DEFOAMERS

1. Introduction

The control or elimination of the foam that occurs in many industrial processes is a vital factor in their efficient operation. Additives for this pupose are the largest single category of process aids used in the chemical industry (1). They are used in low concentration to achieve this effect and are known variously as defoamers, antifoaming agents, foam inhibitors, foam supressants, air release agents, and foam control agents. Defoaming implies breaking a preexisting foam whereas antifoaming or foam inhibition indicates prevention of the formation of that foam. Such distinctions call for different product features. A defoamer is expected to exhibit rapid knockdown of a foam, whereas longevity of action might be the key requirement in many antifoam applications. Despite these varying performance features, many applications require both preventive and control functions, and in practice the same types of materials are used both for antifoaming and defoaming. For this reason, the general term defoamers, as used in this article, is meant to encompass all product types and degrees of action encountered with such process aids. The topic is sometimes known as chemical or physicochemical foam control as opposed to thermal and mechanical foam control approaches, such as centrifuging or spraying of the foam or the use of ultrasound, which are not covered here.

Many industries rely on the efficient and economical use of defoamers both as a process aid in product manufacture and to increase the quality of the finished product in its subsequent application. The most obvious use of defoamers as process aids is to increase holding capacity of vessels and improve efficiency of distillation or evaporation equipment. They are also used to improve filtration,

dewatering, washing, and drainage of suspensions, mixtures, or slurries. Examples of industrial operations that benefit in these ways from the use of defoamers include oil well pumping; gas scrubbing at petrochemical plants; polymer and chemical synthesis and processing, particularly in monomer stripping; textile dyeing and finishing; leather processing; paint and adhesive manufacture; phosphoric acid production; control of wastewater and sewage; food preparation, notably the refining of sugar; the brewing of beer; and penicillin production by fermentation. Among the finished products that are improved in quality or efficacy by the proper inclusion of defoamers are lubricants, particularly cooling lubricants in metal working; diesel fuel, hydraulic and heat-transfer fluids; paints and other coatings; adhesives; inks; detergents; and antiflatulence tablets.

The use of vegetable and mineral oils as defoamers has been known for a long time. However, most modern defoamers are complex, formulated specialty chemicals, whose composition is often proprietary. Numerous reviews of the field have appeared since the previous edition of this article, notably the comprehensive book on the subject by Garrett (2). Other useful reviews include some on foam control principles (3–5) coatings applications (6) and silicones (7,8) Companies involved in the production of defoamers range from large, basic polymer producers to small regional formulators. In addition to control of foam and associated features such as rate of foam knockdown and the persistence of the effects, other frequently needed application requirements of these specialty materials include adequate shelf life, absence of adverse effects on and by the products being treated, ease of handling, lack of toxicity to manufacturing personnel and users, environmental acceptability, and cost-effectiveness. Defoamers range from relatively inexpensive mineral oils to costly fluorinated polymers but it is not the cost per kilogram of defoamer that matters, but rather the cost per unit produced using this processing aid. Another factor that strongly influences the choice of a specific defoamer is its ancillary surface properties such as wetting, dispersion, and leveling.

2. Defoamer Components

Modern defoamers contain numerous ingredients to meet the diverse product requirements for which they are formulated, including a variety of active ingredients in both the solid and liquid states and numerous ancillary agents such as emulsifiers, spreading agents, thickeners, preservatives, carrier oils, compatibilizers, solvents, and water. Not all defoamers contain all classes of components; some complex formulations contain several different materials in a particular category.

2.1. Active Ingredients. These are the components of the formulation that do the actual foam control work. Traditionally, defoamers were single component liquids or homogeneous solutions of vegetable or mineral oils, but nowadays hydrophobic solids are the most effective active ingredients.

Liquid-Phase Components. The four most common liquid-phase components found in defoamers are hydrocarbons, polyethers, silicones, and fluorocarbons.

Many hydrocarbon fluids such as kerosene and other paraffinic and naphthenic mineral oils and vegetable oils such as linseed oil [8001-26-1], corn

oil, soybean oil [8001-22-7], peanut oil, tall oil [8000-26-4], and castor oil [8001-79-4], are used as defoamers. Liquid fatty alcohols, acids and esters from other sources and poly(alkylene oxide) derivatives of oils such as ethoxylated rosin oil [68140-17-0] are also used. Organic phosphates are valuable defoamers and have particular utility in latex paint applications. Another important class of hydrocarbon-based defoamer is the acetylenic glycols (9), such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol, which are widely used in water-based coatings, agricultural chemicals, and other areas where excellent wetting is needed.

Among other organic polymers that have been proposed as foam control agents are polyisobutylene [9003-27-4], poly(alkyl acrylates), polyalkylene polyamines, and polyalkyleneimines. Poly(alkylene oxide) homopolymers and copolymers are frequently encountered in liquid-phase antifoam components. For example, copolymers [106392-12-5] of poly(ethylene oxide) and poly(propylene oxide) are used to reduce foam in the acid-gas scrubbing process (10). High molecular weight adducts of propylene oxide and polyhydric alcohols such as glycerol [56-81-5] and pentaerythritol [115-77-5] have also been reported to have useful antifoaming properties (11). Sometimes the polyether is mixed with other liquids, eg poly(propylene oxide) [25322-69-4] and polydimethylsiloxane [9016-00-6]; sometimes the two materials are copolymerized.

Silicone oils are particularly effective antifoaming agents in nonaqueous systems because of their low surface tension and incompatibility. Polydimethylsiloxane (PDMS) is the most important silicone and is widely used in products for the petroleum industry, where its good thermal stability is very advantageous (12). Other useful silicone defoamers are polytrifluoropropylmethylsiloxanes [25791-89-3] and other fluorosilicones, which are very effective in nonaqueous foaming systems such as organic solvents and crude hydrocarbon stocks.

Fluorocarbons are the most expensive class of antifoam fluid. Fluorocarbon oils and fluorine-containing amides such as the *N*-(alkylamino-trimethylene)-perfluoro-octanamides are used as antifoaming additives to lubricants and jet fuels (13).

Solid-Phase Components.   Dispersed solids are vital ingredients in commercial antifoam formulations. Much of the current theory on antifoaming mechanism ascribes the active defoaming action to this dispersed solid phase with the liquid phase primarily a carrier fluid, active only in the sense that it must be surface-active in order to carry the solid particles into the foam films and cause destabilization. For example, PDMS, despite its considerable effectiveness in nonaqueous systems, shows little foam-inhibiting activity in aqueous surfactant solutions. It is only when compounded with hydrophobic silica [7631-86-9] to give the so-called silicone antifoam compounds that highly effective aqueous defoamers result. The three main solid-phase component classes are hydrocarbons, silicones, and fluorocarbons.

A variety of waxy hydrophobic hydrocarbon-based solid phases are used including fatty acid amides and sulfonamides, hydrocarbon waxes such as montan wax [8002-53-7], and solid fatty acids and esters. The amides are particularly important commercially. One example is the use of ethylenediamine distearamide [110-30-5] as a component of latex paint and paper pulp black liquor defoamer (14). Hydrocarbon-based polymers are also used as the solid components of antifoaming compositions; examples include polyethylene [9002-88-4], poly(vinyl chloride) [9002-86-2], and polymeric ion-exchange resins.

In most cases, these active defoaming components are insoluble in the defoamer formulation as well as in the foaming media, but there are cases that function by the cloud-point mechanism (15). These products are soluble at low temperature and precipitate when the temperature is raised. When precipitated, these defoamer-surfactants function as defoamers; when dissolved, they may act as foam stabilizers. Examples of this type are the block polymers of poly(ethylene oxide) and poly(propylene oxide) and other low hydrophilic–lipophilic balance (HLB) nonionic surfactants. The use of soluble foam control agents has increased in recent years (7).

Pure silicone solids, such as silicone resins, are used in defoamer formulations, but the key material in this category is surface-treated silica, made hydrophobic by treatment with a silicone polymer or silane monomer. The development of these hydrophobic silicas (16) is widely acknowledged as one of the most significant advances in antifoam technology. They are used with a considerable variety of liquid components including hydrocarbons, polyethers, and silicones. The three most common ways of preparing the hydrophobic silica are to spray the silica with silicone oil and heat at 250–350°C, to treat with organochlorosilane vapors in an autoclave, and to disperse the silica in a silicone oil at elevated temperatures. Hydrophobic silica can also be produced by treatment with alcohols, fatty amines, and hydrocarbon waxes. The application of hydrophobic silica formulations as antifoaming agents has been reviewed with an emphasis on mechanism and use in textile dyeing (17).

Fluorocarbon solids are rare in defoamer compositions, presumably on account of their cost. Solid fluorine-containing fatty alcohols and amides are known. The most familiar fluorocarbon solid is polytetrafluoroethylene [9002-84-0]. It is not very effective in conventional hydrocarbon oil defoamer formulations because the particles aggregate strongly together, but in lower surface tension fluids such as silicone and fluorocarbon oils, the powdered polytetrafluoroethylene particles are much better dispersed and its performance is better (18).

2.2. Ancillary Agents. *Surface-Active Materials.* The active defoamer components are necessarily surface active materials, but this ancillary category covers the surfactants that are often incorporated in the formulation for other effects such as emulsification or to enhance dispersion. Emulsifiers are essential in the common oil-in-water emulsion systems but they are also required where mixtures of active liquid components are used. For example, specialized oil-in-oil emulsifiers are needed in defoamers based on silicone–polyether mixtures. Oil-in-water emulsifiers are incorporated in some defoamers even when the final product contains no water, to promote emulsification (self-emulsifiable) or dispersion into aqueous foaming systems. These additives increase the speed of foam decay by promoting rapid dispersion of the defoamer throughout the foaming media. Examples of emulsifying agents used in defoamer compositions are fatty acid esters and metallic soaps of fatty acids; fatty alcohols and sulfonates, sulfates and sulfosuccinates; sorbitan esters; ethoxylated products such as ethoxylated octyl or nonylphenols; and silicone-polyether copolymers.

Carriers. The function of the carrier is to provide an easily handleable, readily dispersible system for delivering the active defoamer components to the foaming system and also to tie the complex defoamer formulation together, ie, coupling agents, compatibilizers, or solubilizers. Sometimes the carrier is used

simply as an extender to lower the cost of the final product. Many of the low viscosity organic solvents that are used also exhibit some antifoaming properties in cases where they are both insoluble and of lower surface tension than the medium to which they are applied. Any of the usual paraffinic, naphthenic, aromatic, chlorinated, or oxygenated organic solvents can be used, but aliphatic hydrocarbons are the most common. Water is often used as a carrier fluid. In these cases, the defoamer product is typically an oil-in-water emulsion. With growing concern over unrecovered solvents, this has become a preferred type of defoamer formulation. Such products usually require preservatives to prevent bacterial spoilage in storage.

Sometimes the defoamer is required in a solid form; eg, to be suitable for incorporation into a low-sudsing detergent powder or agricultural chemical composition. Water soluble inorganic sorbent carriers such as sodium sulfate [7757-82-6], sodium carbonate [497-19-8], or sodium tripolyphosphate [7758-29-4] are used as well as organic polymers such as methylcellulose [9004-67-5]. Sometimes the particles are further encapsulated with a coating that preserves the integrity of the defoamer formulation in storage with the detergents but allows disruption on contact with water in the wash process. When both the antifoam and the solid support are food-grade materials, they can also be used in food processing, brewing, and pharmaceutical applications.

3. Commercial Sources

The defoamer market is large and very specialized; suppliers differ markedly in orientation and in range of product lines. Some suppliers are large, international, polymer producers with a basic manufacturing capability for the specific type of defoamer material they supply, whereas others are small, often regional, formulators who focus on the concerns of particular industries. The diversity of manufacture, supplier, product type, and application makes it impossible to present a comprehensive listing of commercial sources. Compilations such as McCutcheon's (19) are a useful source of available products. Table 1 shows significant defoamer suppliers (over five listings) in this compilation, together with one or two of their associated trade names.

4. Defoaming Theory

Foams are thermodynamically unstable. To understand how defoamers operate, the various mechanisms that enable foams to persist must first be examined. There are four main explanations for foam stability: (*1*) surface elasticity; (*2*) viscous drainage retardation effects; (*3*) reduced gas diffusion between bubbles; and (*4*) other thin-film stabilization effects from the interaction of the opposite surfaces of the films.

The stability of a single foam film can be explained by the Gibbs elasticity E, which results from the reduction in equilibrium surface concentration of adsorbed surfactant molecules when the film is extended (20). This extension produces an increase in equilibrium surface tension that acts as a restoring

Table 1. **Commercial Defoamer Examples**

Supplier	Trade name
Air Products and Chemicals Inc.	Surfynol
Akzo Nobel Chemicals Inc.	Propomeen
Ashland Chemical Co.	Drewplus
BASF Corp.	Mazu, Pluronic
Calgene Chemical Inc.	Calgene antifoam
Creanova Inc.	Serdas
Clariant Corp.	Antimussol, Fluowet
Dow Corning Corp.	Dow Corning antifoam
GE Co.	AF
Graden Chemical Co. Inc.	Rexfoam
Harcros Chemicals Inc.	Harcros antifoam
Henkel Corp.	Foamaster
Huntsman Corp.	Jeffox
ICI Surfactants	Synperonic
Lambent Technologies Inc.	Lambent
Olin Corp.	Poly-Tergent
OSi Specialties, a Crompton Business	Sag
Patco Defoamers Additives	Patcote
Rhone-Poulenc Corp.	Fleetcol, Foamex
Ross Chemical Inc.	Foam blast
Taylor Chemical Co. Inc.	Taylor antifoam
Trans-Chemco Inc.	Trans
Troy Corp.	Troykyd defoamer
Ultra Additives Inc.	Dee Fo, foam ban

force. The Gibbs elasticity is given by equation 1 where σ is surface tension and A is surface area of the film.

$$E = 2A d\sigma/dA \qquad (1)$$

In a foam, where the films are interconnected the related time-dependent Marangoni effect is more relevant. A similar restoring force to expansion results because of transient decreases in surface concentration (increases in surface tension) caused by the finite rate of surfactant adsorption at the surface. Such nonequilibrium surface tension effects are best described in terms of dilatational moduli. The complex dilatational modulus ε^* of a single surface is defined in the same way as the Gibbs elasticity as in equation 2 (the factor 2 is halved as only one surface is considered).

$$\varepsilon^* = A d\sigma/dA \qquad (2)$$

In a dilatational experiment, where the surface is periodically expanded and contracted, ε^* is a function of the angular frequency (φ) of the dilatation as in equation 3 where ε_d is the dilatational elasticity and η_d is the dilatational viscosity.

$$\begin{aligned} \varepsilon^*(i\omega) &= |\varepsilon|\cos\theta + i|\varepsilon|\sin\theta \\ &= \varepsilon_d(\omega) + \omega\eta_d(\omega) \end{aligned} \qquad (3)$$

Table 2. **Dilatational Elasticities and Viscosities of Crude Oil at 1 mHz**[a]

Crude oil	Additive[b] identity	Additive viscosity, $mm^2/s (= cST)$	ε_d, mN/m $(= dyn/cm)$	η_d, mNs/m
North Sea	None		1.34	153
	PDMS	12,500	0.69	90
	PDMS	60,000	0.51	33
	SK 3556		0.99	87
Middle East	none		1.63	105
	PDMS	60,000	1.19	53
	FC 740		4.36	377

[a] Ref. 22.
[b] Concentration = 1 ppm.

A stable foam possesses both a high surface dilatational viscosity and elasticity (21). In principle, defoamers should reduce these properties. Ideally a spread duplex film, one thick enough to have two definite surfaces enclosing a bulk phase, should eliminate dilatational effects because the surface tension of an insoluble, one-component layer does not depend on its thickness. This effect has been verified (22). Silicone antifoams reduce both the surface dilatational elasticity and viscosity of crude oils as illustrated in Table 2. The PDMS materials are Dow Corning Ltd. PDMS fluids, SK 3556 is a Th. Goldschmidt Ltd. silicone oil, and FC 740 is a 3M Co. fluorocarbon profoaming surfactant.

Both high bulk and surface shear viscosity delay film thinning and stretching deformations that precede bubble bursting. The development of ordered structures in the surface region can also have a stabilizing effect. Liquid crystalline phases in foam films enhance stability (23). In water–surfactant–fatty alcohol systems the alcohol components may serve as a foam stabilizer or a foam breaker depending on concentration (23). Alcohol/surfactant ratios less than that corresponding to the liquid crystalline phase enhance film stability; higher ratios produced by contact with alcohol droplets disrupt this phase and cause film instability. Liquid-phase defoamer components may dilute or destroy such stabilizing phases or they may simply contribute lower surface shear viscosities than the foam stabilizing surfactant (profoamer). For example, the very low surface shear viscosity of PDMS (24) is often cited as a contributing factor to its effectiveness in defoamer compositions. On the other hand, too rigid a surface will also be prone to rupture. Thus dilatational moduli that are too high will also result in foam instability, as in the case of diesel fuel antifoaming with a fluorosilicone antifoam agent (25).

Reduced gas diffusion between bubbles delays collapse by retarding bubble-size changes and the resulting mechanical stresses. Consequently single films persist longer than the corresponding foam, but it seems to be a minor factor in practical defoaming situations. The same is true of other thin-film stabilization effects from the interaction of the opposite surfaces of the film. These comprise both electric double-layer repulsion for ionic surfactants and entropic repulsion of polymer chains in the surface for nonionic materials. These effects are of paramount importance in determining the stability of very thin (<10 nm)

films, but in practice the real challenge is usually to defoam films of at least several hundred nanometers in thickness where such effects have not begun to be significant.

All these mechanisms except high bulk viscosity require a stabilizer in the surface layers of foam films. Accordingly, most theories of antifoaming are based on the replacement or modification of these surface-active stabilizers. This situation requires defoamers to be yet more surface active; most antifoam oils have surface tensions in the 20–30 mN/m range, whereas most organic surfactant solutions and other aqueous foaming media have surface tensions between 30 and 50 mN/m, which is illustrated in Table 3.

In addition to having a lower surface energy than the foaming medium, defoamers must be insoluble in that medium, but also readily dispersible in it. There are five basic processes involved in the rupture of foam films by defoamers (7): entering, spreading, bridging, dewetting, and rupture.

The entering and spreading processes are governed by the entering coefficient E and the spreading coefficient S defined in equation 4 and 5, respectively (7), where σ_f is the surface tension of the foaming medium, σ_a the surface tension of the defoamer, and σ_{af} the interfacial tension between them.

$$E = \sigma_f + \sigma_{af} - \sigma_a \tag{4}$$

$$S = \sigma_f - \sigma_{af} - \sigma_a \tag{5}$$

The lower the value of σ_a, the more likely it is that E and S are positive indicating a thermodynamic tendency for the processes to occur.

The displacement of the foam stabilizer and the mechanical disruption caused by these processes is sufficient to explain the function of defoamers, which consist only of insoluble liquids such as silicone fluids used in the defoaming of crude oil. However, practical experience shows that blends of hydrophobic solids dispersed in the insoluble oil are generally necessary to control aggressive foaming, particularly in aqueous foam systems. Materials such as hydrophobic silica (17) or high melting point hydrocarbon amides such as ethylenediamine distearamide are notably effective. As an antifoam particle in a foam film approaches the air interface, an unsymmetrical thin film, known as a pseudoemulsion film (33), forms between the antifoam particle and the air phase. This psuedoemulsion film has a high stability in strongly foaming aqueous systems. Introduction of the hydrophobic particle into the oil drops destabilizes the pseudoemulsion film.

In such systems, bridging and dewetting effects are crucial to the defoaming mechanism. Once a defoamer particle such as hydrophobic silica has entered into a foam lamella, it can then bridge the film. Subsequent dewetting of the particle by the foam film can then cause collapse by causing a small hole to form in the film. This hole rapidly expands, driven by surface tension effects, resulting in rupture of the film (34). The mechanical shock of this event can help propogate the defoaming action. For complete dewetting to occur the contact angle must be greater than 90°, a requirement for defoamer action that has been well correlated for silicone-treated silica in hydrocarbon oil (35). Such dewetting helps thin the film and promote instability, and is particularly effective when sizes are such

Table 3. **Surface Tensions of Surfactants and Defoamers**

Material	CAS Registry number	Surface tension[a] mN/m (= dyn/cm)	Temperature, °C	Reference
		Surfactants		
sodium lauryl sulfate $C_{12}H_{25}SO^-_4Na^+$	[151-21-3]	39.5	25	26
sodium 12-butoxydodecyl sulfate $C_4H_9OC_{12}H_{24}SO^-_4Na^+$	[3694-71-1]	44.0	25	26
lauryl pyridinium bromide $C_{12}H_{25}C_5H_5N^+Br^-$	[104-73-4]	41.2	30	26
$C_{12}H_{25}(OC_2H_4)_nOH$[b]	[9002-92-0]	36.3	23	26
p-t-$C_8H_{17}C_6H_4(OC_2H_4)_nOH$[c]	[9036-19-5]	33.5	25	26
		Surfactant–defoamer		
Surfynol 104[d]		31.4	25	9
Pluronic L62[e]		42.8	25	27
		Defoamers		
poly(oxypropylene), mol wt 3000		31.2	22	28
polydimethylsiloxane, mol wt 3900		20.2	20	28
kerosene	[8008-20-6]	27.5	29	29
mineral oil (MWP paraffin)	[8020-83-5]	28.8	20	30
corn oil	[8001-30-7]	33.4	20	31
peanut oil	[8002-03-7]	35.5	20	31
tributyl phosphate	[126-73-8]	25.1	20	32

[a]Surfactant values are at the critical micelle concentration (CMC) in aqueous solution; surfactant/defoamer values are at 0.1% concentration in aqueous solution.
[b]Lauryl end-capped polyoxyethylene.
[c]Polyoxyethylene end-capped with substituted phenyl group.
[d]Surfynol 104 is an acetylenic glycol, 2,4,7,9-tetramethyl-5-decyne-4, 7-diol [126-86-3] marketed by Air Products and Chemicals, Inc.
[e]Pluronic L62 is a poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene) copolymer marketed by BASF AG.

that the particle occupies both surfaces of the film. In this bridged situation, if the contact angle is large enough, a capillary pressure drop that pushes liquid away from the particle is developed (34). This flow results in migration of the air−liquid−solid interfaces toward each other until they meet and the film ruptures as it pinches off the particle. This concept offers an explanation for observed particle size and shape effects (2,18). Cinephotomicrographic studies are consistent with these dewetting ideas (36).

Debate continues about the detailed mechanisms of antifoaming by these synergistic combinations of insoluble oils and hydrophobic particles. These dewetting ideas imply that the hydrophobic particles become detached from the carrier fluid. This separation accounts for the familiar experience of performance of antifoam compositions diminishing with time. Further additions of defoamer are needed to maintain effective foam control. Adsorption of antifoam components on other available surfaces, particularly in systems containing suspended solids, mutual saturation of foamer and defoamer changing the spreading and dewetting pressures, and coalescense of antifoam emulsions also contribute to this progressive loss of effectiveness. It has recently been demonstrated that exhausted or deactivated oil−silica defoamers segregate into two distinct populations of globules (silica-free and silica-enriched), neither of them being active defoamers (37). In addition, the spread oil layer disappears from the foam solution surface. The defoamer can be reactivated by addition of fresh oil without silica (37), which allows the entering and spreading mechanisms to function again, carrying in particles that can then bridge and dewet. Another interesting aspect of the dewetting/bridging action is its location. Most researchers explain the defoaming action in the foam films, although others (38) claim it occurs in the plateau borders of the foam. This theory can account for the fact that the typical size of antifoam drops (3−50 μm) is much larger than a typical foam lamella thickness, and also that smaller antifoam droplets are ineffective foam breakers.

5. Applications

The main industries and broad product groups that utilize defoamers are indicated by the subheadings in this section. These examples illustrate the wide variety of defoamer applications. Other application areas worthy of mention are agriculture and medical, particularly the use of antiflatulence tablets.

5.1. Adhesives and Sealants. Most industrial adhesives contain surface active components and additives, and air entrainment during their mechanical application can significantly reduce joint strength. Defoamers are usually formulated into adhesives to protect users against such difficulties. Additional benefits, such as improved uniformity of products, increased throughput and reduced labor costs can also result from the use of defoamers during adhesive application. The footwear and nonwoven fabric industries are extensive users of defoamers in this way.

5.2. Chemical Processing. Agitation, distillation, and pressure differences are commonplace in many chemical processes. These are conducive to foam

formation, and even when the plant design minimizes these problems it is still often necessary to employ defoamers. A review of this field (39) lists numerous problems encountered with unwanted foam in chemical processes: increased cost of coping with safety hazards from slippery floors, corrosive residues, or flammable liquids; interference with process instruments, pumps, etc; slow drainage of liquids from products being dried; product rejection due to incompletely filled containers; reduced capacity in vats; premature failure in bearings and other mechanical devices due to loss of lubrication; separation and segregation of critical process ingredients; and perceived negative environmental impact and poor community relations on discharge.

5.3. Cleaning Compounds. A growth area for defoamers is in the formulation of low-foaming detergents and cleaners, which is in response to automation of cleaning equipment and the need to operate it optimally. Changes in detergent composition and washing machine design have also had a significant impact on the need for foam control in this application (40). Incorporation of defoamers in detergents in such a way that the low-foaming property does not drift with storage time is a considerable challenge. The antifoam composition has to survive storage with the surfactants, builders, bleaches, and other auxiliary agents, and yet function properly as soon as the detergent is added to the wash water. The solution is to prevent the defoamer from migrating within the detergent powder matrix such that the droplet size of the defoamer released into the wash water is the same regardless of storage conditions. Numerous patent examples of the four general ways in which this can be achieved have been provided (41): encapsulation in a water-soluble or water-dispersible wax; adsorption onto a carrier prior to wax coating; microencapsulation with film-forming polymers; and adsorption onto specially prepared inorganic salts.

5.4. Construction. Polymer dispersions in cements, mortars, and plastics are being increasingly used in the construction industry (11). Their plasticizing effect allows reduced amounts of water to be used, and they also confer strength and adhesion benefits in certain situations. The emulsifiers and dispersants used in these products can cause air entrainment problems with a detrimental effect on the ultimate stability of the construction. Powdered defoamers that can be directly added to the cement are commonly used. They are usually high surface area, highly absorbent inorganic fillers that have been treated with liquid defoamer compositions, similar to the products used in low-foaming detergents. Another approach to this problem is for the latex manufacturers to formulate low-foaming polymer dispersions with appropriate defoamers having good long-term stability.

5.5. Fermentation Processes. The efficient production of penicillin, yeasts, and single-celled protein by fermentation requires defoamers to control gas evolution during the reaction. Animal fats such as lard [61789-99-9] were formerly used as a combined defoamer and nutrient, but now more effective proprietary products are usually employed. Defoamer application technology has also improved. For example, in modern yeast production facilities, the defoamers are introduced by means of automatic electrode-activated devices. One concern in the use of defoamers in fermentation processes is the potential fouling of membranes during downstream ultrafiltration (qv). Silicone antifoams (42) seem less troubled by this problem than other materials.

5.6. Fertilizers. The fertilizer industry for many years has used tall oil fatty acids for the production of phosphoric acid [7664-38-2] by the digestion of phosphate-containing rocks with sulfuric acid. Carbon dioxide is liberated and presents a difficult, highly acidic foaming problem. Formulated products, many of which continue to contain tall oil fatty acids but that also contain emulsifiers and wetting agents such as dioctyl sodium sulfosuccinate [577-11-7], which greatly increase their effectiveness, are now used. Partially wetted gypsum particles contribute to the foam stabilization, and it is the modification of the gypsum wettability by these wetting agents that makes them so effective in this application.

5.7. Food and Beverages. Defoamer applications in the food and beverage industry include uses in both the preparation and processing of foodstuffs and in the cleaning and disinfecting of containers. Poly(alkylene oxide)-based defoamers have played an important role in satisfying the foam control demands of this industry (43). The sugar beet industry is a prolific user of defoamers, which is now a fully mechanized automated procedure. The sugar is extracted with hot water, treated with limewater and carbon dioxide, filtered, and the filtrate subjected to evaporation. Foaming occurs in many of these steps. Another food processing area with considerable foam problems is the production of chips, fries, mashed potatoes and potato starch. Proteins, starch, and other natural products in potatoes cause troublesome foams in wash baths. Beers and wines are also produced with the aid of defoamers. They permit more efficient use of vats and containers, and permit more controllable bottling procedures. The growth in returnable bottles and the widespread use of automated mechanical cleaning equipment has increased use of defoamers in this industry. They can be used directly or incorporated in low-foaming cleaning agents. It is important to note that foams occurring in food processing are generally stabilized by surface active macromolecules, such as proteins or starch, instead of the more usual small-molecule surfactants and this is reflected in the composition of defoamer products for these applications.

5.8. Leather. Almost every stage in leather processing from the initial rawhide preparation, through tanning and dyeing and other finishing treatments, has the potential for causing foaming difficulties. Many of the preparations used in these steps contain wetting agents and other surfactants, or are applied in the form of emulsions or dispersions. The trend, as with many other defoamer applications, is to formulate the defoamer into the treatment product rather than deal with numerous optimized defoamers at each of the several processing steps.

5.9. Metal Working. The metal working industry encounters considerable foaming problems with the cutting oils and coolants that are sprayed onto the tool–workpiece interface to provide cooling, controlled lubrication, corrosion protection, and increased tool life. These coolants are provided as mineral oil–emulsifier concentrates that are diluted with water by the user. For many years, this industry tolerated the foam difficulty in its many milling, drilling, grinding, rolling, and drawing operations but now uses defoamers such as formulated silicones and dispersions of fatty amides in mineral oils. Calcium soaps are also used as foam inhibitors in coolants. They are formed as a finely divided suspension of insoluble particles when the soaps present in the

cooling lubricant concentrate react with hardening agents added to the dilution water.

5.10. Oil and Petrochemicals. There are a variety of uses for defoamers in oil recovery. They are used in some of the materials used in oil extraction, such as in drilling muds and cement lining, and also directly with the crude oil itself. In its natural state, crude oil contains dissolved gases held by high reservoir pressure. When this live crude oil is extracted and passed into the low pressure environment of a gas-oil separator, the dissolved gases are liberated and can cause troublesome foam that leads to oil losses via the gas stream and downstream equipment damage (44). Foaming is a problem in other petrochemical operations including distillation, cracking, coking, and asphalt processing. Defoamers are also used in the downstream petroleum market in lubricating oils and diesel fuel. The oil and petrochemical application area and the following area of Coatings, are ones where not only the elimination of foam is important, but also the elimination of individual bubbles. This problem of deaeration can only be dealt with using specifically designed products. Foam control agents can break foam lamellae once they are formed between bubbles but the defoamer generally cannot remove or accelerate the movement of individual air bubbles.

5.11. Coatings. Foam problems occur both during the preparation of paints and coatings and in their application. The use of ball mills and other equipment for pigment dispersion provides ideal conditions for mixing in air, and the presence of surfactants in the formulations assures considerable persistence of the foams that are generated. These problems may be controlled during manufacture by mechanical means, but a defoamer is almost always required for foam control during application since application methods vary considerably, eg, roller, brush, dip, or spray methods. The proper choice and minimum use of surfactants such as dispersants, flow agents, and wetting agents can minimize but not eliminate the use of defoamers to prevent surface defects during application such as cratering, pinholes, fisheyes, and orange peel. In addition to the final dried film appearance, the defoamer must not detract from other properties such as color acceptance, gloss, and adhesion.

5.12. Polymers. Foam is often a particular problem in the production of polymers. There are numerous situations where foam can reduce the production capacities of vats and vessels and cause problems in pumps, meters, and other equipment, particularly distillation and evaporation equipment. Foam is frequently a problem when stripping off a monomer from a polymer. Examples are in the production of styrene–butadiene [9003-55-8] and acrylonitrile–butadiene [9003-18-3] rubber latices. These latices are stabilized by surfactants that greatly contribute to foaming difficulties. Another problem foam area is in the stripping of unreacted monomer from poly(vinyl chloride) suspensions. In this process, vinyl chloride [75-01-4], a gas at room temperature, is liquefied by pressure, emulsified in water with surfactants and catalysts, and heated to bring about polymerization. The recovery of unpolymerized monomer by distillation from this mixture produces a severe foaming problem.

5.13. Pulp and Paper. The critical and troublesome foam problems of this industry have led the way in the use of defoamers. It is the world's biggest single user of defoaming agents (45). Early use of large amounts of kerosene or fuel oil has given way for ecological and cleanliness reasons to much more

effective formulated defoamers. Foams are encountered at every stage from pulping, through paper fabrication and coating, to printing. A variety of wastewater streams are generated that are very prone to foaming because of the presence of dissolved soaps. Specific defoamer products are often tailored for each different stream. The so-called black-liquor defoamers were the first hydrophobic silica in hydrocarbon oil products that were then extended to other industries. The use of these defoamers has allowed some Kraft pulp mills to exceed original designed capacity.

5.14. Textiles. Defoamers are required in the jet dyeing of textiles (17). This process, which is mainly used with polyester fibers, is carried out at elevated temperature and pressure, and involves pumped recirculation of the dyeing medium from the reservoir through the jets. When the operation is complete and the pressure released, severe foaming can result in the absence of an effective defoamer. Foam control is needed in other dyeing processes also (17), such as continuous dyeing and beck dyeing. For example, in the dyeing of knitted fabrics of textured polyester fibers, foaming of the dye liquor can cause the material to float resulting in uneven application of the dye. Various surfactant mixtures are used in this area and bring additional benefits such as wetting and solubilization as well as foam control. Acetylenic glycols are very useful in this context (9). Dyeing is only one of several steps where foaming can cause difficulties with fiber processing. Defoamer may be required when any size or finish is applied to a textile material. One example is the pretreatment step in the processing of cotton. The fabric is exposed to strongly alkaline sodium hydroxide and anionic surfactant solution. Phosphate ester defoamers are much used in this application. Textile operations are also notorious for their wastewater foam problems.

5.15. Wastewater Treatment. Defoamers are used extensively to treat wastewater in many municipal and industrial treatment facilities and also in mining and mineral processing. Benefits are aesthetic, environmental, and economic. Aeration basins are rid of unsightly, troublesome foam, and water and energy are conserved, by allowing more efficient use of mechanical equipment. Most foaming problems occur either at the biological treatment step or the effluent discharge step (46). Aeration is necessary in biological treatments to allow microorganisms to breathe, but the agitation produces foam. Defoamers that do not disrupt this process must be selected. Some of the upstream processes may depend on foaming and other surface active phenomena such as flotation and flocculation steps, and care must also be taken to use defoamers that do not interfere with these processes if treated streams are recycled. Effluent foam discharge is illegal in some countries including the United States where the Environmental Protection Agency (EPA) prohibits discharge of floatable materials in the effluent stream (46).

6. Economic Aspects

Accurate information on the size of the defoamer market is impossible to obtain. There are too many types of materials and suppliers involved. Particularly for the more common oils and surfactants, defoaming is a very small part of their total usage, and no public information is available on what fraction of manufacturers'

sales is in the area of foam control. Even for more expensive materials such as the poly(alkylene oxide) block copolymers, there is no way of distinguishing between their use as defoamers and other significant surfactant uses such as de-emulsifiers.

In 1993, the *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed. estimate was a market for defoamers of all types of 150,000–170,000 metric tons per year in the United States, with the rest of the world. slightly exceeding that amount. The principal use area of pulp and paper accounts for between a one-third (47) and one-half (45) of this usage. With modest growth in some markets offset by improvements in efficiency in others, the 1993 estimate remains an adequate one for 2000. No typical selling price for defoamers can be quoted because of the wide diversity of active materials and product types. The cheapest unformulated defoamer types cost as little as $0.6/kg in bulk quantities, whereas some custom-tailored defoamers cost over $5.0/kg. Usages vary from less than 0.1 kg of defoamer per ton of product to over 2.0 kg/ton of product, and it is not the unit cost of the defoamer that matters but the cost per unit of product produced. It often occurs that the controlled use of a relatively expensive defoamer results in a lower cost per unit of product than use of an inexpensive defoamer.

7. Test Methods

The ultimate test of a defoamer is an actual field trial. Occasionally, this is the only testing carried out. More usually some laboratory scale evaluation of several different products is conducted before a recommendation is made for a suitable, economical defoamer for a specific application. Although suppliers have their chosen standard foaming surfactants, it is usual to work with the potential customer's foaming medium. Often this work is done at the plant site to obtain fresh foaming liquors. Establishing that a given defoamer is effective in a particular application is only part of the testing required. The absence of any adverse effect on the final product and the manufacturing and use environments must also be determined. In addition, to be marketable the defoamer must be cost-effective and convenient and easy to handle for the customer. A useful account of the practical selection of defoamers has been given (39).

There are many laboratory methods for testing the relative merits of one defoamer against another. It is a simple matter to measure foam height as a function of time to compare the performance of various foam surfactants and defoamers. Unfortunately, this simplicity has led to a wide variety of methods and conditions used with no standard procedure that would make the measurement of foaminess as characteristic of a solution as its surface tension or viscosity. It has been suggested that the time an average bubble remains entrapped in the foam, Σ, is such a quantity (48), but few workers in the defoamer industry have adopted this proposal. One reason is that the measurement is not practical with strongly foaming materials, the steady-state foam height being very high and hard to reach. Nishioka and co-workers (49) describe dynamic methods for measuring Σ in their review of fundamental methods for measuring foam stability. They also observe that the decay of static foam is measured, most

fundamentally, by the change with time in the size distribution of bubbles in a foam. This measurement can be done by photomicroscopy of flash-frozen samples, a method that although somewhat tedious, is recommended for periodic confirmation of other less direct methods whenever possible. In practice, a wide variety of simpler methods are used that generally fall into one of five main categories:

1. *Pneumatic Methods*. Gas introduction is controlled by injection through capillary tubes, sintered-glass spargers, diffuser stones, and the like.
2. *Dynamic Methods*. This method is a subdivision of the pneumatic class; foam heights or volumes are monitored while the gas continues to produce bubbles.
3. *Shaking Methods*. Agitation is the easiest way of producing foam, but the results are very dependent on the details of the shaking procedure. Foam height, or for more viscous fluids specific gravity changes, are usually measured.
4. *Pour Methods*. The liquid is poured or drained from one vessel into another. This approach is best limited to foams produced from dissolved gases in the liquid.
5. *Stirring and Blending Methods*. Like shaking methods, these are very dependent on procedural and equipment details, but they are simple to use and are widely employed for comparative purposes.

This diversity of test methods is reflected in ASTM recommendations (50). Pour (D1173-53 (reapproved 1986)), shaking (D3601-88), and blending (D3519-88) methods are suggested for aqueous solutions. Pneumatic methods are recommended for lubricating oils (D892-89) and engine coolants (D1881-86). Despite their omission by ASTM, dynamic methods are probably the most satisfactory for defoamer evaluation (12,41). The foaming solution is usually recirculated through a vertical cylinder where foam heights can be measured as a function of time. In such a device, a steady state can be achieved with a given foamer system and defoamer metered in at selected concentrations. The test enables various important defoamer characteristics to be measured such as the knock-down time, the time taken to collapse a preformed foam, and the persistence or hold-down time, the time taken for the foam to recover to some agreed level such as one half of its original height (defoamer half-life).

8. Health and Safety Factors

Defoamers are usually added at low bulk concentrations ranging from a few to 1000 ppm of the foaming medium. Often the health risk posed by such additives is negligible compared to that of the material being defoamed. Such is the case in the defoaming of asphalt (qv) and phosphoric acid. Sometimes a specific defoamer type/foaming medium combination presents a particular problem, so the supplier should always be involved in defoamer selection. Examples are the increase in flammability of polyester textiles with free PDMS (17), and the possibility that

mineral oil antifoams may contain precursors that form dioxins in bleached pulp after chlorination (51). Health and safety concerns arise primarily in applications in the food and drug industries. Defoamers can be incorporated directly in these products, as in the production of sugar from sugar beets or in the defoaming of fats for frying potato products, and indirectly, as in the manufacture of paper or plastic packaging materials.

U.S. government regulations governing the use of additives such as defoamers in food and drugs are listed in the Code of Federal Regulations. Title 21 contains the rules established by the Food and Drug Administration; Title 40 covers those that are the concern of the EPA. For example, part 173.340 of Title 21 deals with defoamers that may be safely used in processing foods, whereas Part 180.1001 of Title 40 lists those materials exempt from the requirement of tolerance levels in pesticide chemicals, including defoamers used therein. Other parts of Title 21 that cover defoamer uses include 176.200 on coatings and 176.210 on the manufacture of paper and paperboard. One defoamer is also used as an active drug ingredient–the antiflatulent silicone, Simethicone [8050-81-5]. Such use is regulated by the FDA under part 332 of Title 21. Regulations are subject to change and the Code of Federal Regulations is revised at least once each calendar year. It is also kept up-to-date by the individual issues of the *Federal Register*, a daily government publication.

Although the intent may be the same, the details of regulatory practice differ in other countries, and a multitude of regulations exist worldwide. Under the auspices of the Joint Expert Committee on Food Additives of the World Health Organization efforts are being made to establish international guidelines. However, given the changing regulatory climate, the differences in practice between countries, and the wide range and regional differences of antifoam components available, the best advice for those interested in health and safety aspects of defoamers is to contact the producers directly. Their skill and experience are the best defenses against safety hazards associated with the use of defoamers.

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