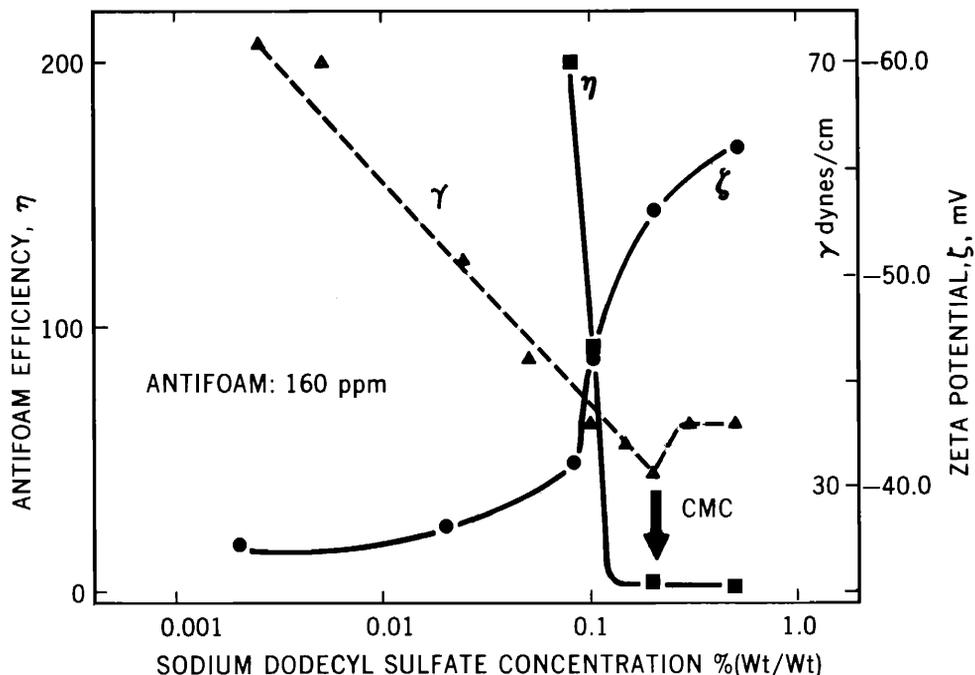
Figure 2. Antifoam effectiveness, η, and zeta potential (ζ) of AF-1 as a function of SDS concentration. Surface tension plot of SDS without antifoam is included.

surfactant, provided an important clue as to the mechanism of step two above (10). When the concentration of the ionic surfactant approached and increased through the CMC, a sharp drop in antifoaming efficiency was observed. At the same time, zeta potential measurements showed that the coulombic charge on the antifoam droplets underwent a rapid increase. The inferred sharp change in the repulsive interaction of the droplets around the surfactant's CMC is attributable to a marked increase in the adsorption of surfactant molecules on the antifoam droplets in this region. Such adsorption is expected to occur through interactions between the surfactant's hydrocarbon chain and the silicone oil droplet, leaving the ionic headgroup of the surfactant still exposed to the solution phase and thereby charging the droplets, as was observed. Under these conditions, the process of droplet movement to the bubble interface involves the transport of a charged droplet towards a similarly charged gas bubble, requiring considerable forces of coulombic repulsion to be overcome. This is clearly illustrated in Figure 2 where antifoam activity is plotted as a function of SDS surfactant concentration along with the SDS solution surface tension (before addition of antifoam), and the surface charge on the antifoam (measured by electrophoresis)—a measure of the repulsive interaction energy, V_m. The sharp change in the antifoam performance accompanying the sharp rise in repulsive interaction energy is quite evident.

In addition to mechanical and diffusion forces, the transport of antifoam droplets from bulk to the interface is thus governed by coulombic and van der Waals' forces. In other words, there is a formal similarity to the bubble/bubble interaction scheme presented in the last section on foaming mechanisms, but it differs since the

interaction in this case is between dissimilar bodies and is therefore more complicated. Details of the calculation allowing the construction of energy/distance plots have been presented elsewhere (8); only the main conclusions will be given here. It was shown that, depending upon the test solution conditions, as an antifoam droplet approaches a foam bubble surface, it can experience either an attractive or repulsive interaction and thereby the antifoaming process will be directly influenced. In particular, in systems containing ionic foaming surfactants the repulsive interactions are important. As pointed out before, the repulsive interaction depends not only on the nature of the surfactants but also on their concentration. It is related (8) to the potential and distance of the particle (subscript 1) and bubble (subscript 2) by the expression

$$E_E = 2.23 \times 10^{-10} \, R_1(\zeta_1^2 + \zeta_2^2)\left(\frac{2P}{(1+P^2)} \ln \frac{(1+\exp(-K\Delta))}{(1-\exp(-K\Delta))} + \ln(1-\exp(-2K\Delta))\right)$$

where the symbols have the same significance as in the previous expression for E_E and P is the zeta potential ratio (ζ_1/ζ_2).

The role of van der Waals' interactions is more complex and is described in detail in the aforementioned publication (8). In short, these interactions will favor antifoaming if the Hamaker constants of the surfactant (A_s), antifoam droplet (A_p) medium (A_m) are such that

$$A_m \geq A_s \text{ and } A_p, \text{ or } A_m \leq A_s \text{ and } A_p.$$

However if $A_s < A_m < A_p$, or $A_p < A_m < A_s$, then one expects an overall repulsive van der Waals' interaction which would diminish the foam inhibition.

Having considered some of the factors governing transport of the antifoam droplet to the bubble interface, it is now appropriate to consider the forces involved during entry into the interface, spreading and rupture. The first two of these are governed ultimately by short range, interfacial energies, as can be inferred from the definition of the so-called "entering" coefficient (e) of the droplet into the interface and its "spreading" coefficient (s) along the interface (19):

$$e = \gamma_w - \gamma_o + \gamma_{ow}$$
$$s = \gamma_w - \gamma_o - \gamma_{ow}$$

where γ_w is the surface tension of the foaming solution, γ_o is that of the antifoam liquid equilibrated with this solution, and γ_{ow} is the interfacial tension between the two equilibrated liquids. For effective antifoaming to occur it is a prerequisite that the antifoam liquid spread spontaneously at the bubble interface, i.e., that s be positive. If s is positive, e must also be positive, i.e., entry of the droplet into the interface is automatically facilitated.

A positive spreading coefficient is favored by a high γ_w value and low values of γ_o and γ_{ow}. The first and third terms, viz., γ_w and γ_{ow}, are both reduced by the presence of (foaming) surfactant; it is the relative effect of the surfactant which is important. It is, however, a matter of experience that the spreading of a liquid tends to decrease as the surface tension of the aqueous subphase is decreased. This fact is in line with our previous statements concerning the requirements of antifoams, which, in fact, become more rigorous the lower the surface tension of the foaming solution. One of the

principle attributes of silicone liquids is their ability to spread on virtually all aqueous surfactant solutions; this ability is directly connected with their low surface tension ($\gamma_o \approx 20$ dynes/cm).

We come now to the last step involved in the antifoaming process, i.e., bubble rupture. In silicone oil-based antifoams it has been clearly shown that the presence of hydrophobic filler particles markedly improves the defoaming ability of the antifoam fluid. It is now believed, with some experimental supporting evidence, that these finely divided hydrophobic filler particles directly participate in the process of bubble rupture. Thus, in the five listed steps of antifoaming, the first four are primarily affected by the properties of the antifoam fluid, but the final step involves the filler in the following way: once the antifoam droplet enters the bubble and spreads, the
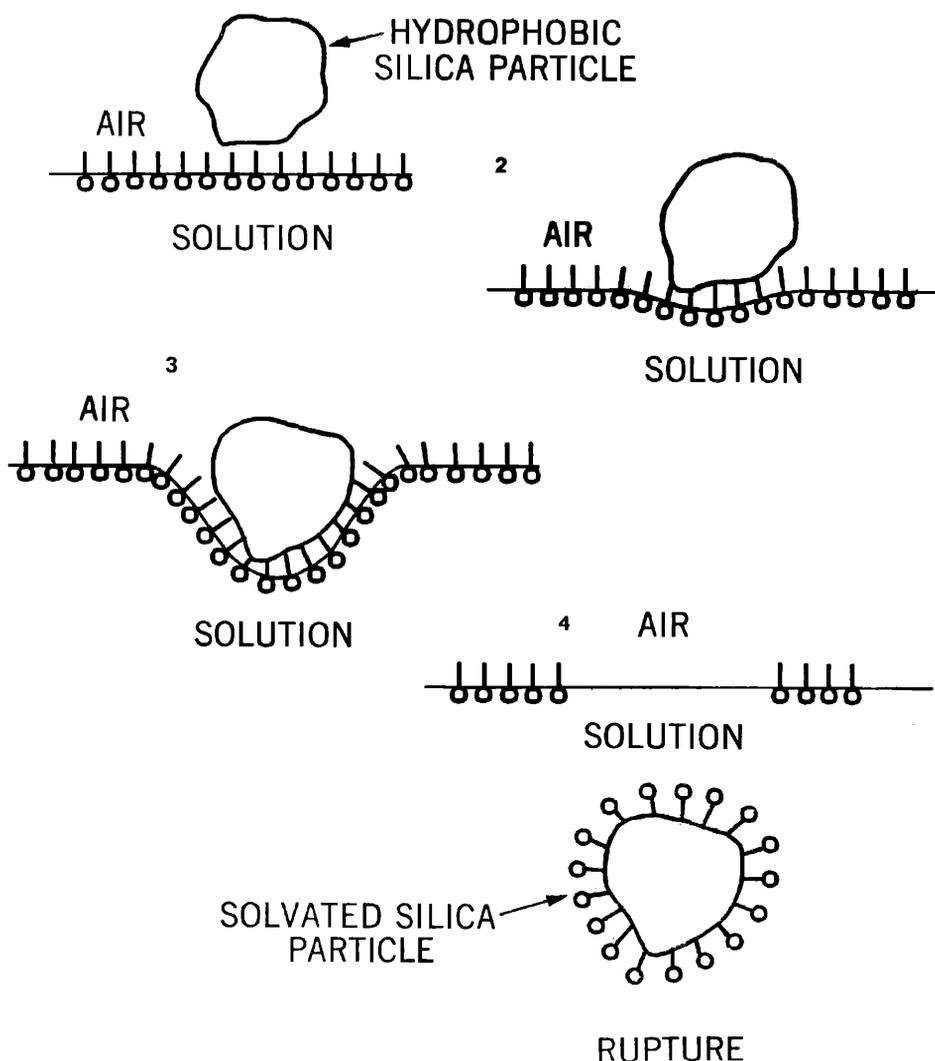

Figure 3. Schematic representation of the mechanism of bubble film rupture by hydrophobic silica particles.

hydrophobic filler particles are swept along the interface. The phenomenon of bubble rupture is explained by the adsorption/depletion of foam stabilizing surfactant molecules by the filler, so causing these particles to become hydrophilic, and ultimately to be extracted into the aqueous phase, as represented in Figure 3. Thus a net transfer of silica from antifoam phase into the aqueous phase is expected and this has, in fact, been experimentally observed (9). It is postulated that if the local depletion of surfactant at the interface is rapid, the resulting surface chemical shock will render the bubble unstable and rupture will occur.

The overall picture which emerges from the above analysis is that, while the hydrophobic silica filler acts as the actual foam breaker, the silicone oil acts as a carrier fluid which prevents the filler particles from coming into contact with surfactant molecules, in this way maintaining their hydrophobicity until they are brought to the point where they exercise their potent antifoaming activity, i.e., in the surface of the foam bubble.

The uniqueness of silicone oil lies in its inertness, in its ability to spread spontaneously on most aqueous fluids and in its ability to maintain the form and size of its droplets in solutions when suitability stabilized. The ability of silica filler particles to act as the foam breaker is primarily dependent on their hydrophobicity and high surface area. A higher degree of hydrophobicity will not only promote potency of the filler particle but will also aid dispersion in the silicone oil. Thus the combination of silicone oil and highly hydrophobic silica particles forms an all-purpose antifoam which can perform effectively in most foaming systems. It is important to mention that the above mechanism has been developed for filled antifoam systems. A different mechanism of action is expected for unfilled antifoams.

CLASSIFICATION AND CHARACTERIZATION
OF FOAMS AND ANTIFOAMS

From the practical viewpoint of antifoaming, foams can be classified in two main ways based on the nature of the stabilizing entity and on the actual mode of foam stabilization. With respect to the former there are five main groups of stabilizers: (a) ionic surfactants, (b) nonionic surfactants, (c) mixed surfactants, (d) polymers, including proteins, and (e) particulate stabilizers. As will be shown later, knowledge of the type of surfactants present facilitates the choice of the antifoam, but it provides only partial mechanistic insight into a potential antifoam's performance. As regards the second classification, four stabilization modes can be listed, namely: (a) by electrical charge, i.e., repulsion force, (b) by entropy, i.e., steric forces, (c) by viscosity, i.e., control of drainage rate, and (d) by a combination of the preceding stabilization mechanisms.

In addition to the above-mentioned classification of foams, there are several specific foaming media characteristics which should be known in order to predict the performance of added antifoams and facilitate their choice. These characteristics are: (1) the state of the foaming system, i.e., its homogeneity, (2) the solution viscosity, (3) the surfactant concentration in relationship to the critical micelle concentration (CMC), (4) the surfactant type, i.e., ionic, nonionic or mixed, (5) γ, the solution surface tension, i.e., low (≤ 38 dynes/cm), medium (38–45 dynes/cm) or high (≥ 45 dynes/cm), and (6) the operating temperature. These factors will be elaborated upon

later. However we stress here that the state of the foaming system is important because heterogeneity of the foaming solutions, as brought about by suspended solids, can accelerate antifoam loss from the system through adsorption or coalescence. This will eventually result in lower antifoam performance. At the same time, suspended solids can sometimes aid foam stabilization and thereby interfere with the antifoaming process. We note here also that the relevance of solution viscosity in antifoaming comes from the fact that, in addition to affecting the rate of foam drainage, it will influence the transport of the antifoam droplets to the interface—a vital step in the overall antifoaming process.

A general classification of antifoams is presented in Figure 4. As seen in this compilation, there are two main types of antifoams, viz., (1) filled and (2) unfilled antifoams. Filled antifoams refer to those which comprise an antifoam base fluid and a small amount (generally 3–10% by weight) of finely divided inorganic filler. In most cases the filler is a fumed silica such as Cab-O-Sil (Cabot) having an average particle

GENERAL CLASSIFICATIONS OF ANTIFOAMS

(Represents Broad Guidelines Only)

ANTIFOAM TYPE	SILICONE	ORGANIC	MIXED
		FILLED ANTIFOAMS	
ANTIFOAM COMPOSITION*	SO, SiO_2	MO, SiO_2	MO/SO/SiO_2
WHERE EFFECTIVE**	A, B, C	B, C,	B, C,
		UNFILLED ANTIFOAMS	
ANTIFOAM COMPOSITION*	S-G	PG	SO, S-G, PG
WHERE EFFECTIVE**	C	C	B, C

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*   SO = Silicone Oil; SiO_2 = Silica, MO = Mineral Oil

S-G = Silicone-Polyglycol Copolymers; PG = Polyglycol (e.g., PPG)

**   A: Ionic Surfactant, High Conc., Low S.T.

B: Ionic Surfactant, Low Conc., Nonionic Surfactant Solution, Medium-Low S.T.

C: Solutions of Polysaccharides, etc., High-Medium S.T.

Figure 4. General classification of antifoams.

size from 100–2000 Å and a surface area of 50 to 350 m^2/gm. The base fluid is generally a nonpolar fluid such as mineral oil or a polydimethylsiloxane oil without any pendant groups. Incorporation of silica markedly improves the antifoaming properties of the base fluid. These antifoams require predispersion for effective action.

Unfilled antifoams, on the contrary, are self-dispersible by virtue of the presence of a hydrophilic-hydrophobic group combination in the molecule. Such antifoams can be highly effective, but only in specific systems; they also tend to be inexpensive.

In each of the above two categories there are antifoams made either from silicone fluids, organic fluids or mixed fluid systems. The choice of the particular fluid system, of course, depends upon the nature of the foaming system and the type of control intended. In the antifoam classification of Figure 4, each of the listed categories is accompanied by a typical foaming system in which the antifoam will perform efficiently. The listing reflects solely performance and not necessarily cost effectiveness. Note, for example, that the silicone based antifoams are effective in a high concentration anionic foaming system, such as 0.5% sodium dodecyl sulfate, whereas antifoams belonging to the other categories will either be ineffective or less effective in defoaming this system. However for a protein stabilized foam all of the antifoams, including silicone/silica, are listed as being effective but will naturally have different efficiencies.

SILICONE ANTIFOAM PREPARATION

There are two major steps in the preparation of silicone antifoams: (a) preparation of the active mixture and (b) processing of the active mixture to a stable form.

The active mixture preparation requires dispersion of hydrophobic fumed silica or other finely divided solid in silicone oil. This can be done by mixing prehydrophobized solid filler with the fluid or, alternatively, by mixing hydrophilic filler and hydrophobizing it either by heat treatment in situ or by incorporation of a hydrophobizing agent followed by heat treatment.

As stated earlier, the active mixture so produced is unsuitable for direct use owing to its poor dispersibility. Therefore the second step in the antifoam making process is the conversion of this compound into an aqueous emulsion or otherwise appropriately formulated form. Proper emulsification of these silicone antifoams is necessary for their overall effectiveness. Nonetheless, the preparation of an acceptable grade of emulsion is still an art and is successfully practiced by only a few companies.

Note: AF-1 and TAF-1 are designations for representative conventional and transient antifoam types, respectively, and will be used throughout this report to illustrate performance variations in different foaming systems.

ANTIFOAMING TESTING

Depending upon the particular end application, several antifoam tests are in use today. Most of these tests are, however, qualitative and, although generating sufficient information for the intended purpose, do not provide fundamental insight into the phenomenon of antifoaming. For the latter purpose, the "nitrogen bubbling" test is
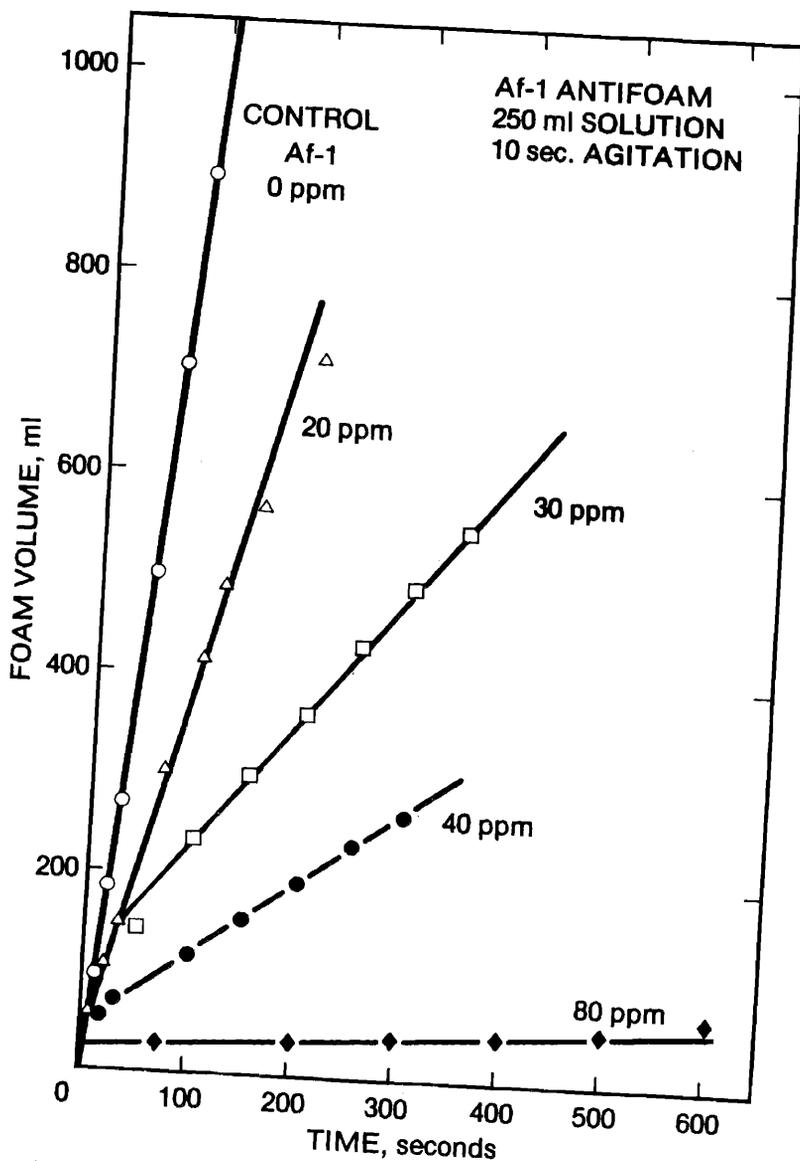
Figure 5. Foaming behavior of protein-based foaming system in the presence of varying concentrations of antifoam, AF-1.

more satisfactory and it also provides quantitative information. The test is simple and involves bubbling nitrogen through the foaming liquid under controlled conditions. In our version of the test, nitrogen is supplied at a constant flow rate through a coarse glass frit ($20-50\mu m$ pore size) immersed in 250 ml of test foaming solution contained in a 1000-ml graduated cylinder. The rise of foam is noted as a function of time; typically, a linear increase in foam volume with time is obtained (see Figure 5). The foaming solution is tested alone and with increasing concentrations of antifoam which are chosen so that the foaming is only partially inhibited. The "antifoam efficiency" (η) is calculated for each dosage of antifoam, as $\eta = K_o/K$, where K_o and K are the

foaming rates without and with antifoam present. In well dispersed antifoam systems the foaming rates are generally constant for at least the first 15 min, allowing determination of a single η value which is representative of the performance of the antifoam at the particular dosage employed. Mechanistically, η represents the degree to which the foaming rate has been reduced by the antifoaming action. Thus a value of η equal to unity means either the absence or total ineffectiveness of an antifoam; $\eta = 10$, for example, means that one would obtain only one tenth of the normal foam volume in a given time.

It should be noted that the comparison of various antifoams by the above test procedure will be valid only if foam production is strictly reproducible in terms of bubble size and size distribution. In this connection it is extremely important to standardize the glass frit and maintain it scrupulously clean so that the pores are always well wetted by the foaming solution and are completely unblocked.

In certain cases, especially in the presence of antifoams, a linear increase in foam volume with time may not be obtained. Such deviation from normal behavior is typical of systems in which the antifoam is either lost from the solution or changes its effectiveness during the course of the test. For example, a poorly dispersed antifoam will tend to "cream" and/or coalesce, eventually growing large enough to suffer
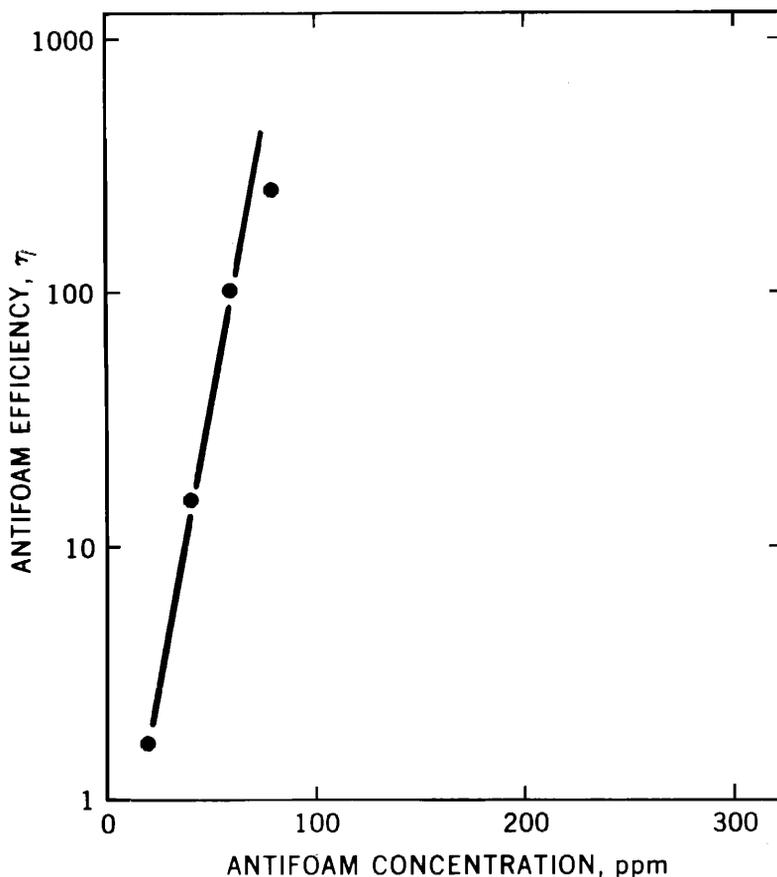

Figure 6. Antifoam efficiency of antifoam, AF-1, in a protein-based foaming system.

serious separation from the system. Another possibility is the adsorption of antifoam onto other available surfaces; this is especially significant in systems where suspended solids are present. All the above conditions will lead to a net decrease in availability of antifoam during the course of the test and result in an apparent decrease in η. Yet, on the other hand, in some instances an increase in antifoam efficiency as a function of test time is possible. This is true in those systems where antifoams become better dispersed, so causing a change in the number of droplets present in the system.

Figure 6 depicts a typical plot of efficiency versus antifoam (AF-1) concentration in a protein foaming system. The relationship can be expressed as $\log \eta = AC + \log B$ or $\eta = Be^{AC}$, where A and B are constants related to the effectiveness of the antifoam in the given medium and C is the concentration of added antifoam. This relationship is valid unless the concentration of antifoam becomes excessive, as would be the case if it reaches and exceeds the point where no foam is formed. For a given antifoam the value of A changes with the quality of its dispersion and A will be constant as long as the degree of dispersion remains unchanged. A nonlinear plot of $\log \eta$ versus C can reflect an increasing tendency of the antifoam to aggregate with increase in concentration.
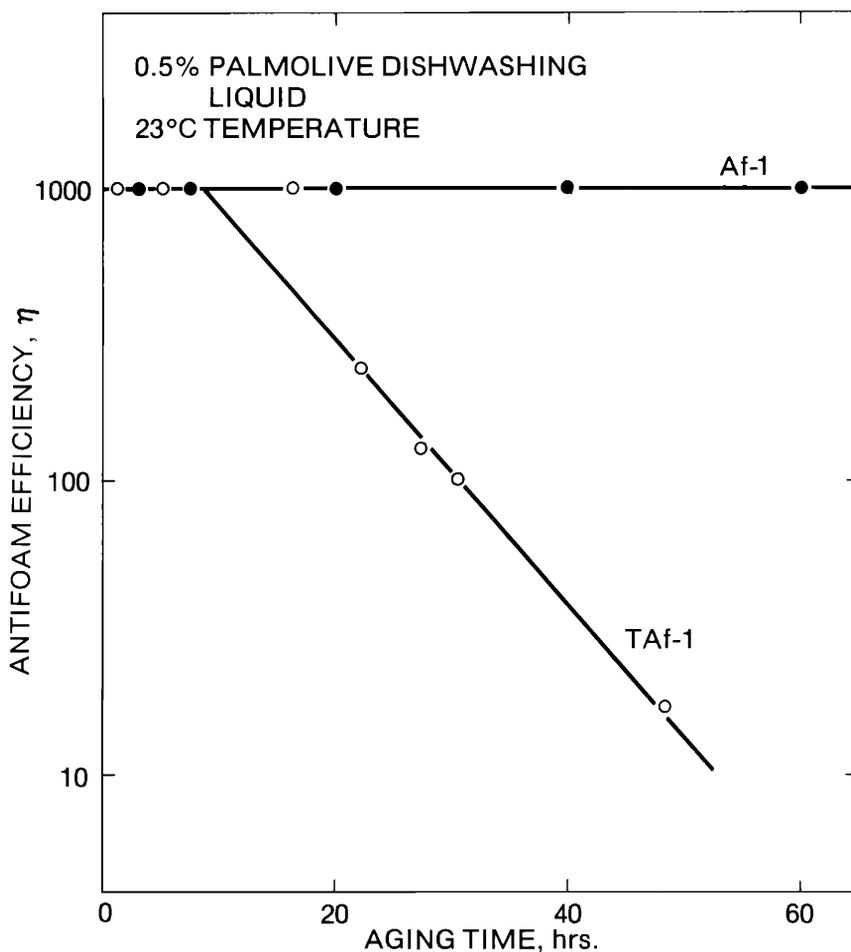

Figure 7. Demonstration of transient nature of TAF-1 antifoam.

The practical factors affecting the performance of silicone antifoams, in general, have been given (8–10) and will be elaborated upon elsewhere. Certain experimental aspects of the behavior of transient antifoams are now presented.

SPECIALTY ANTIFOAMS: THE "TRANSIENT" ANTIFOAM

Over the past 20 years, several specialty antifoams have evolved. They have been developed both on an ad-hoc basis, i.e., for specific foaming systems, or as generic specialty types. The most recent example of the latter type is the transient antifoam which is in contrast to practically all the antifoams described thus far which, in general,
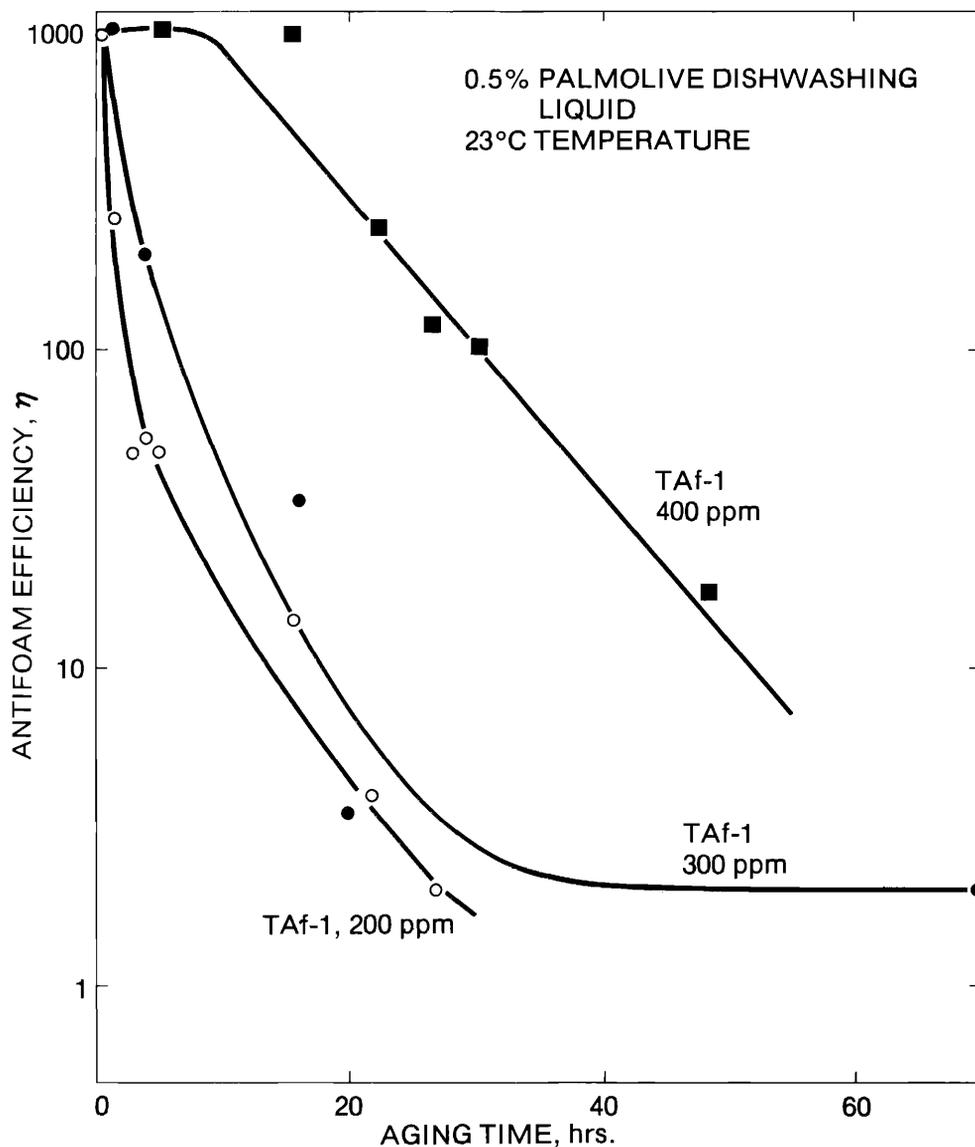

Figure 8. Effect of transient antifoam concentration on its performance in 0.5% Palmolive dishwashing liquid.

lead to lasting reduction of the foaming power of a given system. For certain process or product applications, the foam inhibition or control requirement may be only temporary and subsequent regeneration of foaming characteristics is either highly desirable or essential. For example, during handling of liquid surfactant systems such as shampoos or dishwashing liquids or in plant operations such as filling, temporary foam inhibition would significantly aid overall processing efficiency, but restoration of foaming power is essential thereafter. Transient antifoams have been developed with these applications in mind: after use and exerting their action they destroy themselves
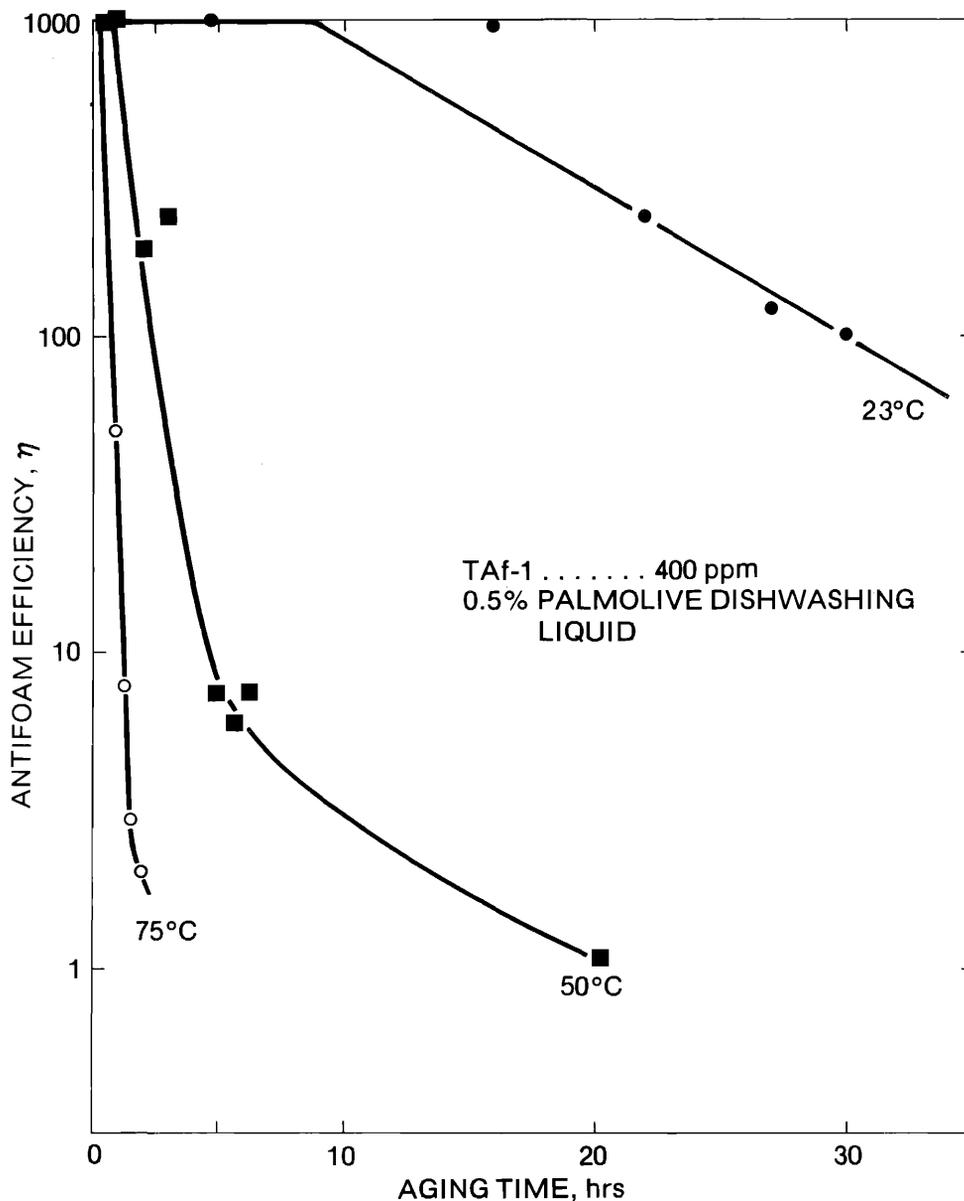

Figure 9. Effect of aqueous aging temperature on the performance of the transient antifoam.

producing an inert, finely divided residue which is sensibly undetectable. These transient antifoams, which represent the latest development in antifoaming technology, are based on an active component, with limited stability in aqueous foaming systems and dispersed silica particles. The antifoam is formulated to be stable.

Figure 7 compares the effectiveness of two different antifoams at the 400 ppm level as a function of aging time in 0.5% Palmolive dishwashing liquid solution. In this particular study, the antifoam was mixed with the foaming solution and then was aged for the stated time period before testing. The temperature and the mixing conditions
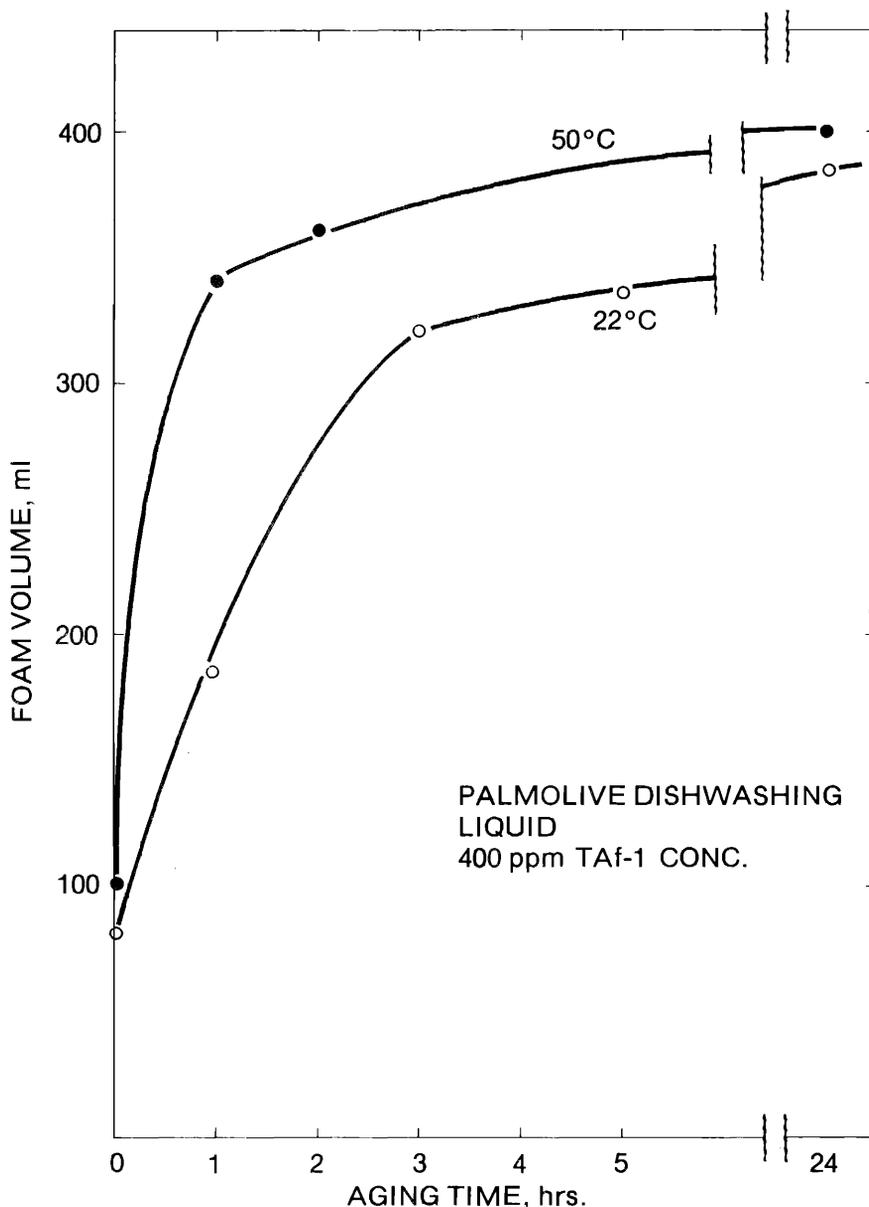

Figure 10. Temperature dependence of transient antifoam, as tested in "T-2" test.

were carefully controlled. As seen in this figure, the transient antifoam evinces a distinct time decay property, dropping in efficiency by a factor of ten in about 30 hr. However, as expected, the conventional silicone oil based antifoam, AF-1, did not show any noticeable change in performance during aging. Similar results were obtained when other foaming systems such as SDS, protein, etc., were tested.

The transient properties of TAF-1 type antifoams are expected to be dependent on several bulk solution parameters such as (a) pH, (b) temperature and (3) composition and concentration of the antifoam. As an example, Figure 8 shows the effect of TAF-1 concentrations on its antifoaming decay rate in 0.5% Palmolive liquid solutions and, similarly, Figure 9 demonstrates the temperature dependence of rate of loss of antifoaming of TAF-1 in the same system. In these experiments the test samples were aged at the stated temperature but the actual test was run at room temperature (22°C). The following observations can be made from these figures: (1) The operating life span of a transient antifoam in a system can be changed by adjusting its concentration: the higher the antifoam concentration, the longer will be its useful life span. (2) The logarithm of the η value tends to fall exponentially with time except at higher concentration where a linear decay law is followed. (3) The transient property is highly sensitive to the aging temperature: for example, a reduction in antifoam efficiency from 500 to 10 requires 30 hr at 25°C, 2.6 hr at 50°C and 0.8 hr at 75°C.

Figure 10 depicts similar temperature sentivity of transient antifoams tested in a different manner. This test ("T-2") was performed by mixing the antifoam with Palmolive dishwashing liquid of full strength, aging at the desired temperature and then producing foam by agitating for 3 min the full strength fluid in a Hobart bowl mixer. The total volume of foam produced at room temperature was measured and plotted, as shown in this figure. Restoration of foaming is faster at the higher temperature.

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