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The mechanisms of antifoam action

P M Kruglyakov

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Abstract. The homogeneous and heterogeneous mechanisms of antifoam action are examined. The homogeneous mechanism involves the adsorption displacement of the molecules of the foam-forming agent from the surface layers of foam films with formation of mixed layers of the foam-forming agent and the antifoam; in this case, the foam films are in a nonequilibrium state. The heterogeneous mechanism of the destruction of the foam consists in the formation of unstable asymmetric aqueous films and the subsequent appearance, after their disruption, of 'bridges' consisting of drops or solid particles of the antifoam passing through the foam film. It is shown that the most important factors governing the instability of the asymmetric film are the low degree of adsorption of the foam-forming agent on the interface between the films and the drops of the antifoam and the solid particles, as well as the presence of rough regions on the solid particles. The antifoam action of solid particles or drops forming the 'bridges' is determined by the wetting angles. The foam film is ruptured when the establishment of an equilibrium three-phase foam film – antifoam – gas contact is impossible. In many systems, both mechanisms of the destruction of the foam operate simultaneously. The bibliography includes 66 references.

I. Introduction

Many industrial processes are accompanied by the formation of a foam, which creates serious difficulties in the technological process or spoils the product. The formation of a foam in the cellulose and paper industries, in the enzymic synthesis of antibiotics and other medicinal preparations, in the electroplating industry, in the dyeing of fabrics, in the preparation of food yeast, baker's yeast, and tomato juice, in blood transfusion, and in the pumping and treatment of bore hole, boiler, industrial, and domestic waste water is a list of only some examples of undesirable foam formation.[1,2]

In order to diminish foam formation, various measures are undertaken. Technological procedures (diminution of the entrainment of air, change in the composition of the solutions or their pH) are usually insufficient and it is necessary to resort to various physical (usually mechanical) and chemical methods to combat foam formation (antifoam action).

Mechanical antifoam equipment includes various rotating devices (stirrers, discs, blades, centrifuges, separators, etc.); in air, steam, or liquid streams, the foam is disrupted by the critical stresses and deformations in the film or as a consequence of the acceleration of the syneresis (drying) of the foam. A rational classification of these procedures for the destruction of the foam and the methods used in the design calculations for mechanical antifoam devices have been examined in detail by Vetoshkin.[3]

The physical procedures include the disruption of the foam by thermal action (heating, treatment with hot steam, freezing), by an electric current, by acoustic waves (mainly ultrasound), by vibration, by exposure to α-particles, by the creation of a high capillary pressure in the foam, etc.[1,2,4]

The most widely used procedure in the fight against foam involves the introduction into the foam-forming solution (or into the foam) of special substances — antifoams (chemical antifoam action). Fats, oils, waxes, aliphatic alcohols, acids, amines, ethers, organophosphorus compounds (in particular, tributyl phosphate), organosilicon compounds (silicone oils), nonionogenic surfactants with a low hydrophilic – lipophilic balance (HLB) [with a HLB number less than 6 (usually 1 – 3)], solid hydrophobic particles, as well as numerous types of waste containing the above and other components†.

'Filled' antifoams (hydrophobic particles, usually hydrophobic silica, dispersed in an oil), which can be emulsified in an aqueous medium, are regarded as some of the most promising.

Hitherto antifoams have been selected mainly empirically taking into account the purposes and nature of the industry. The mechanism of the action of antifoams, especially in the form of a separate phase (drops or hydrophobic particles), remains in many respects obscure.[2]

In terms of the principle governing their action, antifoams can be divided into two groups. The first includes substances that interact chemically with the foam-forming agent, which leads to the formation of insoluble or sparingly soluble compounds. Thus, when soluble aluminium or calcium salts are added to a foam or a foam-forming solution of the sodium or potassium salts of aliphatic acids or when cationic surfactants are added to a solution

P M Kruglyakov Department of Chemistry, Penza State Architectural and Building Institute, ul. Titova 28, 440028 Penza, Russian Federation, Fax (7-841) 262 04 10

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† A detailed list of antifoams and their applications may be found in the relevant books.[1,5].

of anionic surfactants, insoluble compounds are obtained, whereupon the foam is disrupted or ceases to form. The effectiveness of the antifoam is determined in this case by its ability to bind the foam-forming agent, converting it into a precipitate.

A procedure intensifying the disruption of an existing foam involves the supply of antifoams in the form of a foam.[2] For example, a foam produced from a solution of a cationic surfactant with added calcium and aluminium salts is supplied to a foam produced from a solution of anionic surfactants which it is proposed to destroy. The disadvantages of antifoams of this group are the large consumption of the substance and contamination of the working solution by the insoluble compounds formed. For this reason such antifoams are used very rarely.

The second, more common group of antifoams includes substances which do not interact chemically with the foam-forming agent. They disrupt the foam or prevent foam formation as a result of various physicochemical processes, so that they should probably not be referred to as chemical antifoams.

The mechanism of the action of the antifoams of the second group is more complex: it depends not only on the nature of the substance (composition, structure, etc.) and its concentration, but also on the state in which it exists in the foam-forming solution (in the form of molecules or ions or as a separate phase) and many other factors.

The mechanism of the antifoam action of dissolved antifoams will be referred to henceforth as homogeneous (or adsorption) and that of antifoams forming a separate phase will be called heterogeneous. The mechanism of the heterogeneous antifoam action operates in a pure form when liquid, nonpolar, and water-insoluble hydrocarbons or solid hydrophobic particles (Teflon, hydrophobic glass, or silica) are used. When diphilic sparingly soluble compounds are used, the foam may be destroyed as a result of the joint operation of the homogeneous and heterogeneous mechanisms of the antifoam action.

Antifoams in the form of a separate phase (such as drops of a pure substance, solutions in organic solvents, or emulsions) have long been used.[6] There exist various treatments of the mechanisms of the antifoam action including a homogeneous treatment involving the monolayer spreading of the antifoam on the surfaces of foam films and the adsorption displacement of the molecules of the foam-forming agent from their surfaces. The drops can then be regarded (like surfactant micelles) merely as an absorber (or 'reservoir') of the antifoam.

Various qualitative ideas concerning the operation of a special heterogeneous mechanism of antifoam action have been put forward in discussing the role of the spreading of drops in antifoam processes and in the prevention of the formation of optically black spots in microscopic foam films.[7,8]

An explanation of the heterogeneous mechanism of the antifoam action of drops, based on the conversion of stable foam films into unstable aqueous films on an antifoam support owing to the sharp decrease in the degree of adsorption of the foam-forming agent on one of the surfaces of the asymmetric film, was first put forward by Kruglyakov and coworkers.[9,10]

Another mechanism of the heterogeneous antifoam action has been proposed for hydrophobic solid particles.[11,12] Subsequently it was developed in detail in many other investigations.[13–16] This treatment came to be used also in relation to liquid drops.[13,15,16] Different mechanisms of antifoam action have not so far been compared.

The problem of the stability of foams (like that of other disperse systems) and of its regulation (increase in some systems and decrease in others) is crucial in colloid chemistry. Many aspects of this problem have not yet been elucidated.[2,17]

As a consequence of the excess surface energy, a foam is as a whole in a state of thermodynamic nonequilibrium. A consequence of this is spontaneous processes involving the segregation of the liquid from the foam (syneresis of the foam), diffusional transport of gas from small bubbles into larger ones, rupture of films with local coalescence, and the destruction of the foam as a whole, i.e. the separation of the disperse system into a liquid and a gas. However, individual constituents of the foam, in particular films and Plato–Gibbs channels, may be in equilibrium and may possess true stability (metastability).

Analysis of these processes and equilibrium states is outside the framework of this review (although it is important for the understanding of the mechanism of the action of antifoams). Individual questions concerning directly the influence of antifoams on the equilibrium in films or on the kinetics of the syneresis and disruption of the foam will be considered in the analysis of the mechanisms of the antifoam action.

The rate of syneresis of the foam as a function of time or simpler parameters, for example, the time required for the segregation of half of the initial volume of liquid, are used as characteristics of stability in relation to the segregation of the liquid.

The main parameter characterising the rate of internal disruption (aggregative instability) is the rate of decrease in the specific surface of the film and the parameter characterising the disruption of the foam as a whole is the rate of decrease in its volume or of the height of its column (provided that the cross-section of the column is identical along its height). The corresponding characteristics of the stability may be the reciprocals of the rates of the internal disruption and of the disruption of the foam as a whole. The simplest integral characteristic of the stability of a foam is the lifetime of the entire foam or of part of it.

The equilibrium in foam films and hence the prolonged existence of a foam are ensured, on the one hand, by the molecular, electrostatic, and short-range (adsorption or structural) components of the disjoining pressure (Π). On the other hand, various kinetic factors exert a significant influence on the rate of equilibration, the rate of the internal disruption of the foam (as a consequence of diffusion and coalescence), and on the response to the effect of various external perturbations (compressive and stretching deformations, changes in temperature, local changes in surfactant concentrations, etc.). These factors are determined by the stabilising effect of the surfact adsorption layers and by the volume properties of the solution[2]—the equilibrium and dynamic elasticity, the retardation of the rate of flow of the liquid along the films and the Plato–Gibbs channels with different mobilities of the adsorption layers, the volume and surface viscosities, and the electroosmotic pressure—as well as other properties combined in the concept of the structural-mechanical barrier.[18]

External physical influences (a change in temperature, an increase in capillary pressure, irradiation by a stream of α-particles, etc.) alter the rates of the above processes and lead to the breakdown of equilibria. The study of the mechanisms of certain influences helps to achieve a better understanding of the nature of the kinetic processes and equilibrium states and a specific regulation of the stability of the foam.

The method involving the creation of large pressure drops in the liquid phase of the foam and of the corresponding capillary (P_σ) and disjoining pressures in the foam films proved very effective in the study of various physicochemical processes and equilibria in a foam.[2,19,20] In this method, the foam is brought into contact with a porous hydrophilic partition under which a reduced pressure (relative to the atmospheric pressure), not exceeding the capillary pressure in the pores of the partition, is established. Only the liquid but not the gas flows out of the foam under these conditions. This form of external action is most 'natural' for a foam, since a reduced pressure in the Plato–Gibbs channels is an essential condition for the formation of any polyhedral foam. By regulating the pressure drop, it is possible to reduce the positive component of the disjoining pressure by $\Pi - P_\sigma$.

Comparison of the properties of microscopic foam films and the films in a real foam showed that the behaviour of the films in a foam and their response to external influences are more complex than in model films. This is associated both with the difference between the kinetics of various processes in the foam and with the

influence of the dimensions of the films, on the one hand, and with the existence of 'collective effects', arising as a result of the transmission of perturbations due to the rupture of individual films by neighbouring films and bubbles, on the other.[19,20] Various factors stabilising a real foam have been surveyed in a monograph.[2]

II. Methods for the investigation and estimation of the antifoam activities of substances

Various ways of using antifoams are known. They can be introduced beforehand into the working medium (foaming solution) in a pure form or as solutions and dispersions of solid particles in organic solvents (kerosene, turpentine, liquid paraffin) and also as emulsions of different composition in order to prevent the undesirable foam formation. Antifoams are sometimes introduced directly into the foam. The efficiency of antifoams is not the same under these conditions.[1,2]

In view of this, in estimating the antifoam activities of antifoams it is essential to distinguish their effectiveness in disrupting a foam which has already been formed (antifoam action proper) and in preventing foam formation in the foaming process. Substances which are effective in preventing foam formation usually effectively disrupt an existing foam at the same time. On the other hand, many antifoams which effectively disrupt a foam become relatively ineffective in preventing the formation of a foam when introduced into a solution. For example, when drops of butanol and silicone oil are added to a 0.024% solution of saponin, the foam is rapidly destroyed.[21,22] However, when the solution is subsequently shaken with butanol, abundant foam formation again takes place and the resulting foam is stable. On the other hand, the shaking of a solution containing a drop of the silicone antifoam does not induce foam formation.

Various methods are used to estimate the antifoam activities of substances. In the study of the mechanism of antifoam action and of the prevention of foam formation, a comprehensive qualitative assessment of the antifoam activity is very important. This is done in the first place by observing the behaviour of a model foam film (usually macroscopic) when a drop of the antifoam is deposited on it.[23,24] It can involve the observation of the characteristics of the behaviour of the foam or the foam film after the introduction of the antifoam (the nature and rate of attenuation, the lifetime, etc.) and of the behaviour of the antifoam (the form of spreading, fragmentation, the formation of 'bridges', etc.). The film is obtained by withdrawing frames of different size (for example 2 × 1.5 cm) or rings (6–10 mm in diameter). A drop of the test substance or a hydrophobic particle is deposited on the film or the latter is touched with a needle wetted with the antifoam. The film is also obtained from a solution containing the antifoam[13,14] and the nature and rate of its attenuation and disruption are observed.

Similar observations are also carried out when a drop of the antifoam is added directly to the foam investigated immediately after its formation or after a certain time (for example, after 2 or 20 min) or to a solution on the surface of which 'islands' of foam bubbles have been obtained.[7] This permits conclusions concerning the mechanisms of the antifoam action (homogeneous or heterogeneous), the rate of disruption of the foam, the role of the spreading of the antifoams, the influence of solvents on the antifoam activity, etc.

Yet another method for the investigation of the antifoam activity, useful in elucidating the mechanism of the antifoam action, involves the study of the suppression of the formation of optically black spots in microscopic foam films and the influence of the added antifoam.[8,9] This method is based on the fact that a sharp transition to films with a high stability with increase in the concentration of the antifoam is associated with the appearance of black spots in microscopic foam films.[2]

For the film to remain stable after the addition of the antifoams, i.e. in order to ensure the appearance of black spots, it is necessary to increase the concentration of the foam-forming agent. Conversely, with increase in the concentration of the foam-forming agent, the concentration of the antifoam necessary to suppress the formation of black spots must also be increased. Comparison of the ratio of the concentrations of the antifoam and of the agent producing black spots makes it possible to find a measure of the antifoam activity. Such a method for the estimation of the effectiveness of antifoams was first proposed by Ekserova and Buleva.[25]

A direct or indirect determination of the decrease in the stability (lifetime) of the foam or of the decrease in its volume under the influence of a definite dose of the antifoam are used to obtain quantitative characteristics of the antifoam activity. These are usually determined from the average lifetime of the foam or of the relative (compared with the foam without additives) lifetime of the foam in the presence of the antifoam.[1,2] The effectiveness of substances in preventing foam formation is frequently estimated from the decrease in the rate of foam formation for a constant supply of the gas, from the decrease in the height of a column of the foam compared with the height of the foam without the antifoam, etc.[1,2]

For industrial purposes, the antifoam activity (for example, the decrease in the volume of the foam) is referred to a unit volume or mass of the antifoam and sometimes the consumption of the antifoam is compared with the consumption of a standard substance.[1,2] The most complete estimate of the antifoam activity must take into account not only the effectiveness of the substance for different ways of its application but also the influence of the duration of its action (since the effectiveness usually diminishes greatly on contact with the solution) as well as the influence of the solvent and the form and concentration of the foam-forming agent.

III. The homogeneous (adsorption) mechanism of the antifoam action

Any decrease in the lifetime of a foam as the composition of the solution is altered may be regarded as the manifestation of antifoam activity and in this sense the process can be regarded as part of the problem of the stability of foams. However, antifoam action has come to be regarded as the rapid disruption of the foam by special additives and such a process and the mechanisms inducing it constitute a special theoretical and applied problem in colloid chemistry. It is at present difficult to predict theoretically the rate of disruption of a foam even in the simplest systems, for example, in foams for which the type of foam films and the internal structure and capillary (disjoining) pressure, determining the thickness of the films in the absence of an antifoam, are known. One of the main reasons why the mechanisms of the antifoam activity have not yet been fully elucidated is associated with this factor. Furthermore, antifoam activity is caused by many factors on which the effectiveness of antifoams also depends.

One of the possible mechanisms of the action of antifoams involves the adsorption displacement (complete or partial) of the molecules of the foam-forming agent from the interfaces of the foam films and the formation of mixed adsorption layers, which exhibit a poor stabilising activity.

The idea of the adsorption mechanism of the antifoam action was put forward in early studies by Quinke to account for the disruption of the foam on beer by ether vapour.[1] This idea is extremely widespread and is used to explain antifoam activity and de-emulsification,[1,4,26,27] although special studies designed to confirm and determine the details of the adsorption mechanism have been scarcely carried out.

As mentioned above, the disruption of a foam by antifoams introduced into the foam or the foam-forming solution as drops of the pure antifoam or its solutions in organic solvents immiscible with water or directly in the form of emulsions has been investigated in most of the studies. The spreading of the antifoam on the foam-forming solution (for a positive spreading coefficient

or a positive spreading pressure) does not permit an unambiguous conclusion concerning the mechanism of the antifoam action: it can be both homogeneous and heterogeneous.

The only reliable indication of a homogeneous mechanism of the antifoam action is provided by the results of a direct study of the decrease in the stability of foams in foam-forming systems containing an antifoam in an amount not exceeding its solubility (the true solubility or the colloidal solubility in the form of a solubilised system).

The disruption of foams by ethanol was already known to Plato. However, the antifoam activity of alcohol is low: the complete prevention of foam formation requires a concentration of about 25%. The properties of the solvent (mixture of water and alcohol) are markedly altered at such a high concentration.

The prevention of foam formation and the disruption of a foam obtained from a solution of sodium dodecyl sulfate (DDSNa) has been investigated under conditions where after the introduction of the antifoams (19 kinds in all) it was known exactly whether the system was homogeneous or heterogeneous.[28] When certain homogeneous systems (ethyl acetate, oleic acid) were used to prevent foam formation, virtually no decrease in the volume and stability of the foam was observed, but when the system became heterogeneous an appreciable suppression of foam formation was noted.

An almost complete prevention of foam formation in the homogeneous region is characteristic of other homogeneous systems (phenol, pentyl and butyl alcohols, butyric acid, ethyl ether, and triethyl phosphate)—when the antifoam was introduced, the height of the foam after 10 min did not exceed 0.4–0.5 cm, while the height of the foam in an aqueous DDSNa solution without additives was 10 cm. This confirms unambiguously the homogeneous mechanism of the antifoam action.

The antifoam activities of readily soluble antifoams—lower saturated alcohols—have been compared[29] over a wide range of concentrations, including the region of the transition from the homogeneous to the heterogeneous system. The effectiveness of the antifoams was estimated from their ability to prevent foam formation. The dependence of the decrease in the lifetime of the foam on the concentration of the antifoam is illustrated in Fig. 1 for certain foam-forming agents.

Comparison of the stabilities of foams in the homogeneous region showed that, in order to decrease the lifetime of the foam to the same value, for example to 20 min, the amount of butyl alcohol required is ~10–30 times greater than that of hexyl alcohol (depending on the nature and concentration of the foam-forming agent). This means that the antifoam activity of the lower homologous alcohols is approximately directly proportional to the surface activity of the alcohol. According to Traube's rule, the surface activity increases by a factor of 12 on passing from butyl to hexyl alcohol.[30] The most effective suppression of foam formation in the homogeneous region has been observed in a solution of saponin, which is probably associated with the fact that it has the lowest surface activity and with the poor stabilising activity of mixed adsorption layers. These results confirm, at least qualitatively, the fact that in the given homogeneous system the antifoam activity of the antifoam is determined by its adsorption capacity and that in a number of systems (DDSNa–isovaleric acid, OP-10‡–butyl alcohol) virtually complete suppression of foam formation is observed after the attainment of the concentration corresponding to the solubility limit (saturation). However, in other systems, for example DDSNa–hexyl alcohol and OP-10 (0.1%)–tributyl phosphate (TBP) and in all cases where higher homologues of alcohols are used,[29,31] an appreciable stability of the foam is retained (the lifetime is 10–25 min) up to the instant of saturation, but the subsequent increase in the concentration of the alcohols and transition to the heterogeneous region lead to the complete disruption of the foam and prevention of foam formation.

Convincing evidence for the inadequacy of the adsorption displacement of the foam-forming agent in antifoam action has also been obtained in studies of the suppression of the formation of black spots in microscopic foam films by the addition of aliphatic alcohols and acids.[8,9] It was shown experimentally[8,9] that this effect (i.e. the conversion of foam films into an unstable form) occurred in all the systems investigated only after the attainment of the limiting solubility of the antifoam in the solution of the foam-forming agent. These and the results mentioned previously[23,28] indicate the possible operation of two mechanisms of the antifoam action different from the adsorption-displacement mechanism and associated with the appearance of a new phase. In a number of systems (for example, in a mixture of saponin and soap), the antifoam action can be accounted for within the framework of the homogeneous mechanism but in a more complex specific form[32] with allowance for chemical interaction.[2]

In the homogeneous mechanism of the antifoam action, the effect of the antifoam reduces mainly to the alteration of the properties of the adsorption layers of the foam film, the rate of adsorption,[26,33] the elasticity, the surface viscosity,[26,34] and the positive component of the disjoining pressure. Antifoams sometimes influence indirectly the surface properties of foam films by altering the solubility of the foam-forming agent or its critical concentration for micelle formation (CCM). Thus it has been established[35,36] that the addition of 2-ethylhexanol, TBP, and tetradecanol increased the CCM of the foam-forming agent (sodium oleate, DDSNa, etc.) and hence reduced the surface activity.

Ross and Young[37] divided all antifoams into two groups: the first (for example, TBP) mainly accelerate the syneresis of foams by decreasing the surface viscosity and elasticity, while others (for example, isobutylcarbinol) increase the critical thickness of the films or more precisely convert the metastable foam films into unstable ones, which are ruptured at a certain critical thickness (in conformity with theory§; for further details, see Kruglyakov and Ekserova[2]).

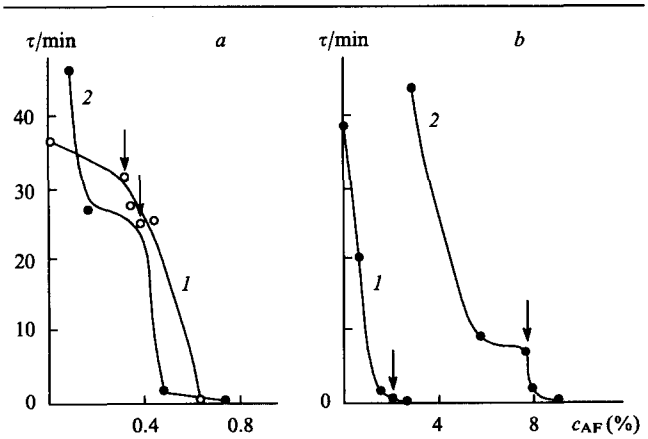


Figure 1. Dependence of the lifetime of the foam on the antifoam concentration. Antifoam: (*a*) 5 × 10^{-1} M DDSNa + 0.4 M NaCl + hexyl alcohol (curve *1*); 0.1% OP-10 + 0.1 M KCl + hexyl alcohol (curve *2*); (*b*) 5 × 10^{-5} M DDSNa + 0.4 M NaCl + isovaleric acid (curve *1*); 2.5 × 10^{-4} M DDSNa + 0.4 M NaCl + butyl alcohol (curve *2*). The limiting solubilities of the antifoams are indicated by arrows.

‡ Technical hydroxyethylated alkylphenol with ten hydroxyethyl groups.

§ See A Scheludko *Adv. Colloid. Interface Sci.* **1** 391 (1967); A Vrij *Discuss. Faraday Soc.* **42** 23 (1966).

IV. The spreading of antifoams and the effectiveness of the antifoam action

Antifoams frequently spread on the surface of the foam-forming solution (and foam films produced from this solution), destroying foam thereby, and for this reason many investigators explain the antifoam activity as being due to spreading.[2,21,25] Leviton and Leighton[38] were among the first investigators to relate the effectiveness of an antifoam to the spreading pressure. Ross and coworkers,[35,37,39] who investigated the influence of spreading on the antifoam action in greatest detail, concluded that there are several types of effects by the spreading substance on the stability of foam films.

The first type of effect involves the formation of a polymolecular spreading film. A condition for polymolecular spreading is a positive value of the initial spreading coefficient ($S_{B/A}$)¶:

$$S_{B/A} = \sigma_A - \sigma_{AB} - \sigma_B \ , \qquad (1)$$

where σ_A and σ_B are the surface tensions of the foam-forming solution A and of the antifoam B, while σ_{AB} is the interfacial tension between A and B.

Rapid spreading of an organic film on the surface of water is usually observed when this liquid has low surface and interfacial tensions. The coefficients $S_{B/A}$, calculated by Eqn (1) for several typical antifoams with a positive initial value of $S_{B/A}$ on the surface of foam-forming solutions, are listed in Table 1.

Table 1. Initial spreading coefficients.[7,31]

Antifoam	Surface tension of antifoam/mN m^{-1}	Foam-forming solution	
		I	II
Alcohols			
Butyl alcohol	24.6	3.0	4.7
Hexyl alcohol	25.3	1.1	1.7
Organosilicon compounds			
Polymethylsiloxane PMS-200	20.4	4.8	3.5
Polyhydrosiloxane liquid PGZh-891	20.2	6.3	6.9

Note. (I) σ_A = 28.5 mN m^{-1}; 1% solution of sulfonol (technical alkyl arenesulfonate) + 0.1% carboxymethylcellulose; (II) σ_A = 31.0 mN m^{-1}; 1% OP-10 solution.

Some time after the addition of the antifoam, the liquids are mutually saturated (at least in a thin layer) and the tensions σ_A and σ_{AB} vary up to the equilibrium values (σ'_A and σ'_{AB}), while the equilibrium spreading coefficient $S''_{B/A}$ becomes negative. Thus, for positive coefficient $S_{B/A}$, the liquid spreads in the form of a polymolecular film and soon after saturation the main bulk of the substance assumes the form of a lens, while the remainder exists in the form of a saturated monolayer.

The characteristic form of the lens is presented in Fig. 2. The shapes of such lenses and the equilibrium condition have been investigated in a number of studies (see, for example, Adamson[40]).

According to the Neuman equation, we have at equilibrium

$$\sigma'_A \cos\gamma = \sigma'_B \cos\beta + \sigma'_{AB} \cos\alpha \ . \qquad (2)$$

¶ A similar condition was used for a hypothetical film of condensed ether vapour in an early study by Quinke as a condition governing the displacement of the foam-forming agent by the antifoam.[4]

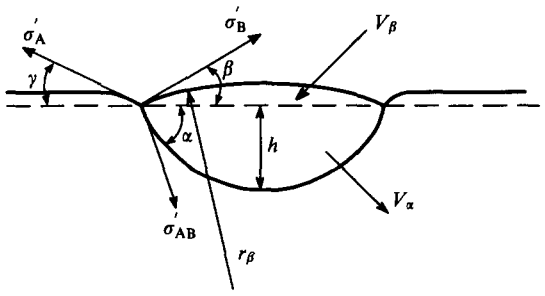


Figure 2. Profile of the organic liquid lens on water (for explanation, see text).

The angle γ is usually small and may be neglected in calculations of equilibria. The lens may be represented in the form of two spherical segments with volumes V_α and V_β. The volume of a segment is

$$V = \pi\left(r - \frac{h}{3}\right)h^2 \ , \qquad (3)$$

where h is the height of the segment and r the radius of curvature.

Furthermore, the radii of curvature of the upper (r_β) and lower (r_α) segments are related by the Laplace equation

$$r_\beta = r_\alpha \frac{\sigma'_B}{\sigma'_{AB}} \ . \qquad (4)$$

Table 2 presents the angles α and β for lenses floating on the surface of water.[41,42]

Table 2. The surface and interfacial tensions as well as the wetting angles for the lenses floating on the surface of water.

Substance	σ'_A/ mN m^{-1}	σ'_B/ mN m^{-1}	σ'_{AB}/ mN m^{-1}	α/ deg	β/ deg
Benzene	62.3	28.8	35	6	7.3
Chloroform	59.4	27.1	32.6	4.7	5.7
Heptyl alcohol	28.5	26.8	7.7	67	16
Octyl alcohol	28.8	26.2	8	70.5	16.7

Comparison of the data in Tables 1 and 2 shows that the tensions σ'_A and σ'_B in alcoholic systems are similar. Thus the angles α and β in typical antifoam systems (Table 1) are the same as for alcohols on the surface of water (Table 2). These angles may be used to predict the behaviour of the film (rupture or equilibrium) with a lens which covers the film.

The second type of effect is monomolecular spreading equivalent to the adsorption penetration by the molecules of the antifoam into the surface layer of the foam-forming agent. A necessary condition for monomolecular spreading is a positive surface pressure[40]

$$\pi^0_{BA} = \sigma_A - \sigma'_A = RT \int_{P(\Gamma=0)}^{P_0(\Gamma_\infty)} \Gamma \ln p \ , \qquad (5)$$

where Γ is the degree of adsorption of substance B, Γ_∞ the limiting degree of adsorption of substance B, and p the saturated vapour pressure of substance B for a negative initial spreading coefficient $S_{B/A} < 0$.

The surface pressure can also be determined from the difference between the initial ($S'_{B/A}$) and final (equilibrium $S''_{B/A}$) spreading coefficients:[40]

$$\pi^0_{B/A} = S'_{B/A} - S''_{B/A} \cdot \quad (6)$$

According to Ross's data, polymolecular spreading is most effective for the disruption of a foam, although Ross did not discover the mechanism of the action of such a film. Among the numerous systems investigated by Ross and coworkers,[21,37,39] Robinson and Woods,[43] and Pattle,[44] very many of those for which the conditions $S_{B/A} < 0$ and $\pi^0_{B/A} < 0$ hold proved to be effective antifoams (see, for example, Tables 3, 1, and 6 in the papers of Ross and Young,[37] Ross,[39] and Robinson and Woods[43] respectively). The effective disruption of a foam for $S_{B/A} < 0$ was also noted in later investigations.[7,13,45]

The possibility of the direct preparation of stable aqueous films on a support comprising certain antifoams[9] demonstrates that the condition for polymolecular spreading is not by itself either necessary or sufficient for the antifoam activity. Nevertheless, in a later study Ross[46] and a number of other investigators (see, for example, Pletnev[47] and Kozhanov et al.[48]) continued to assume that the antifoam activity in heterogeneous systems is a consequence of polymolecular spreading and suggested that the condition $S_{B/A} > 0$ be used as the principal criterion for the selection of effective antifoams. It is therefore useful to consider in greater detail the role of the spreading of antifoams in the prevention of the formation of foams and in the destruction of foams.

A study has been made[7] of the antifoam activity of aliphatic alcohols, acids, and polysiloxanes in two foam-forming systems with a high surfactant concentration (0.1% of OP-10 and 1% of sulfonol) with exact monitoring of the spreading. The antifoam activity was estimated both from the rate of disruption of the foam and from the ability to prevent its formation. The condition $S_{B/A} > 0$ served as the criterion of polymolecular spreading, while $\pi^0_{B/A} > 0$ combined with $S_{B/A} < 0$ served as the criterion of monomolecular spreading. In addition, the Wilhelmy balance was used to monitor the spreading directly.

An effective antifoam activity has been observed also for polymolecular (hexyl alcohol, PGZh-891) and monomolecular (heptyl and decyl alcohol in both systems, oenanthic and caprylic acids in solution in sulfonol) spreading and also in the absence of any spreading (caprylic and pelargonic acids). The nonpolar polysiloxane PMS-200 (without filler), having a high positive spreading coefficient, exhibits a very low antifoam activity.

In other experiments, the influence of antifoam drops on the disruption of foam 'islands' on the surface of the solution was observed.[7] It was established that only direct contact between the antifoam drops and the bubbles leads to the effective disruption of the foam. It was noted that polymolecular spreading of the polysiloxane PGZh-891 is completed by the fragmentation of its film into small droplets, which is an important factor, increasing the effectiveness of the antifoam.

It has also been shown that the antifoam activity of dispersions of solid stearic and palmitic acids[13] and of trialkylmelamine[49] is not due to spreading.

The results of a series of investigations[7,13,45,49] permit the conclusion that the effective action of antifoams in heterogeneous systems is not associated with any particular form of spreading and that an explanation of the partial association of positive values of $S_{B/A}$ and $\pi^0_{B/A}$ with effective antifoam activity can probably be found by comparing these conditions with the condition governing the instability of asymmetric aqueous films.

Yet another condition necessary for the manifestation of antifoam properties is believed to be a positive value of the so called disruption coefficient R,[26,43] for which the drops of the antifoam are believed[43] to penetrate the foam film between the bubbles. The positive disruption coefficient is given by[43]

$$R = \sigma_A - \sigma_B + \sigma_{AB} = -(\sigma_B - \sigma_A - \sigma_{AB}) > 0. \quad (7)$$

Evidently R is a negative coefficient for the spreading of the foam-forming solution on the antifoam, i.e. condition (7) is the condition for the nonwetting of B by a solution of A ($S_{A/B} < 0$). Condition (7), in the form of the negative spreading coefficient $S_{A/B}$, describes[50] yet another possible mechanism of the antifoam action, in which nonwetting is considered as a condition for the instability of the aqueous film.

However, it is known from the analysis of the stability of asymmetric films[51] that the fulfillment of the thermodynamic condition (7) is sufficient for the instability of an aqueous film on an antifoam support. It is then possible to obtain long-lived metastable aqueous films on an antifoam support stabilised by surfactant adsorption layers (similarly to stable foam films). The possibility of effective antifoam action should therefore be sought in the conditions for the instability of metastable films.

V. The antifoam effect of drops of organic liquids

Various organic liquids, sparingly soluble in water, appreciably diminish the stability of a foam on coming into contact with the latter.[28,45,48,50,52]

When a foam is formed in the presence of drops of an organic phase immiscible with the aqueous solution, there is a possibility of the formation of asymmetric aqueous films bounded by the gaseous medium on one side and by the antifoam phase on the other. Such aqueous films on an antifoam support can be obtained in the course of the attenuation of foam films if the solution of the foam-forming agent contains drops of an antifoam in the form of an emulsion (Fig. 3) and also when a solution of the antifoam is atomised in the form of an aerosol over the foam or when it spreads on the surface of the films and when the films containing drops of the antifoam are ruptured. The formation of an asymmetric film from a foam film containing drops of an organic liquid is promoted to a large extent by the absence of a charge on the drops, by a high concentration of the disperse phase, and by other conditions influencing heterocoagulation.

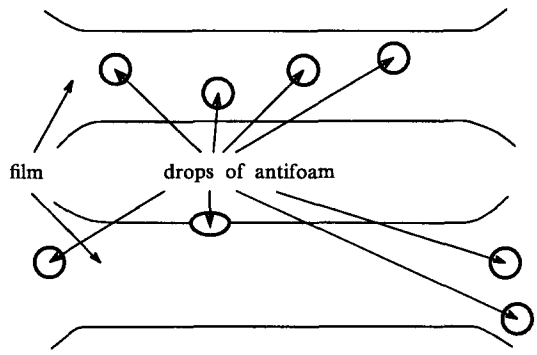


Figure 3. Schematic explanation of the formation of asymmetric films.

The asymmetric film (film on an antifoam support) can be part of the foam film or it can be fully bounded on one side by the organic phase, as in the polymolecular spreading of an antifoam on a film. If the asymmetric film formed is in a state of nonequilibrium for all thicknesses and is ruptured following the attainment of a critical thickness, its rupture leads to the disruption of the entire foam film of which it was a component. On the other hand, if the asymmetric film reaches equilibrium at a certain thickness (h), its influence on the stability of the foam film will depend on the height of the barrier on the disjoining pressure isotherm $\Pi(h)$. For the same height of the barrier, the lifetime of the foam film will evidently remain virtually unaltered. However, in the presence of antifoam drops the concentration of the foam-forming agent usually decreases in the aqueous phase as a consequence of its extraction by the drops of the organic liquid

and the additional adsorption on the drops. The adsorption of the surfactant on the water–antifoam interface is as a rule much smaller than on the water–gas interface, so that the energy repulsion barrier, generated by the interaction of the adsorption layers of the foam-forming agent on the water–antifoam and water–gas interfaces is significantly reduced compared with that in a two-sided film with adsorption layers on the water–air interface. Thus in this case too the antifoam exhibits a definite foam destroying capacity.

Analysis of the stability conditions shows that aqueous films on a support consisting of an organic phase are thermodynamically unstable.[4,51] Metastable asymmetric aqueous films can be obtained under certain conditions when the adsorption (Π_{ads}) or electrostatic (Π_{es}) components of the disjoining pressure, arising in the course of the attenuation of the film, exceed the molecular attraction Π_{vw} within a certain range of thicknesses:[51]

$$\Pi_{es}+\Pi_{ads} > \Pi_{vw}.$$

Model films of this type were first obtained from a solution of a nonionogenic surfactant—20-hydroxyethylated nonylphenol [NP-20, concentration $(1-5) \times 10^{-2}$%] with added magnesium sulfate on a cyclohexane support.[53] As in the case of foam and emulsion films, two types of equilibrium films were obtained in this case depending on the electrolyte concentration: the usual films and Newtonian black films.

In such films, the minimum surfactant concentration (c_{st}), necessary to obtain stable films (with a lifetime in excess of 10 min), depends greatly on the polarity of the organic phase (Table 3).

Table 3. Surfactant concentrations ensuring the formation of stable aqueous films on the surfaces of organic liquids.[9]

Organic phase	Surfactant concentration × 10^3 (%)	
	OP-10	Saponin
n-Decane	–	4
Benzene	3	3
Decyl alcohol	4	2
Heptyl alcohol	7	8
Butyl alcohol	Unstable films	

Note. The minimum surfactant concentrations for which thin (grey) films with a lifetime not less than 10 min were obtained.

In the case of a nonpolar organic phase, c_{st} does not differ greatly from the minimum concentration required to obtain a stable foam film, i.e. the concentration for the formation of black spots c_{bl} ($c_{bl} \approx c_{st}$). For example, $c_{bl} = 7 \times 10^{-4}$ % for a saponin solution and $c_{bl} = 1.2 \times 10^{-4}$ % for an OP-10 solution. This means that the effective disruption of the foam by nonpolar hydrocarbons due to the formation of unstable films is possible only at very low concentrations of the foam-forming agent (less than 0.003%–0.004% for saponin and OP-10). At higher concentrations of the foam-forming agent, the foam destroying capacity of the antifoam is determined by the slight decrease in the energy barrier and certain kinetic factors (for example, by additional adsorption).

The lifetime of a foam on an organic support diminishes greatly following the establishment of a reduced pressure in the Plato–Gibbs channels as a consequence of the decrease in the repulsion forces barrier by the amount $\Pi - \Delta P$ (where ΔP is the decrease in the pressure within the channels).[2,54] For alcohols, the difference between c_{bl} for foam films without and with added antifoam becomes significant and, on a support comprising lower alcohols, it is altogether impossible to obtain stable aqueous films as a consequence of the sharp decrease in the adsorption of the foam-forming agent on the water–antifoam interface (Table 3).

The simplest mechanism of the action of an antifoam (with barrier-free rupture whereupon the asymmetric film is in a state of nonequilibrium for all thicknesses) operates when highly polar organic liquids with a high affinity W_A for the aqueous medium are employed:

$$W_A = \sigma_A + \sigma_B - \sigma_{AB}.$$

In this case, the adsorption of the foam-forming agent at the water–antifoam interface is impossible (or its extent is very low) over the entire range of concentrations up to and including the CCM, because in such systems

$$\sigma^0_{AB} \approx \sigma_{AB} \approx 0, \quad (8)$$

where σ^0_{AB} is the interfacial tension on the antifoam–water interface and σ_{AB} is the interfacial tension on the interface with the aqueous solution of the foam-forming agent.

A low degree of adsorption of the foam-forming agent on the water–antifoam interface occurs in various foam-forming systems,[10] where lower alcohols (propyl and butyl) are used as antifoams at concentrations which exceed their solubility, and $\sigma^0_{AB} \sim 0$.

The same heterogeneous mechanism of the disruption of the foam with formation of unstable films on a support operates when the foam is introduced into highly polar liquids (partially or fully soluble in water): lower alcohols and acids, ketones, ethers, etc.[45] The rate-limiting stage in the disruption of the foam may be determined in this instance by various kinetic factors (the suction of the organic liquid into the foam, the rate of its dissolution in water, etc.), but the instability of the films is due to the sharp decrease or complete loss of the surface activity of the foam-forming agent on the water–antifoam interface.[45]

A heterogeneous mechanism of the antifoam action of drops has been described.[2,9,10,55] The second stage of the disruption of the foam film after the rupture of the asymmetric film and the appearance of a two-sided (symmetrical) antifoam lens within the foam film was not considered because the instability of such a system was regarded as evident.

Fig. 4 illustrates the possible behaviour of the antifoam lens after the rupture of the asymmetric film. It is seen that, when the lens shape is retained, the drop is continuously extended as a consequence of the inequality

$$\sigma'_B \cos\beta < \sigma'_A + \sigma'_{AB} \cos\alpha,$$

and is converted into a planar film of the substance. Without attaining mechanical equilibrium, the film of substance B and the foam film will be ruptured. On the other hand, if the drop rapidly assumes a shape close to spherical after the rupture of the asymmetric film, then, under the conditions of a temporary local mechanical drop–film equilibrium, the foam film forms a convex meniscus with an increased capillary pressure within it. The outflow of the liquid from the meniscus leads to a further rapid approach of the surfaces of the foam film and the drop until they touch and the foam film is then separated from the drop (slips off) and is destroyed. The instability of liquid drop 'bridges' within the foam film has also been indicated by Garrett.[12]

The disruption of a foam by diphilic antifoams as a consequence of the surface activity on the water–air interface takes place with the joint operation of two mechanisms–homogeneous (adsorption displacement) and heterogeneous. This is yet another of the causes of the greater effectiveness of diphilic antifoams compared with nonpolar liquids.

The contribution of the heterogeneous mechanism in the disruption of the foam in such systems can be isolated and estimated only in a quantitative study of the dependence of the foam destroying capacity of the antifoam on its concentration when passing from a homogeneous to a heterogeneous system.[29] The contribution of the heterogeneous mechanism usually increases at high surfactant concentrations, whereupon the homogeneous mechanism proves to be relatively ineffective.

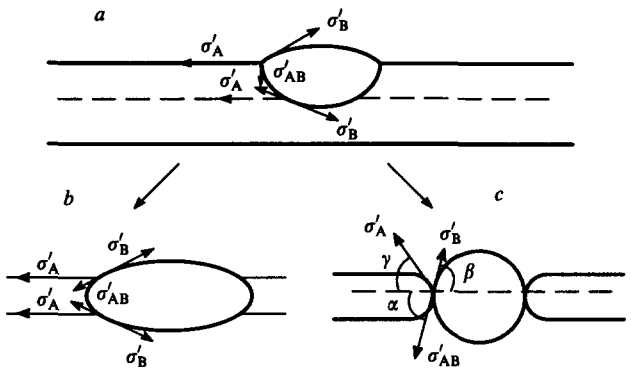


Figure 4. Schematic illustration of the behaviour of the antifoam lens on formation of a 'bridge' in the foam film: (*a*) initial stage after the rupture of the asymmetric film (the second side of the film is shown dashed); (*b*) extension of the lens with retention of the initial shape; (*c*) formation of a convex spherical meniscus near the antifoam drop.

A series of important features of foam formation and destruction in heterogeneous systems have been explained on the basis of the mechanism of the heterogeneous antifoam action:[2,55,56] the temperature dependence of the stability of foams produced from solutions of nonionogenic surfactants in the region of their turbidity temperature, the influence of solvents on the foam-destroying capacity of antifoams when they are used in the form of solutions, and, especially, the inversion of the antifoam activity in the series of aliphatic alcohols.[10]

VI. The antifoam effect of solid hydrophobic particles

Kurzendorfer[49] reported that, when particles of solid trialkylmelamine in suspension in alkyl benzenesulfonate fall on the surfaces of films, they cause their rapid rupture, which is not associated with the formation of mixed layers comprising trialkylmelamine and sulfonate molecules (with the adsorption displacement mechanism).

It has also been reported[57] that, when atomised silica particles which have been rendered hydrophobic enter a foam, they lead to the rapid disruption of the films in those bubbles which are in contact with the particles. Garrett later showed[11] that the chemically inert 5–40 μm particles of dispersed Teflon act as an effective antifoam on contact with a foam. He explained their antifoam properties by the appearance of hydrophobic 'bridges' made up of such particles and passing through the film and by their nonwettability. The formation of 'bridges' with subsequent rupture of the film near the hydrophobic particles (glass beads which have been rendered hydrophobic, lead sulfide, etc.) was demonstrated by Dippenaar[58] using a high speed filming technique.

The studies of the influence of hydrophobic particles on the stability of foams generated from aqueous surfactant solutions were later continued by other investigators.[12–16] The influence of the method used to form the foam and of the state of aggregation of the particles and of their shape on the effectiveness of the disruption of the foam was examined and the joint action of solid and liquid particles was investigated. In Garrett's experiments,[11] the foam was obtained from solutions of surfactants of different types (6-hydroxyethylated tetradecyl alcohol, tetradecyltrimethylammonium bromide, and DDSNa) by shaking in a 250 ml cylinder for 15 s. The three-phase contact wetting angles θ, measured on a plate wetted with water, were $\theta = 108° \pm 5°$ (incoming flow angle) and $\theta = 97° \pm 5°$ (outgoing flow angle). The volume of the foam in the presence of Teflon particles (40 mg per 50 ml of the solution) diminished by a factor of 2 and at low surfactant concentrations the foam was not obtained at all.

Garrett[11] deduced a thermodynamic justification of the critical value of the wetting angle at which the film ruptures spontaneously as a consequence of the formation of the hydrophobic particle 'bridge' between both surfaces of the foam film and the subsequent 'slipping off' (separation) of the menisci from the particles.

Garrett's analysis was based on the calculation of the change in the Helmholtz free energy when the particle passes from the incompletely or completely wetted state (immersion in the liquid) to a state where the foam film does not wet the elliptical particle at all, forming a point contact with the particle. An improved more realistic model of the rupture as a consequence of the nonwetting of the particle was developed by Frye and Berg.[14]

The mechanism of the rupture of the foam film by hydrophobic particles is explained by the scheme presented in Fig. 5. If the surfactant solution contains poorly wettable particles, then one (or several) may find itself on the surface (flotation by the surface), where it is rapidly oriented, occupying an equilibrium position. After the rupture of the asymmetric film under the particle, the latter moves, as shown by Dippenaar's direct measurements,[58] and occupies a symmetrical position relative to the film, so that the wetting angles on either side of the film are closer to the equilibrium values. the subsequent behaviour of the film around the particle depends on the equilibrium wetting angle. If $\theta < 90°$ (for a sphere), then the initially convex meniscus around the particle is converted, after the attainment of the equilibrium wetting angle, into a concave meniscus with a reduced pressure, which prevents further attenuation. If $\theta > 90°$, then after the formation of a 'bridge', a convex meniscus with an increased pressure $\Delta p = 2\sigma/R$, where R is the radius of curvature of the surface of the meniscus, appears. The increased pressure expels the liquid from the menisci and, since equilibrium is not attained under these conditions, the mutual approach of the surfaces around the particles continues until they come into full contact. This leads to the 'slipping off' (separation) of the meniscus, the 'liberation' of the particle, and the rupture of the film. This model has been used by Frye and Berg[14] to calculate the time required to disrupt such films. This time is made up of the attenuation time until the formation of a 'bridge' and the time required for the dewetting of the particle (direct rupture of the film). According to the authors,[14] the rupture time must be sufficiently short for the particle to behave as an effective antifoam. The attenuation time (τ) up to the formation of a 'bridge' was determined from the

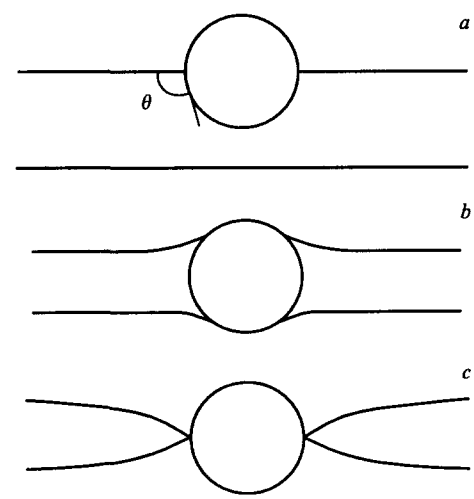


Figure 5. The influence of a solid hydrophobic spherical particle on the behaviour of the foam film: (*a*) equilibrium position on the surface; (*b*) local thickening of the film near the particle for $\theta < 90°$; (*c*) local attenuation of the film near the particle, inducing the rupture of the latter, for $\theta > 90°$.

Reynolds equation[2,14] on the assumption that the surface of the film is fully retarded (immobile):

$$\tau = \frac{3\mu R}{2\Delta p h^2}, \quad (9)$$

where R is the radius of the circular film, μ the dynamic viscosity, Δp the capillary pressure, and h the thickness of the film at the instant of the appearance of the 'bridge'.

In the calculation of the rupture time (the time required for contact between the surfaces of the two menisci), it is assumed that the particle occupies a symmetrical position relative to the surfaces of the film. Fig. 6 illustrates the region of contact between the film and the particle and presents the designations of the quantities used to calculate the rupture time.

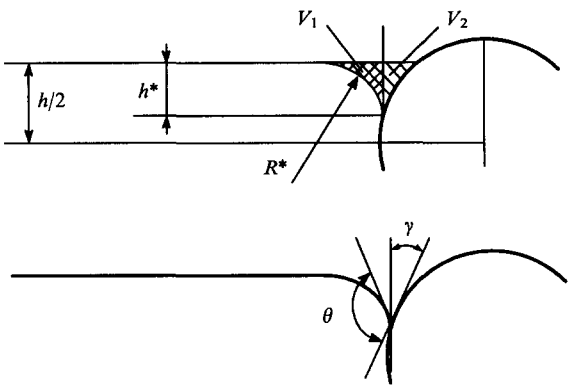


Figure 6. Schematic explanation of the significance of the parameters used to calculate the film rupture time.

In the initial state, the surface of the film is planar until there is contact with the solid particle; while at the instant of rupture, at which point the edges of the menisci come into contact, the thickness of the film becomes $h = 2h^*$. The rate of the mutual approach of the menisci depends on the volume rate of attenuation of the film and on the excess volume of the liquid ($V_1 + V_2$).

The calculation was based on Eqn (9) with substitution of the capillary pressure given by

$$\Delta p = \frac{\sigma}{R^*} = \frac{\sigma[1 - \sin(\theta + \gamma)]}{h^*}, \quad (10)$$

where γ is the angle between the vertical and the tangent at the point of contact between the surfaces of the solid and liquid phases. In this calculation, it is assumed that the excess liquid flows from the meniscus through the entire film, although Dippenaar's observations have shown[58] that the liquid flows only a short distance away from the particle at the instant of rupture. For particles with smooth surfaces without sharp angles (spheres, discs, ellipsoids, and rods oriented at right angles to the surface of the film), the calculation predicts the rupture of the film at $\theta > 90°$. A strong antifoam activity (a rupture time of the order of milliseconds) should be observed already for $\theta = 95° - 100°$.

Among particles of all shapes (to simplify the calculation, only figures of rotation are considered), conical particles alone are effective for $\theta < 90°$. The rupture time for conical particles depends both on the wetting angle θ and on the angle at the apex of the cone (β) and it is essential that $\beta < \theta$. The influence of the initial thickness of the film, the particle size, and other parameters on the film rupture time has also been considered.[14]

The results of the calculation agree well with experiment. The experiments involving the rupture of films obtained on a frame, by piercing the films with thin rods (d = 1 mm) of different materials, are especially instructive. In these experiments, only the shape, size, and orientation of the particles were known. The wetting angle could be measured accurately and it was an incoming flow angle. Furthermore, the problem of the probability of the penetration (entry) of particles onto the surface, which is not entirely evident in the disruption of a foam obtained from a suspension of particles, was in this instance solved unambiguously.

The results of such experiments are presented in Fig. 7. Despite some scatter in the range of angles 95° – 105°, it is readily seen, that for $\theta < 95°$, none of the films is ruptured and, for $\theta > 105°$, all the films are ruptured. Experiments with suspensions of solid particles (Teflon, glass beads which have been made hydrophobic, and ground glass) showed that in the case of 'smooth' particles, the antifoam activity begins to be manifested for $\theta = 35° - 45°$ and complete prevention of the formation of foam occurs for $\theta = 85°$. In the case of rough ground glass particles, effective antifoam action occurs already for 25° – 30° and, when $\theta = 50° - 55°$, a foam is not formed. The quantitative treatment of experiments with suspensions is more complex as a consequence of some uncertainty in the determination of the wetting angle during the rupture of films (owing to its uncertainty as the angle approaches the outflow value), the adsorption kinetics, and other factors.

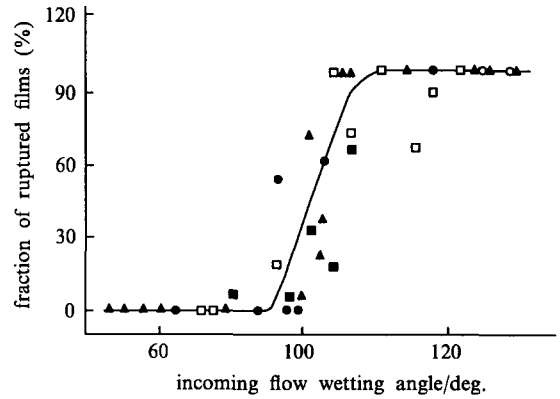


Figure 7. Dependence of the proportion of ruptured films on the incoming flow wetting angle. Antifoam: (*1*) hexadecyltrimethylammonium bromide; (*2*) sodium dodecylbenzenesulfonate; (*3*) Triton X-100. Open symbols — Teflon; filled symbols — glass which has been made hydrophobic.

The influence of the state of aggregation of the particles on the antifoam activity has been investigated by Aronson.[13] It was shown that, regardless of the type of solid particles (hydrocarbon or saturated aliphatic acids), the antifoam activity falls sharply with increase in temperature over a narrow range corresponding to the melting point.

Aronson believes that the most important cause of the large difference between the antifoam activities of liquids and solid particles is the influence of roughness on the stability of asymmetric films. Regardless of their shape, solid particles always have rough regions, which make it possible to overcome the energy barrier hindering the rupture of asymmetric films. However, the heights of the barriers are no less important for the wetting films on solid and liquid supports.

Various synergistic effects in the joint action of solid and liquid hydrophobic particles have been examined on the basis of the model of antifoam action described above.[15,16] In particular, it has been shown[16] that an increase in the effectiveness of the antifoam action by solid particles in the presence of dodecane is associated with the decrease in the wetting angle θ required to disrupt the foam, while the decrease in the effectiveness of antifoams with increase in the concentration of the foam-forming agent is a consequence of the adsorption of the surfactant on the solid particles and the acquisition of hydrophilic properties by their surfaces.

Comparison of the two mechanisms of the antifoam action in heterogeneous systems permits the following conclusions. A necessary condition for the rupture of foam films in the model of drop antifoams is the instability of the film on the support as the drop approaches the interface. The cause of the instability may be a change in any of the components of the disjoining pressure. The simplest and clearest case of instability occurs when the energy barrier disappears due to the complete loss of surface activity at the water–polar antifoam (aliphatic alcohol or acid) interface.

The rupture stage after the formation of the drop 'bridge'-lens through the foam film is assumed to be evident in this case in view of the instability of the system produced for both lens-shaped and spherical initial drops (Fig. 4).

The second attenuation stage — extending from the formation of the hydrophobic 'bridge' up to equilibrium or rupture — is decisive for the mechanism of the antifoam action by solid particles. The first stage — the rupture of asymmetric films — is assumed to be evident at least for films on solid hydrophobic supports as a consequence of the influence of rough regions, although it has been shown experimentally [13] that, in the absence of such regions, films may be thermodynamically stable (metastable).

In the theory of the rupture of films by hydrophobic particles, the question of the influence of the particle size on the effectiveness of the antifoam action for $r < 1$ μm is not entirely clear. It follows from calculation [15] that the time required to attain rupture shortens with decrease in the particle size (from $r = 10^3$ to $r =$ 1 μm) as a consequence of the decrease in the volume of the meniscus and of the thickness of the film at the instant of formation of the 'bridges'. The experiments in which large particles ($r > 1$ μm) were separated by filtration demonstrated a sharp (almost complete) fall in the antifoam activity in systems without these particles. [13] Furthermore, when very small hydrophobic particles were used ($r = 20-1000$ nm), their pronounced stabilising action was observed and, according to data of Tang et al., [59] such particles behave to some extent like molecules, diminishing the surface tension.

VII. Concentration effects in antifoam processes

The effectiveness of antifoams in preventing foam formation diminishes sharply with increase in the concentration of foam-forming agents. However, as noted above, at high surfactant concentrations many substances effective in destroying foam lose this capacity fully or partially on entering the solution. These changes in antifoam activity, which are frequently extremely significant, may be a consequence of various physicochemical processes.

The mechanisms of antifoam action examined make it possible to explain, at least qualitatively, the various concentration effects in the prevention of foam formation and in the disruption of a foam by the addition of antifoams.

We shall consider certain characteristic instances of changes in antifoam activity following a change in the composition of the foam-forming agent and in the methods used to apply antifoams.

In the development of foam-forming compositions, used to extinguish fires arising on inflammation of liquids which are miscible with water, experiments are carried out on the disruption of the foam by these 'corrosive' liquids, the foam being supplied on to the surface of the liquid. The rate of such contact antifoam action is extremely high, but at the same time, when comparatively large amounts of these liquids (5%–10%) are added to aqueous solutions of surfactants, they cause a comparatively small decrease in the stability of the foam. A marked decrease in stability is observed only with increase in the concentration of the liquids to 20%–30%. The cause of the significant difference between the antifoam activities of these liquids in their contact interaction with the foam and when they are added to an aqueous solution in the given systems is evident: when a foam comes into contact with such liquids, unstable asymmetric films arise in the heterogeneous antifoam process [owing to the complete loss of surface activity by the foam-forming agent on the water–alcohol (ether, acetone) interface]. Furthermore, the surface is 'unstable' as a consequence of the complete miscibility of the phases in contact.

When such solvents are added to water, the stability of the foam does not change, owing to the low surface activity, until the foam-forming agents cease to be surface-active on the liquid–gas interface at very high concentrations owing to the marked change in the composition of the mixture (solvent). For this reason, the foam becomes completely unstable under these conditions.

Another example is the characteristic case involving the use of sparingly soluble diphilic additives (for example, aliphatic alcohols — pentyl, hexyl, heptyl, etc. [31]) as antifoams. With increase in the concentration of the foam-forming agent in systems [10, 31, 60] containing added antifoams in a molecular or drop form, the lifetime of the foam increases and the time required for the formation of its specified volume (Fig. 8), necessary to suppress the formation of black spots in foam films, achieving thereby the complete prevention of foam formation (Fig. 9), diminishes (or the amount of the antifoam increases). For low-molecular-mass diphilic antifoams (alcohols, acids, ethers, etc.), the loss of effectiveness is largely a consequence of the solubilisation of large volumes of the antifoam [31] which decreases the thermodynamic activity (for the dissolved component) and the number of drops, while for initial concentrations of the antifoam less than its colloidal solubility, it is a consequence of the change in the mechanism of the antifoam action (from the joint homogeneous and heterogeneous mechanism in the presence of drops to the homogeneous mechanism after dissolution).

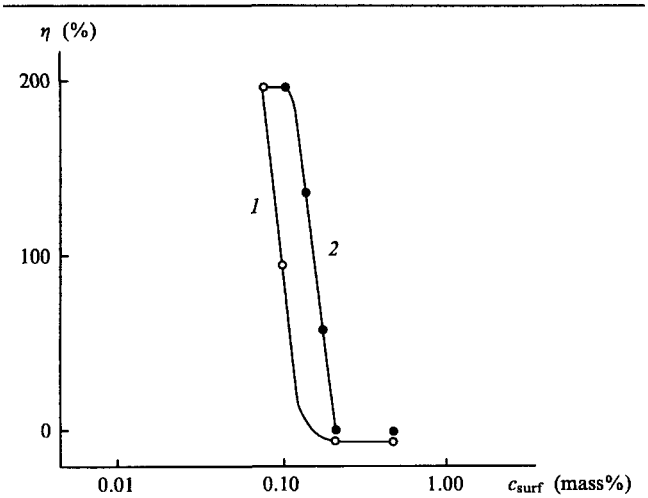


Figure 8. Dependence of the effectiveness of the antifoam action (η) on the concentration of the foam-forming agent (η is the ratio of the rate of foam formation without the antifoam to the rate in the presence of 0.016 vol.% of a 10% emulsion of polydimethylsiloxane as the antifoam): (*1*) 1% DDSNa solution; (*2*) 1% dodecylammonium chloride solution.

Another cause of the decrease in the antifoam activity may be an increase in the stability of the asymmetric films at high surfactant concentrations owing to the increase in the degree of adsorption on the interface between the solution of the foam-forming agent and the antifoam drops. [9, 10]

Yet another important cause of the loss of antifoam activity with increase in the concentration of ionogenic foam-forming agents, particularly when nonpolar (for example siloxane) antifoams are employed, is the appearance of a charge on the drops. Such a case has been studied in detail. [60]

The antifoam activity and the ζ-potential change markedly in the region of the 0.1% concentration of DDSNa, which corresponds approximately to the CCM (Fig. 10). Similar results have been obtained also for a solution of a cationic surfactant. The appearance of a charge stabilises the asymmetric film, the

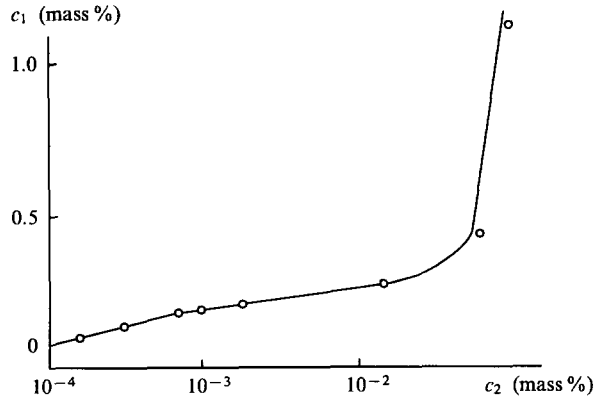


Figure 9. Dependence of the concentration of heptyl alcohol required to prevent foam formation (c_1) on the concentration of the OP-10 foam-forming agent (c_2).

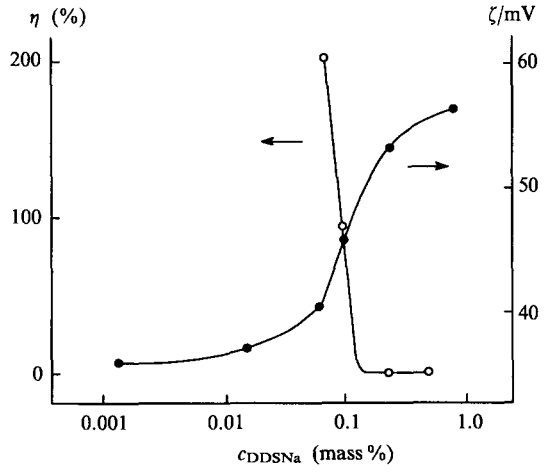


Figure 10. Dependence of the electrokinetic potential ζ and of the antifoam activity η on the DDSNa concentration (amount of added antifoam 0.016 vol.%).

drops cease to fall onto the surface, and the heterogeneous mechanism of the antifoam action becomes relatively ineffective.

The inversion of the antifoam activity in the series of aliphatic alcohols is associated with concentration effects. Systematic studies on higher aliphatic alcohols have shown that, at low concentrations of the foam-forming agents (OP-10, DDSNa, etc.), the effectiveness of the antifoam activity, estimated from the amount of alcohol required for the complete prevention of foam formation, increases along the homologous series with increase in the molecular mass of the alcohol (from butyl to undecyl).[9,10,55] With increase in the concentration of foam-forming agent, the maximum in the antifoam activity begins to shift towards lower homologues and finally, at the very highest concentrations, the lowest member of the series (butyl alcohol), which is fully insoluble in aqueous solution, becomes most effective.

The inversion of the antifoam activity of alcohols and the maximum in the antifoam activity corresponding to the middle homologues at 'medium' concentrations have been explained within the framework of the heterogeneous drop mechanism of the antifoam action.[10]

The effectiveness of the heterogeneous antifoam action is largely determined by two factors: the solubility of the antifoam (the lower the solubility, the sooner the heterogeneous mechanism is 'switched on') and the ability to prevent the adsorption of the foam-forming agent on the interface between the foam film and the antifoam and to destabilise thereby the asymmetric aqueous films.

The solubility of alcohols in the aqueous phase diminishes with increase in their molecular mass and the ability of the alcohols to prevent the adsorption of surfactants, which is determined by the interfacial tension on the interface between the aqueous solution of the foam-forming agent and the alcohol, decreases in the same direction.

At low concentrations of the foam-forming agent, when a minimal excess of any alcohol (relative to its solubility) is sufficient to destabilise foam films, the higher homologues are most effective. Conversely, at high concentrations of the foam-forming agent, the degree of its adsorption on the interface between the film and the alcohol drops is a maximum for the higher homologues, and it is sufficient to stabilise the asymmetric films, so that only films on supports comprising lower alcohols, for which the degree of adsorption of the surfactant is low, are unstable. This is precisely the reason why lower alcohols are the most effective. The inversion of the antifoam activity has been discussed in detail by the present author.[10,55]

In aqueous solutions with a high content of a solubilised organic phase, a marked influence of the amount of the oil on the solubility of foams is observed. By regulating the hydrophilic–lipophilic balance for the foam-forming agent by adding hydrophobic surfactants (for example, the esters of aliphatic acids and anhydrosorbitol, xylitol, and glycerol, aliphatic alcohols, acids, and amines) and also by varying the number of hydroxyethylene groups in the surfactant molecule and the electrolyte concentration, it is possible to obtain a water–oil–surfactant phase three-phase system in such solutions with high water and oil contents.[61,62] A significant increase in the stability of the foam with increase in the concentration of the oil is observed in systems of this kind already in the homogeneous micellar region. For example, the stability of the foam in a 15% solution of DDSNa with added butyl alcohol (up to 16%) decreased greatly on solubilisation of xylene: for a 20%–25% content of xylene, the foam became completely unstable.[63]

Similarly, in a foam formed from a solution of a mixture of technical alkylphenols (OP-10 and alfapol-4)[61] with an average number of hydroxyethyl groups $n = 7.8$ in the absence of an oil (kerosene), the lifetime of the foam exceeded two days, while for a kerosene content of ~20% (still in the homogeneous region) it was only 3 min. In another system,[61] water–kerosene–mixture of volgonate† and FM emulsifier‡ (concentration 30%), the lifetime of the foam fell from tens of hours when the volgonate : emulsifier concentration ratio was 4 : 1 and the kerosene content was 3.5% to 6 h for a concentration ratio of 2 : 3 and a kerosene content of 27%.

With increase in the concentration of pentyl alcohol in the system containing 1% of DDSNa, 1.75% of NaCl, and kerosene, the volume and stability of the foam fell sharply in the region of the hydrophilic–lipophilic balance close to the region corresponding to the appearance of the micellar phase of the surfactant, falling to zero on formation of this phase. The stability of the foam diminished similarly in a number of other systems on formation of the micellar phase.[62]

It is noteworthy that, also in the absence of oils, the stability of the foam is appreciably lower in this region of the hydrophilic–lipophilic balance compared with neighbouring regions. This means that not only the formation of the surfactant phase and the associated significant depletion of the aqueous solution in the surfactant, but also radical changes in the properties of the adsorption layers of the foam films are the causes of the instability of foams (and emulsions). As in many of the other cases considered above, in this instance the foam is disrupted via a mixed mechanism. The instability of asymmetric films is determined by the behaviour of the multilayer metastable foam films formed in these systems.

† Technical alkyl sulfate.
‡ Ester of oleic acid and triethanolamine.

The attenuation of the multilayer films does not take place continuously but with a discrete separation of the layers (stratification) with a thickness which is equal to (or is a multiple of) two surfactant bilayers containing a certain amount of a solubilised oil. [64] In conformity with this, the $\Pi(h)$ isotherm has an oscillating form. [65]

In nonaqueous nonpolar solutions, highly stable foams are usually obtained only in the presence of liquid crystals. [66] In such systems, water and certain other phases may be effective antifoams. The mechanism of the action of such antifoams is unknown.

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