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The Mechanism of Action of Antifoams

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Abstract: The aim of this study was to summarize the mechanisms of foam destruction by antifoams and the influence of various factors on this phenomenon. For this purpose, first the so-called bridging mechanisms together with spreading-fluid entrainment mechanism are discussed then the importance of various factors such as oil viscosity, the presence of hydrophobic particles within compound antifoams and concentration of antifoams is discussed from the viewpoint of the mechanisms of antifoaming.

Key words: Antifoams, mechanism, bridging-stretching, bridging-dewetting, spreading-fluid entrainment

INTRODUCTION

Foaming in many industrial plants might reduce the process efficiency and cause environmental problems in waste discharge. That is why various additives called antifoams or defoamers are widely used to reduce the volume of undesired foam in different technologies such as pulp and paper production, food industries, textile dyeing, gas sweetening and dehydration, waste water treatment and many separation processes^[1-3].

Antifoams or foam inhibitors are usually added to the foaming solution prior to foam formation and act to prevent formation of excessive foam. In contrast, defoamers or foam breakers are substances sprinkled over existing foam with major aim to induce rapid foam collapse. The activity of antifoam is strongly depend on entry barrier, which indicates how difficult is for predispersed antifoam entities to pierce the gas-water interface and to appear on the solution surface. However, in the case of defoamers the entry barriers is less important because the defoamers are introduced from the gas phase and there is no barrier to prevent the emergence on the gas-water interface.

A typical antifoam or defoamer consists of oil, hydrophobic solid particles or a mixture of both. Nonpolar oils (mineral oils, silicone oils) and polar oils (fatty alcohols and acids, alkyl amines, alkyl amides, tributyl phosphate (TBP), tioethers and many others) have been successfully used. The solid particle could be inorganic (silica, Al₂O₃, TiO₂), wax (e.g. Mg stearate) or polymeric (e.g. poly amides, poly propylene)^[3].

The aim of this study is to summarize our current understanding of the mechanism of the foam destruction by such substances and the influence of various factors on this phenomenon.

MARANGONI EFFECT

Near the end of the nineteenth century, Gibbs and Reyleigh^[4] point out independently that even under isothermal conditions, a surface active solute might create a surface tension gradient by the variation of excess surface concentration of the solute as the solution flows, for whatever cause. One such cause is the action of gravity on a liquid film; another is the Laplacean suction exerted by a difference in curvature of Plateau borders. The gradient in surface produces a motion of the liquid surface from region of low to a region of higher surface tension, a phenomenon known as the Marangoni effect^[5]. The motion of the surface drags underlying liquid along with it and so offsets the thinning of the liquid film.

If someone touches a bubble with finger, it will break. This little every day experience of a defoamer is in fact Marangoni effect. Remember that the surface tension of a liquid also measure its Helmholtz free energy. The skin of the finger introduces a gradient of surface energies: the skin with its low surface energy, which is the result of a natural exudation, can not be covered by higher surface energy of the aqueous solution, which withdraws spontaneously (dewets) and in so doing ruptures the bubble. The thermodynamic reason is that the free energy change at the interface is negative. The same dewetting

action can be obtained by means of solid particles of low surface energy such as hydrophobic silica.

Early workers ascribed the foam-inhibiting action of insoluble droplets to their ability to spread on the surface of foamable solutions and so destroy lamella as soon as they form. Robinson and Woods^[6] ascribed the foam-inhibiting effect to an entering coefficient which turned out to have exactly the same criterion as that for the dewetting of droplets by withdrawal of the profoaming solution. These suggested mechanisms of foam-inhibiting action depend on the motion of surfaces, either the spreading of a liquid foam inhibitor or the withdrawing of the solution from a low-energy solid or liquid surface. Any liquid motions that depend on gradients of surface energy are Marangoni effects.

ANTIFOAMING MECHANISMS

Hydrophobic solid particles: The foam breaking efficiency of solid particles is mainly determined by their hydrophobicity, quantified by the value of the contact angle (α_{AW}). It was shown experimentally that hydrophobic particles can rupture the foam film by the so-called bridging-dewetting mechanism^[3,7-11]. This mechanism implies that first the solid particle comes in contact with two opposite surfaces of the foam film,

forming solid bridge between them (Fig. 1). If the particle is sufficiently hydrophobic (α_{AW} is greater than a certain critical value), it is dewetted by the liquid and the three phase contact lines eventually come in direct contact with each other and the foam film gets perforated at the particle surface.

Various theoretical and experimental studies^[7,10-12] showed that the critical contact angle is 90° for complete dewetting of solid particles which have smooth convex surfaces, sphere, ellipsoid, disks and rods. Particles of contact angle 90° induce foam film rupture and collapse. Less hydrophobic smooth particles ($\alpha_{AW} > 90^\circ$) do not cause foam film rupture and they can even stabilize the foam by blocking the Plateau channels and reducing the rate of water drainage from the foam. Interestingly, some experiments showed that foam film rupture can be induced by less hydrophobic particles (α_{AW} well below 90°) if they have sharp edges and are properly oriented in the foam film^[9].

At α_{AW} below critical contact angle as the film drains, it attains a critical thickness where the film is planar and capillary pressure becomes zero. At this point, further drainage reverses the sign of the radii of curvature causing an unbalanced capillary force which prevents drainage occurring.

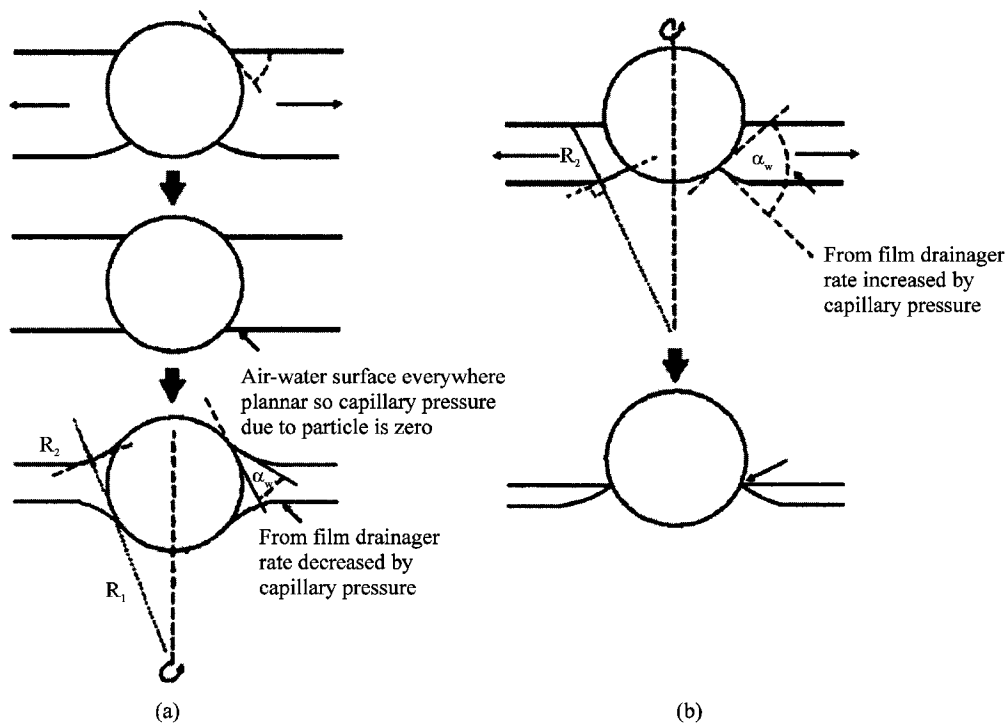


Fig. 1: Schematic presentation of the bridging of foam film surfaces by spherical smooth solid particle (a) $\alpha_{AW} < 90^\circ$ (b) $\alpha_{AW} > 90^\circ$

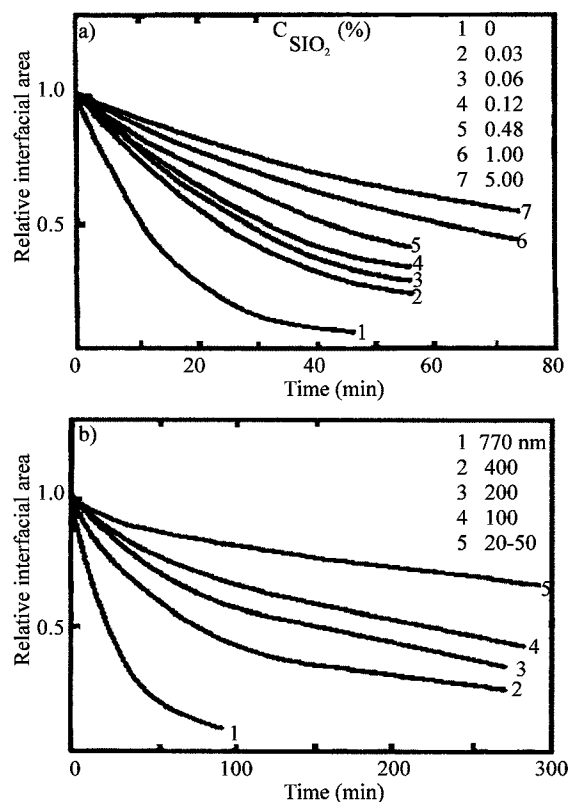


Fig. 2: Stabilization of foam with silica particles (hydrophobized with tetraethylorthosilicate treatment). (a) Influence of concentration of SiO₂ particles on foam stability. (b) Effect of particle size of hydrophobic SiO₂ particles on foam stability. The foam was produced by sodium dodecyl sulphonate in alkaline

Usually, the lower the concentration of particles and the larger the particle size, the more effective the antifoaming mechanism. Fang *et al.*^[13] demonstrated this effect for monodispersed silica particles with diameters ranging from 20 to 70 nm (Fig. 2). In the present study it was suggested that the particles may cause a decrease in surface tension but a change in viscosity was not detected. There exists a possibility that the tightly packed adsorbed layer can slow down the gas diffusion process.

In surfactant solutions of concentration around and above the cmc, high contact angles for particles were difficult to achieve and it was preferential to use rough shaped particles which gave sharp angles^[14].

Oil based antifoams: The synergistic antifoaming effect of mixtures of oil and hydrophobic solid particles (typically 2-6 wt.% solid) when dispersed in aqueous medium has been well establish in the patent literature from early

1950s. Such mixture of oil and particles are usually termed antifoam compounds.

The optical observations show that two types of antifoam entities are usually present in foamy solutions and play a role in foam destruction^[15]: (i) antifoam globules dispersed in the bulk and (ii) lenses floating on the solution surface. Often a layer of oil is present on the solution surface and could be also important for the foam action. Sometimes the antifoam globules enter the surfaces of the foam films and destroy these films soon after globule entry^[3]. Moreover the antifoam globules may first escape from films into the neighboring Plateau borders and get trapped there^[16]. According to this mechanism antifoam globules are compressed by walls of shrinking Plateau borders (as a result of water drainage from the foam) and eventually the globules enter the walls of Plateau borders causing rupture of the neighboring foam films (Fig. 3).

Essentially three different film destruction mechanisms have been proposed for the oil based antifoams:

Bridging-stretching mechanism: The experiments with foam films in the presence of antifoams^[17] showed that a biconcave oil bridge was formed in the foam lamella, with the thinnest region being in the bridge center (Fig. 4). The stretching of this bridge in a radial direction as a result of uncompensated capillary pressures at the oil-water and gas-water interfaces led to the eventual formation of a thin unstable oil film in the bridge center. The rupture of this oil film resulted in the perforation of the entire foam lamella. This mode of foam film rupture was termed the bridging stretching mechanism. An important requirement for realization of this mechanism is the possibility for deformation of the antifoam globule. That is why this mechanism can not be realized with hydrophobic solid particles.

Bridging-dewetting mechanism: Once an oil bridge is formed between the two surfaces of the foam film, this bridge is dewetted by the aqueous phase due to the hydrophobic surface of the oily globule. This idea was suggested^[3,18] in analogy with bridging-dewetting mechanism which was observed with hydrophobic solid particles^[9]. In contrast with hydrophobic solid particles, when the antifoam globule is deformable (oil drop or oil-olid mixture with large excess of oil), it acquires a lens shape after the first entry on one of the film surfaces (Fig. 5C). Simple geometrical consideration shows^[3] that such a lens can be dewetted by the opposite foam film surface, in the moment of bridge formation, if no significant change of the lens shape takes place during dewetting, (Fig. 5D and E).

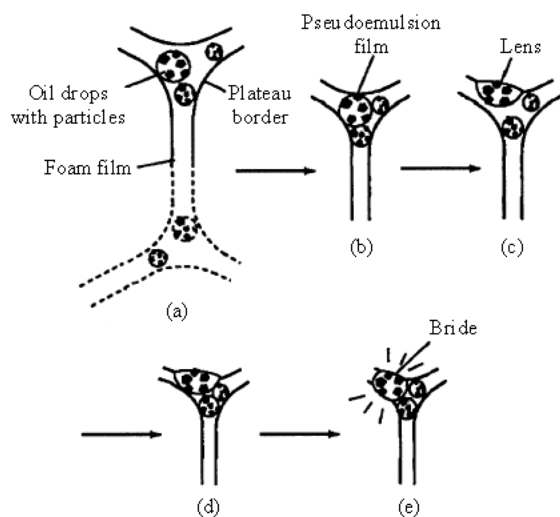


Fig. 3: Suggested antifoaming mechanism for mixed type antifoam: (a) oil drops (containing solid particles) collect in the Plateau border; (b) they become trapped in the thinning border; (c) the pseudo-emulsion film breaks and a drop enters and forms a solid + oil lens; (d) the lens becomes trapped during thinning; (e) the lens bridges the film at the Plateau border and the bridge

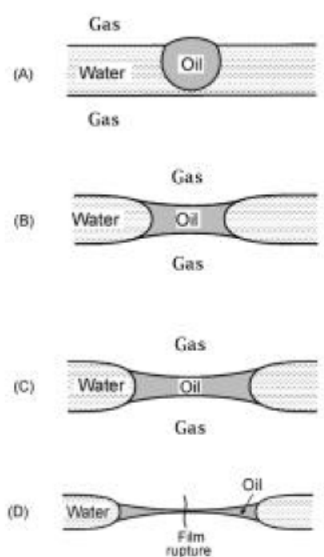


Fig. 4: Bridging-stretching mechanisms of foam film rupture. (A-B) Bridging of the foam film surfaces by antifoam globule leads to an oil bridge with non-balanced capillary pressures at the oil-water and gas-water interfaces. (C-D) The bridge stretches with time until a thin, unstable oil film is formed in the bridge center. The rupture of this oil film leads to destruction of the entire foam lamella

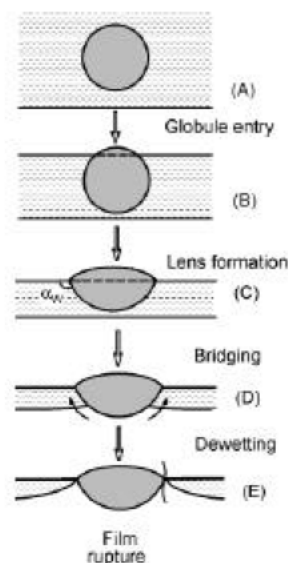


Fig. 5: Rupture of foam operating through film bridging-dewetting mechanism. The oil drop first enters one of the film surfaces and forms a lens. On further thinning of the film the lens enters the opposite film surface and an oil bridge is formed. The bridge is unstable because the capillary forces dewet the film from the bridge and the film ruptures. The arrows in the film indicate the direction of capillary forces

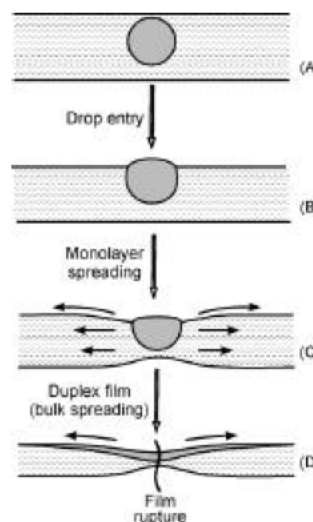


Fig. 6: Schematic presentation of the spreading-fluid entrainment mechanism of foam film rupture: an antifoam globule enters the foam film surface (A-B). The oil spreading is assumed to cause a Marangoni-driven flow of water, directed radially from the oil lens, which leads to local thinning of the foam film and its eventual rupture (C-D)

Spreading-fluid entrainment mechanism: One of the classical mechanisms for film destruction relies on the Marangoni-driven flow (fluid entrainment) produced by oil spreading along gas film interface^[3,19]. The basic idea is that when a monolayer of oil spreads over the surface of a film, it drags subsurface fluid with it, causing local film thinning which can rupture the film (Fig. 6). Assuming equilibrium values of the surface tensions, this radial spreading behavior can be described^[20,21]:

$$r = kt^{3/4}$$

$$k = \left(\frac{4S}{3\rho^{1/2}\mu^{1/2}} \right)^{1/2} \quad (1)$$

where, r is radius of the spreading monolayer, ρ the density of subsurface fluid, μ the viscosity of the subsurface fluid, t is the time and S the spreading coefficient. Important to antifoaming action is the penetration depth of the subsurface flow, $m = \sqrt{\rho/\mu t}$, predicted by the model. This depth must be on the order of the foam film thickness before a spreading layer can influence film thinning and/or rupture.

Requirements of the oil based antifoams: First and foremost the antifoaming globules must enter the gas-water interface to have an effect on the foam film. The key thermodynamic quantity that expresses the necessary conditions for this to occur is called the entering coefficient, $E^{[6]}$, which is similar to the spreading coefficient, $S^{[22]}$. Both quantities are simply determined from the interfacial tensions in the system:

$$E = \sigma_{gw} + \sigma_{ow} - \sigma_{go} \quad (2)$$

$$S = \sigma_{gw} - \sigma_{ow} - \sigma_{go} \quad (3)$$

where, σ_{ij} corresponds to the surface or interfacial tension and the subscript o , w and g signify oil, water and gas respectively. For a positive E , oil penetrates the gas-water interface from aqueous side while a negative S implies that the oil droplet will form oil lenses (for a positive or zero S oil spreads over the gas-water interface). Situations where, $S > 0$ are necessarily transient. They arise because the relevant influences are not at mutual equilibrium. Thus, if initially $S > 0$ then we find, after equilibrium, formation of either a stable duplex film (where, $S = 0$ at equilibrium) or a thin liquid film in equilibrium with an oil lens (where, $S < 0$ at equilibrium). This causes some ambiguity in assessing the relevance of transient spreading in antifoam action. The process will depend on the relevance of the pre-equilibrated interfacial tensions.

Irrespective of such ambiguity, it seems probable, however that reduction of oil-gas surface tensions so that $S > 0$ will, if anything, produce enhanced effectiveness relative to situations where, $S < 0$.

Antifoams with positive E may bridge aqueous foam films. Such bridging lenses are necessarily unstable provided the condition:

$$B = \sigma_{gw}^2 + \sigma_{ow}^2 - \sigma_{go}^2 > 0 \quad (4)$$

is satisfied; where, B is the so-called bridging coefficient first formulated by Garret^[7]. To assess the bridge stability, Garrett assumed that the Neumann triangle was satisfied at the three phase contact lines oil-water gas and then he checked whether the capillary pressure jumps across the oil-gas and oil-water interfaces can be balanced. His analysis showed that if α_w , the angle formed between the gas-water and oil-water interfaces at there phase contact line (Fig. 5C), is larger than $\pi/2$ the capillary pressure across the oil-water interface is always smaller than the capillary pressure across the oil-gas interface. This means that it is impossible to satisfy simultaneously the Neumann triangle and the capillary pressure balance which are both necessary conditions for mechanical equilibrium in the system. Therefore the oil bridge was considered unstable. If $\alpha > \pi/2$ then it is easy to show that $B > 0$ ^[3]. It can also be proven mathematically that positive value of bridging coefficient guarantees positive entry coefficient, however the reverse is not true. When the bridging coefficient of an oil lens is positive, any axial contraction along its axis of symmetry (due to local transient decrease of the foam film thickness in the bridge region) would lead to increase of the equatorial radius of the bridge. As a result, the capillary pressure balance across the oil-water and gas-oil interface is violated and a process of spontaneous expansion of the equatorial radius of the bridge is induced. This expansion continues until a thin oil layer is formed in the center of the bridge which eventually ruptures perforating in this way the entire foam film.

Both mechanisms of bridging-stretching and bridging-dewetting are in principle possible, if the bridging coefficient is positive and which of three mechanisms would be realized, in a given system, depends on the relative velocities of lens dewetting and lens deformation. The process of bridge dewetting is probably much faster than the process of bridge stretching and a bridging-dewetting mechanism is more probable for viscous oils because the low oil viscosity favors the lens deformation, which is the configuration corresponding to the bridging-stretching.

The experiments^[15,17,23] show that there is no direct relation between the magnitudes of the entry, E, spreading, S and bridging, B, coefficients, on one side and the antifoam efficiency, on the other side. The only requirement for having active antifoam, with respect to the bridging mechanisms, is that B should be positive. On the other hand, the barrier preventing the emergence of pre-emulsified antifoam globules on the solution surface (so-called entry barrier) is of crucial importance for the mode of foam destruction and for the antifoam efficiency. Measurements of the entry barrier show that antifoams possessing low entry barriers act as effective antifoams, where low barriers correspond to inactive antifoams. Entry barrier is important for the emergence of the pre-emulsified antifoam globules on the gas-water interface and also for the formation of an oil bridge from a lens, which initially floats on one of the film surfaces.

EFFECTS OF VARIOUS FACTORS ON ANTIFOAMING

Viscosity: The spreading of the monolayer film in precursor film spreading is associated with the kinetics of disentanglement of the oil molecules from the bulk macroscopic oil drop. At high oil based antifoams viscosity, dislodging the oil molecules from the bulk oil becomes the rate limiting steps in the precursor film

spreading process ($r \propto \mu^{1/4}$) and dynamic non-equilibrium oil bridges are more possible, that is lenses which bridge the film before the bulk oil has had a chance to spread^[23]. This type of dynamic bridge can occur when the combined-bridging and pinch-off time is faster than the bulk oil spreading, or in systems that display pseudo partial wetting behavior. The former situation may occur when the oil viscosity is rather high and larger than that of the aqueous surfactant solution. When non-equilibrium bridges are formed pinch-off and oil spreading as a precursor film will occur at the same time and act synergistically to destroy the films.

It is noticeable that more viscous oils retain a drop-size distribution that is enriched with larger drops. This is due to large energy requirement needed to deform and break the more viscous oil^[24]. On the other hand a significant loss of antifoam performance correlates only with antifoam globules size reduction over the time of action, because wetting coefficients (E, S and B) after the systems lose their antifoam performance are not changed significantly from their initial values. The size decrease is caused by continued emulsification of the oil upon agitation and break up of thin oil layers spread on the film.

Hydrophobic particles: Hydrophobic particles added to the oil destabilize the pseudo-emulsion film separating the oil droplet from the gas and accelerate the crucial drop

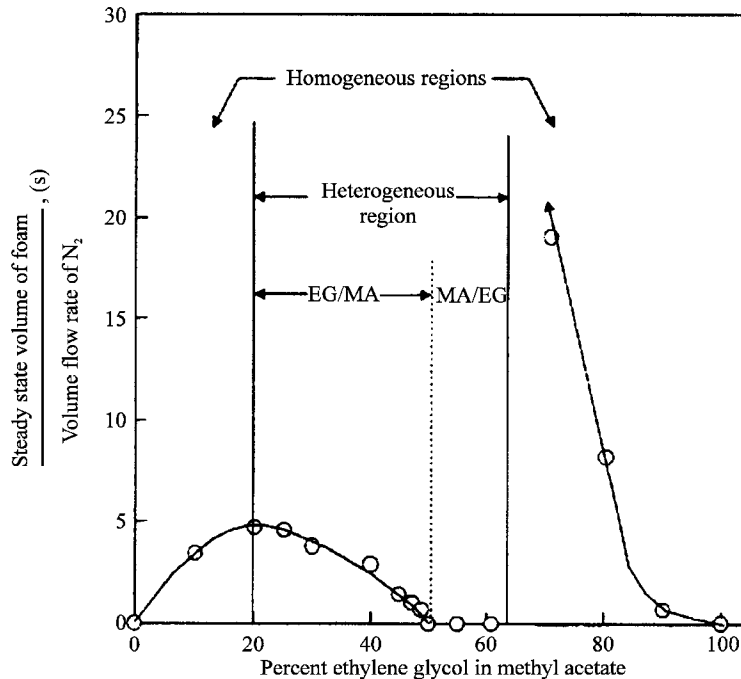


Fig. 7: The Ross-Nishioka effect in a two-component system at 20°C (methyl acetate and ethylene glycol). As the solutions approach a phase boundary, bubble stability increases, until phase separation create a foam inhibitor

entry step^[3,8] and increase the penetration depth of oil lenses^[15,16,18]. Video microscopy of pseudo-emulsion film thinning as antifoam globules approach the gas-water interface revealed that particles located at the oil-water interface produce irregularities at this surface which pierce the film and facilitate drop entry^[23]. The resulting increase in the drop entry rate is one of the main factors leading to increased antifoam performance of particle doped oils. In addition, particles increase the effective viscosity of the oil which helps prevent excessive emulsification and size reduction.

Concentration of antifoam: The discovery of the incidence of capillarity (i.e. various manifestations of surface activity) in systems described by certain defined locations within phase diagrams was first made by Ross and Nishioka^[25]. The characteristic of this effect, particularly in systems of two components or more whose phase diagram contain a region of partially miscible liquids, is the gradual growth of the surface activity of solutions as their compositions approach the limits of their separation into two phases. On the nucleation of the conjugate solution, however the increasing foaminess of the solutions, a reflection of their increasing surface activity, is replaced by a dramatic break to zero foam stability. In fact the insoluble conjugate liquid of lower surface tension, once nucleated, acts as an inhibitor of foam (Fig. 7). Therefore, antifoaming effects will result only when the solubility limit exceeded and separated conjugate phase has surface energy low enough to be dewetted by the medium.

It was demonstrated experimentally^[26,27] that a given oil antifoam usually increases foaminess when added at concentrations below and around its solubility limit (the reduced surface tension is more important than the antifoam effect at these concentrations), whereas the same oil could significantly suppress foaming when added at higher concentrations which is present in the form of dispersed oil drops. This phenomenon is consistent with Ross-Nishioka effect.

CONCLUSIONS

In this study the mechanism of action of antifoams and the mode of foam destruction by antifoams were discussed. First the hydrophobic solid particles were investigated and then mechanisms of action of oil based antifoams were explored. In the course of study on the oil based antifoams bridging-stretching, bridging-dewetting and spreading-fluid entrainment mechanisms were discussed in details. Eventually the effect of factors such

as oil viscosity, presence of hydrophobic solid particles within compound antifoams and concentration of antifoams on the antifoam performance were explained.

REFERENCES

1. Exerowa, D. and P.M. Kruglyakov, 1998. Foams and Foam Films: Theory, Experiment, Application. Elsevier, Amsterdam.
2. Abdolahi, F. and A. Vatani, 2004. Unstable operation in an acetaldehyde purification tower. Chem. Eng. Technol., 27: 1027-1029.
3. Garrett, P.R., 1993. Defoaming: Theory and Industrial Applications. Marcel Dekker, New York.
4. Gibbs, J.W., 1906. Scientific Papers of J. Willard Gibbs: Thermodynamics, Vol. 1, Longmans Green and Co., London, pp: 229-231.
5. Marangoni, C., 1872. Il Nuovo Cimento Ser., 2: 239.
6. Robinson, J.V. and W.W. Woods, 1946. A general method of selecting foam inhibitors. National Advisory Committee for Aeronautics, Technical Note No. 1026, Washington.
7. Garrett, P.R., 1980. Preliminary consideration concerning the stability of a liquid heterogeneity in a plane-parallel liquid film. J. Colloid Interface. Sci., 76: 587-590.
8. Garrett, P.R., J. Davis and H.M. Rendall, 1994. An experimental study of the antifoam behavior of mixtures of a hydrocarbon oil and hydrophobic particles. Colloid Surfaces A: Physicochemical and Engineering Aspects, 85: 159-197.
9. Dippenaar, A., 1982. The destabilization of froth by solids, I. The mechanism of film rupture. Intl. J. Mineral Process, 9: 1-14.
10. Aveyard, R., B.D. Beake and J.H. Clint, 1996. Wettability of spherical particles at liquid surfaces. J. Chem. Soc. Faraday Trans., 92: 4271-4277.
11. Aveyard, R. and J.H. Clint, 1995. Liquid droplets and solid particles at surfactant solution interfaces. J. Chem. Soc. Faraday Trans., 91: 2681-2697.
12. Aveyard, R., P. Cooper, P.D.I. Fletcher and C.E. Rutherford, 1993. Foam breakdown by hydrophobic particles and Nonpolar oil. Langmuir, 9: 604-613.
13. Fang, Q., X. Zheng, T. Ji-an and J. Long, 1989. The effect of SiO₂ particles upon stabilization of foam. J. Colloid Interface Sci., 131: 498-502.
14. Frye, G.C. and J.C. Berg, 1989. Antifoam action by solid particles. J. Colloid Interface Sci., 127: 222-238.
15. Denkov, N.D., 1999. Mechanisms of action of mixed solid-liquid antifoams. 2. Stability of oil bridges in foam films. Langmuir, 15: 8530-8542.

16. Koczo, K., J.K. Koczona and D. Wasan, 1994. Mechanisms for antifoaming action in aqueous systems by hydrophobic particles and insoluble liquids. *J. Colloid Interface Sci.*, 166: 225-238.
17. Denkov, N.D., P. Cooper and J. Martin, 1999. Mechanism of action of mixed solid-liquid antifoams. 1. Dynamics of foam film rupture. *Langmuir*, 15: 8514-8529.
18. Frye, G.C. and J.C. Berg, 1989. Mechanisms for the synergistic antifoam action by hydrophobic solid particles in insoluble liquids. *J. Colloid Interface Sci.*, 130: 54-59.
19. Ross, S., 1950. Inhibition of foaming II. A mechanism for the rupture of liquid films by antifoam agents. *J. Phys. Colloid Chem.*, 54: 429-436.
20. Bergeron, V. and D. Langevin, 1996. Monolayer spreading of polydimethylsiloxane oil on surfactant solutions. *Phys. Rev. Lett.*, 76: 3152-3155.
21. Fay, J.A., 1969. The Spread of Oil Slicks on a Calm Sea. In *Oil on the Sea*. Ed. by Hoult, D.P., Plenum Press, New York, pp: 53-56.
22. Harkins, W.D., 1941. A general thermodynamic theory of the spreading of liquids to form duplex films and of liquids or solids to form monolayers. *J. Chem. Phys.*, 9: 552-568.
23. Bergeron, V., P. Cooper, C. Fischer, J. Giermanska-kahn, D. Langevin and A. Pouchelon, 1997. Polydimethylsiloxane (PDMS)-based antifoams. *Colloid Surfaces A: Physicochemical and Engineering Aspects*, 122: 103-120.
24. Clift, R., J.R. Grace and M.E. Weber, 1978. *Bubbles, Drops and Particles*. Academic Press Inc., New York, pp: 321-325.
25. Ross, S. and G. Nishioka, 1975. Foaminess of binary and ternary solutions. *J. Phys. Chem.*, 79: 1561-1565.
26. Kruglyakov, P.M. and T.A. Koretskaya, 1974. Inversion of antifoam ability in the fatty alcohol series. *Kolloidn. Zh.*, 36: 627-634.
27. Arnaudov, L., N.D. Denkov, I. Surcheva, P. Durbut, G. Broze and A. Mehreteab, 2001. Effects of oily additives on the foamability and foam stability. 1. Role of interfacial properties. *Langmuir*, 17: 6999-7010.