Foam and its Control in Pulp and Paper Manufacturing: A Review of Chemical Principles and Governing Factors

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This review article considers factors contributing to the development of problematic levels of foam, as well as ways to control foam, with emphasis on two critically important unit operations in pulp and paper manufacturing plants, namely the brownstock washing system and the paper machine. In general terms, hard-to-break foam bubbles can be expected when an aqueous system is subject to a means of air entrainment (such as agitation), when an air phase is present, when there are surface-active agents present, and when the solution also contains significant levels of water-soluble polymers. Brownstock washers and paper machines have all of these ingredients, and sometimes they are at problematic levels. The resulting stabilized foam bubbles can hurt production rates, interfere with displacement of pulping liquor from the fiber mat during washing, and contribute to blemishes in paper products. Considerable progress has been made over many years in understanding these phenomena and also in understanding the work of foam-control products. Engineers in modern pulp and paper mills can make use of efficient foam-control products as well as monitoring equipment. This article provides a tutorial review of such issues, based on published findings.

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INTRODUCTION

Motivations to Control Foam in Pulp and Paper Mills

Foam-control agents, which are often called defoamers or antifoams, are among the most commonly applied additives in pulp and paper mill operations. Though they are added in relatively low amounts, they can have a big effect on operational efficiency and product quality. According to Allen *et al.* (1993), the paper industry is the world's largest user of these agents. Of this amount, about 60% of the usage is for brownstock wasing, *i.e.* the separation of lignin-rich water from the fibers after kraft pulping. This review article mainly considers their applications in brownstock pulp washing (Pelton 1989; Santos and Hart 2014) and in the paper machine forming section (Allen *et al.* 1993). Foam-control agents are also used at the size press of the paper machine (Vines *et al.* 1997) and during preparation of coating formulations for paper (Hudson 1968; Reinhardt *et al.* 1998). The term "defoamer" has often been used to denote relatively fast-acting foam-control agents (Denkov 2004; Denkov *et al.* 2014), which are often needed in pulp and paper mill applications. The alternatively term "antifoam" has often been used to denote agents that are intended to suppress the later development of foam. It has been noted that many foam-control agents comprise both fast-acting and long-term efficacy, and their modes and speeds of action often depend on details of the industrial environment to which they are being added (Denkov *et al.* 2014).

A key motivation to use foam-control agents in the pulp and paper industry is to maintain a suitably high rate of production, which can depend strongly on the rate of release of water from a wet mat of fibers. Defoamers have been shown to increase rates of dewatering in brownstock washing (Hakamäki and Kovasin 1985; Pelton 1989; Lobo and Bolton 2013; Bolton *et al.* 2014; Santos and Hart 2014) and the forming of a paper sheet (Allen *et al.* 1993). In the case of brownstock washing, foam bubbles in the fiber mat not only can lower the rate of filtration, but they also interfere with the displacement of lignin-rich water by the rinse water (Pelton 1989). On the paper machine, by occupying a variable proportion of volume in a suspension of fibers, foam bubble can interfere with process control, thereby leading to variability in paper properties such as basis weight (mass per unit area) (Mudaly 2007).

Types of Foam

As illustrated in Fig. 1 (Hubbe and King 2009), three categories of air can be found within the brownstock washer systems and paper machine system, namely dissolved air, entrained air, and large bubbles. Bubbles that are small enough to move along with a fiber suspension are called entrained. Poschmann (1962) observed that the fibers in a flowing suspension can constrain such bubbles so that they are unable to collide and coalesce with each other and thereby become larger. Because the volume of a fiber-water suspension is increased by the presence of air bubbles, without appreciably contributing to the weight, there can be a loss of accuracy in the pumping and metering of flows (Mudaly 2007). Under severe cases, there can be undesired swings of basis weight due to too much compressibility of the mixture as it passes through fan pumps. Because the fiber suspension in a paper mill is under pressure, during its approach to the forming section, there will be a tendency for at least part of the entrained air to become temporarily dissolved in the process water (Matula 2000). However, the tiny bubbles form again quickly during depressurization as the jet of furnish emerges from the headbox slice, just before the dewatering process begins.

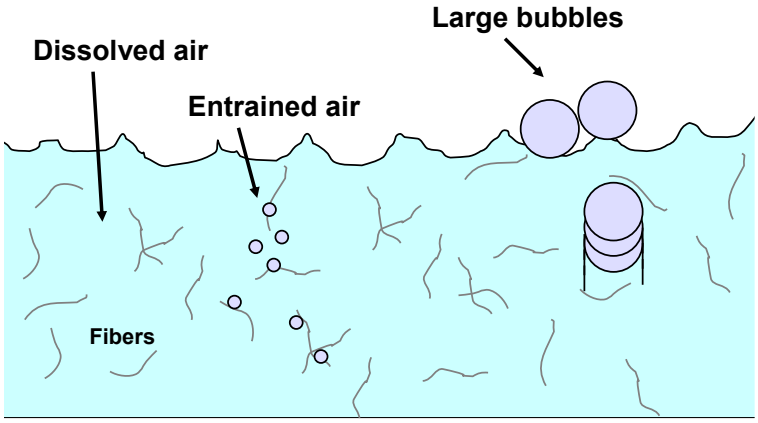

Fig. 1. Three general categories of air that are present in pulp and paper mill aqueous systems (Figure adapted from a version by Hubbe and King 2009)

Once air bubbles present in industrial processes become large, *e.g.* 2 mm or greater in diameter, they are expected to rise rapidly and separate themselves from the aqueous phase in response to gravity or centrifugation effects in various processes (Melzer and Poschman 1973). Visible foam becomes apparent especially at the surfaces of chests, including the trays below Fourdrinier forming sections, as well as seal pits and white water silos in a paper mill (Mudaly 2007). Not only can such foam be unsightly, but it can contribute to the concentration and subsequent deposition of pitch-like materials onto process equipment and spots in the paper product (Allen *et al.* 1993). When the foam is severe enough to overflow to top of a seal chest or elsewhere in a pulp and paper mill (Pelton 1989), there can be a loss of yield, since the foam can be expected to carry some otherwise valuable cellulosic fibers into sewer drains. Pinholes in paper can develop in cases where vacuum suction boxes, which are intended to remove water from the paper web, pull bubbles of air through the wet web (Allen *et al.* 1993).

The structure of banks of foam bubbles, often resting at the surface of water, has received detailed attention (Langevin 2008). Garrett (1993) noted that recently formed banks of foam, following agitation, often consist of polyhedral bubbles on top, with round, smaller bubbles down below, where there may still be a greater proportion of water between adjacent bubbles. Because of the interfacial tension, the smaller bubbles will have a higher pressure of gas within them. Because air is able to gradually diffuse through walls of bubbles, one can expect a gradual disappearance of the smaller bubbles in favor of growth of adjacent larger ones (Denkov *et al.* 2020; Brondi *et al.* 2022).

Intentional Foam

Though the main focus of this article is on the control and destruction of foam bubbles, it is important to point out at least two circumstances where papermakers intentionally encourage the production of foam. One is in the flotation deinking of recovered fibers (Shrinath *et al.* 1991; Heindel 1999). Such operations often are carried out by dissolving air into pressurized water, which is then discharged at the base of a shallow chest containing the ink-laden wash water from the deinking process. The bubbles of air attach themselves onto the hydrophobic surfaces of typical ink particles, *e.g.* from the offset lithographic printing process (Hutchinson 1995). By contrast, it has been found that air bubbles do not nucleate on or adhere strongly to the generally hydrophilic surfaces of

papermaking fibers (Ajersch and Pelton 1994). Analogous dissolved-air-floatation (DAF) treatment is used in paper recycling operations to remove fine contaminants such as stickies from the process water (Hubbe 2026). Surfactants used in such processes, to the extent that they become recycled back to paper machine systems, may contribute to foam problems in other operations due to their tendency to stabilize bubbles.

In so-called "foam forming" processes, paper machines can be run using foam rather than water as the suspending medium (Alimadadi and Uesaka 2016; Hjelt *et al.* 2022; Nechita and Nastac 2022). Such processes might be considered for preparation of long-fibered paper sheets in cases where it is desirable to have fibers oriented relatively evenly in three dimensions (Alimadadi and Uesaka 2016), *i.e.* specialty paper grades. The control of the level of foaming in such systems is outside of the scope of this article.

Earlier Review Articles

As shown in Table 1, review articles have described various aspects of aqueous foam and its control. The present article aims not only to cover more recent findings, but also to provide needed emphasis on paper machine applications of defoamers.

Table 1. Selected Review Articles Focusing on Aspects of Foam and its Control

Review Article Highlights	Citation
Practical effects of air in papermaking	May & Buckman 1975
Brownstock defoamer fundamentals	Pelton 1989
Mode of action of antifoam products, emphasizing beds of foam	Garrett 1993
Foam control mechanisms for oil-based antifoams	Denkov 2004
Physical chemistry of foam drainage and coarsening	Saint-Jalmes 2006
The science of foam, its stability, chemistries, and structure	Langevin 2008
Foam control, with an emphasis on silicone antifoam products	Owen 2010
Mechanisms of foam-control agents	Denkov *et al.* 2014
Brownstock washing, including the usage of defoamers	Santos & Hart 2014
Theories of foam growth, stability, and breakdown	Wang *et al.* 2016

FACTORS CONTRIBUTING TO FOAM IN PULP & PAPER SYSTEMS

Pulp and paper mills can be regarded as favorable environments for the occurrence of unwanted entrained air and visible foam. This section will consider such foam-promoting and stabilizing factors as agitation (*i.e.* the mixing of aqueous solutions with air), the leaking of pump seals, variations in pressure leading to the generation of air bubbles, the role of surfactants, the role of dissolved polymers, and a possible influence of particles and emulsion droplets present in the process water or pulp and paper mills.

Agitation

Foam has been defined as gas dispersed in liquid with a sufficiently high ratio that it can have a density approaching that of a gas (Avery-Edwards *et al.* 1994). Though that definition does not include entrained air, it well describes the most obvious episodes of out-of-control foam that occur in pulp and paper mills during upset conditions or when there is a lack of optimized foam control technology. From a thermodynamic standpoint, every instance of foam is unstable and expected to break down over the course of time in a stationary system. A bank of foam, with no additional input of agitation or movement, will gradually collapse due to drainage of water from the bubble walls (Saint-Jalmes 2006;

Langevin 2008; Wang *et al.* 2016). It follows that the occurrence of unwanted foam requires there to be some form of mechanical energy leading to the initial entrainment of bubbles.

In a paper machine system, water is released from the freshly formed mat of fibers as a cascade of droplets (Allen *et al.* 1993). A similar effect takes place during brownstock washing, especially when using rotating screen drum washing equipment (Santos and Hart 2014). Figure 2 provides a schematic illustration of a series of three conventional drum washers connected in series, such that the rinse water can be used efficiently to displace the lignin-rich water from the fiber mat and return it to the chemical recovery system of the pulp mill with a minimum of dilution. Note, however, that the rinse water is applied at the top of the drum, such that the filtrate has to fall through the air and land on a pool in the lower part of the drum interior. Both the spraying and the cascading action are expected to contribute to entrainment of air.

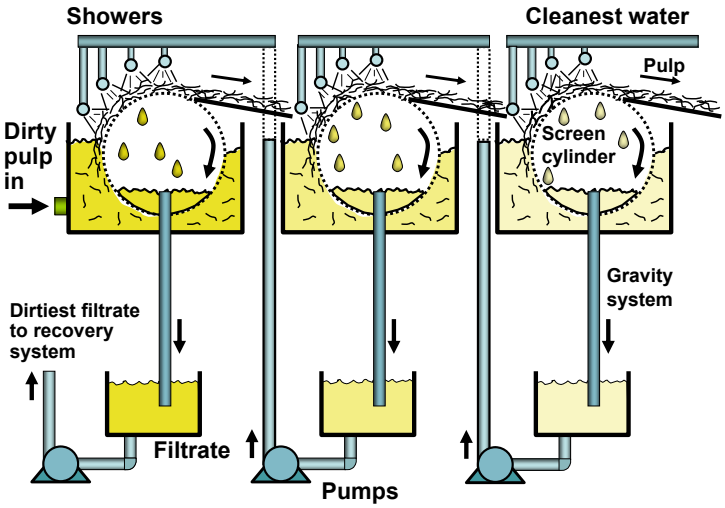

Fig. 2. Schematic illustration of a drum washing system set up with counter-current flow of the rinse water; figure copyrighted by the author and previously published in (Hubbe 2021)

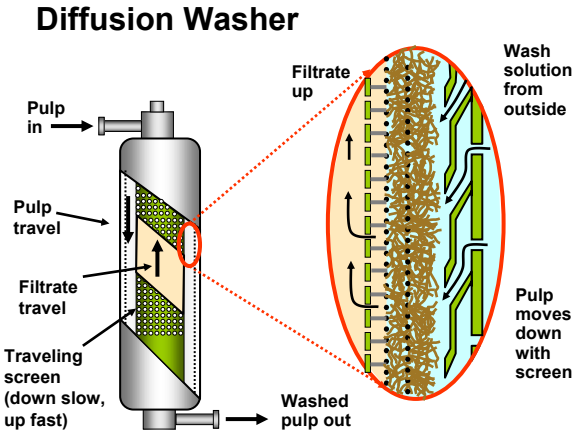

Fig. 3. Schematic diagram of a continuous diffusion-type pulp washer in which the whole operation is completely immersed (figure redrawn from an original by Pikka *et al.* 1999)

An advantage of modern continuous diffusion-type pulp washing equipment is avoidance of splashing and thereby minimization of air entrainment (Allen *et al.* 1993). As diagramed in Fig. 3, such equipment allows the rinsing action to take place in a completely immersed situation. An observed advantage of such methods and equipment has been a reduced need for consumption of foam-control agents (Johnson 1985).

Banks of hydrocyclones, which are commonly called cleaners, are used in the approach flow to most paper machine headboxes (Bliss 1994). As shown in Fig. 4, their primary purpose is to remove dense particles, especially sand, from the fiber suspension. In addition, their design and action provide a high potential for the entrainment of air into the papermaking stock. The accepted stock from a set of hydrocyclone cleaners has only a few more seconds before it becomes formed into a paper mat, which is often a point of major concern related to entrained air.

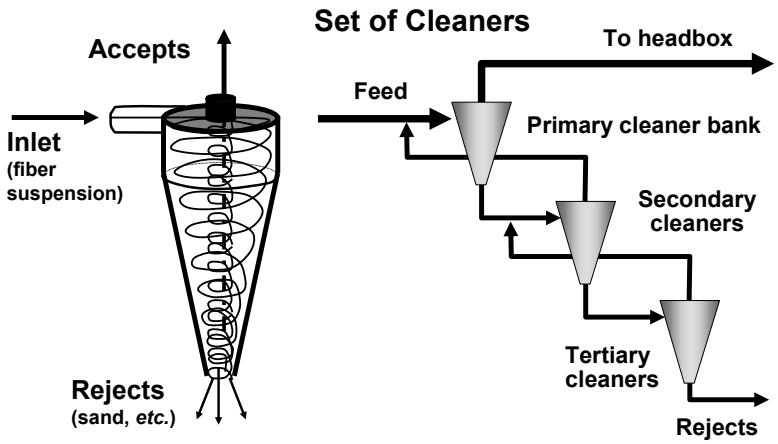

Fig. 4. Hydrocyclones (cleaners), as commonly used in the approach flow to a paper machine's forming section

Leaking at Pump Seals

Depending on the types of pump seals and how they are maintained, various amounts of air can leak and become entrained during the usage of modern pumping equipment (Gülich 2020). Only in the case of specialized pumps, such as diaphragm-type positive displacement pumps, can well-maintained equipment completely remove the possibility of air entrainment (Jackson *et al.* 2018). For the much more common centrifugal pumps, the rates of leakage during normal operations can be predicted (Gülich 2020). In addition, the wearing out or failure of seals on such pumps can lead to much larger amounts of air entrainment (Melzer and Poschman 1973; Allen *et al.* 1993). In fact, as a stop-gap measure to avoid adverse consequences of such a situation it has been proposed to add a defoaming agent to the fiber suspension feeding into such pumps (Melzer and Poschman 1973).

Depressurization at the Headbox Slice

In the course of industrial papermaking, the fiber suspension passes through a large pump (the fan pump), where it is combined with and diluted by filtrate that has recently been drained and pulled by vacuum from freshly formed web of paper. The elevated pressure continues to be maintained within the suspension as it travels through such devices as hydrocyclones (cleaners) and screens on its way to the headbox. During this period of

pressurization, much of the air that had earlier been entrained in the slurry as small bubbles becomes dissolved in the aqueous phase. Additional air is likely to become entrained as the furnish passes through the hydrocyclones, and some of this additional air may become dissolved as well. Then, when the jet of furnish emerges from the headbox slice, there is an immediate release of pressure, which induces a re-emergence of entrained air in the form of small bubbes (Matula 2000). This situation is illustrated in Fig. 5.

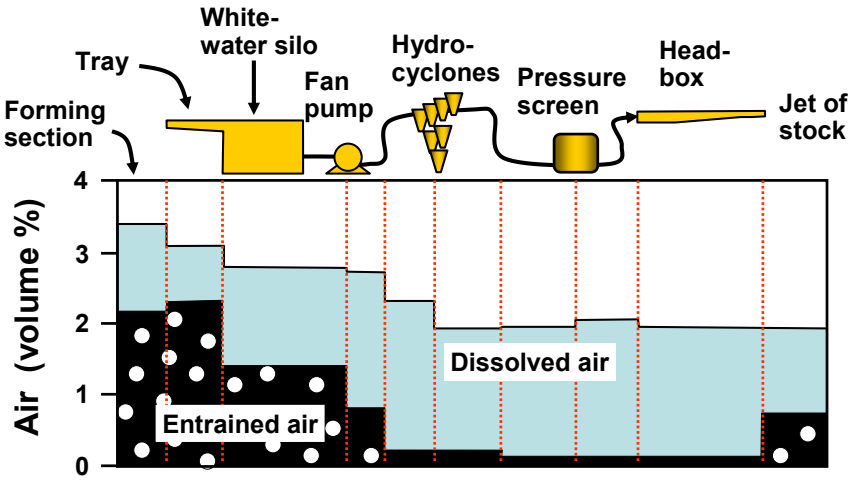

Fig. 5. Schematic diagram of expected levels of entrained (while bubbles with back background) and dissolved (blue background) air in a Fourdrinier paper machine system (figure redrawn based on an original by Matula and Kukkamäki 1998)

The information in Fig. 5 came from a paper machine system in which a foam-control product was being added at the white-water silo. It also is common to inject a foam-control agent before the inlet to the hydrocylone (cleaner) system. Only a matter of seconds will pass between the time when stock is passing through the cleaners and when it is being formed into paper. A modern paper machine may run at the speed of a car on a highway or racetrack (up to 2000 to 3000 m/min for commodity grades of paper). If one assumes a 10 m length of a Fourdrinier forming section, that implies that only 0.2 to 0.3 seconds for the defoamer to act, following depressurization of the stock at the headbox slide. The time available for foam breakage is even much more constrained in the case of gap formers (paper machines in which the sheet is formed between a pair of continuous fabrics). In such systems, the water is removed over a very short distance, depending on the design of the equipment.

Surfactants

In the absence of a stabilizer, a bubble formed in water will collapse immediately. This phenomenon is well known to swimmers on a pristine beach with breaking waves. Though a foam-like appearance occurs during the breakage of each wave, most of the bubbles may be gone moments later, depending on the levels of any natural or synthetic surfactants that may be present.

Soaps from kraft pulping

Especially in mills where there is primary production of kraft pulp, the process water is likely to contain certain compounds that had been extracted from the wood under

hot alkaline conditions. The most important of these are illustrated in Fig. 6. As shown, these include triglyceride fats, which are highly hydrophobic, but which can be naturally converted by enzymes to become fatty acids. Another class of surface-active compounds in kraft black liquor are the resin acids, including abietic and levopimeric acids. These two are converted to their soap forms when the pH is neutral or alkaline. In addition, there will be some compounds, such as α-pinene and β-sitosterol, which have an insufficient number of polar groups to render meaningful surface-activity. The hypothetical mycel structure shown in the middle of Fig. 6 envisions such nonpolar components as mainly occupying the center positions of pitch-like emulsion droplets or particles in the aqueous suspension, whereas the more surface-active compounds can be expected to be suitably oriented at the surface, if one were to take a snapshot in time.

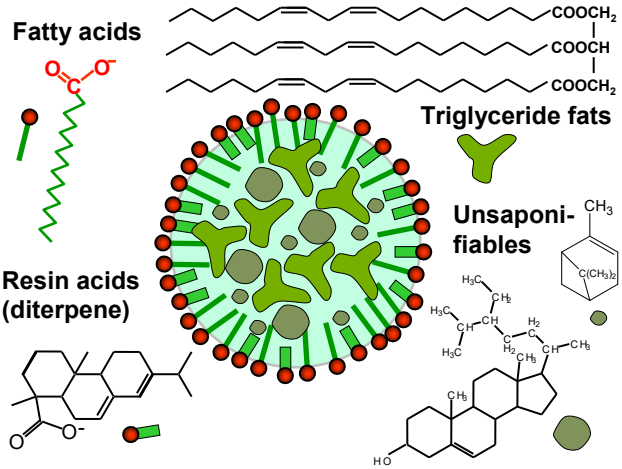

Fig. 6. Types of extractives commonly found in black liquor from kraft pulping of softwood chips, as well as a hypothetical emulsion droplet that is being stabilized by the most surface-active components

While Fig. 6 shows the fatty acid and resin acid soap molecules stabilizing an emulsion of other wood extractive compounds, it is reasonable to envision them also acting as stabilizers for bubbles of foam. Figure 7 describes three relevant situations to consider. First, as diagrammed in part A, the surfactant molecules will tend of form a condensed monolayer at air-water interfaces (Hubbe *et al.* 2020a). The molecules within that layer are expected to be in equilibrium with surfactant molecules dissolved in the water. If the concentration is high enough, then there will be additional molecules of surfactant present as micelles. The presence of a monolayer at the air-water interface lowers the interfacial tension (Prosser and Franses 2001), as can be measured by standard tests (Lunkenheimer and Wantke 1981; Sjökvist *et al.* 2018). Part B of the figure describes a group of bubbles that have risen to the surface of the bulk water. In this case, each bubble, in locations above the level of the bulk water, is composed of a surfactant bilayer, with a film of water sandwiched in the middle. Part C of the figure shows the cross-sectional profile of a group of three bubbles that happen to be fully immersed in the water phase. As shown, each bubble is expected to have an approximately spherical shape, except that the shapes are modified in places where any two bubbles are in contact. Details of these shapes have been the subject of study (Koczo *et al.* 1994; Denkov 2004; Wang *et al.* 2016; Anazadehsayed *et al.* 2018).

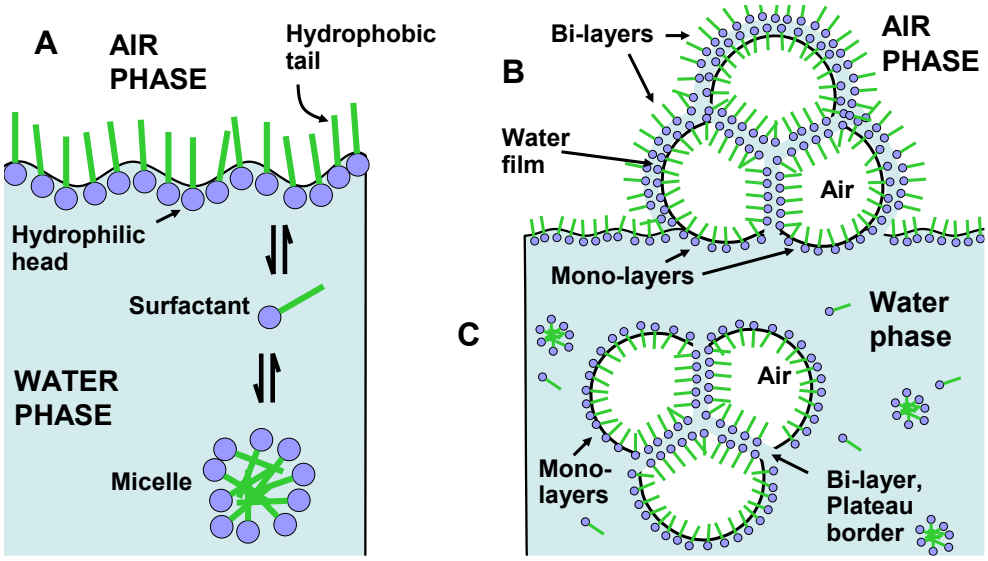

Fig. 7. Diagram highlighting different expected locations of surface-active molecules in a water-air system that has been recently subjected to agitation, leading to air entrainment: A. Surfactant molecules at an air-water interface and also in equilibrium with molecules in the water's bulk phase and with micelles; B. Three bubbles of foam (in profile) at the water surface; and C. Some bubbles (in profile) within the bulk water phase

Deinking surfactants

Surfactants also are widely used in the removal of ink from recovered printing paper. In such operations, one of the roles of the surfactants is to promote detachment of the ink from fiber surfaces (Shrinath *et al.* 1991; Heindel 1999; Theander and Pugh 2004). This takes place, to a large extent, during agitation of the fiber suspensions in a pulper, *i.e.* a chest provided with a large, robust impeller at its base. The pulping operation is often followed by a washing stage, in which the ink-laden process water is displaced from a mat of fibers (*i.e.* similar to what was shown in Fig. 2). The next step is to remove both the ink and much of the surfactant content of the process water in a dissolved air flotation (DAF) operation, as illustrated in Fig. 8.

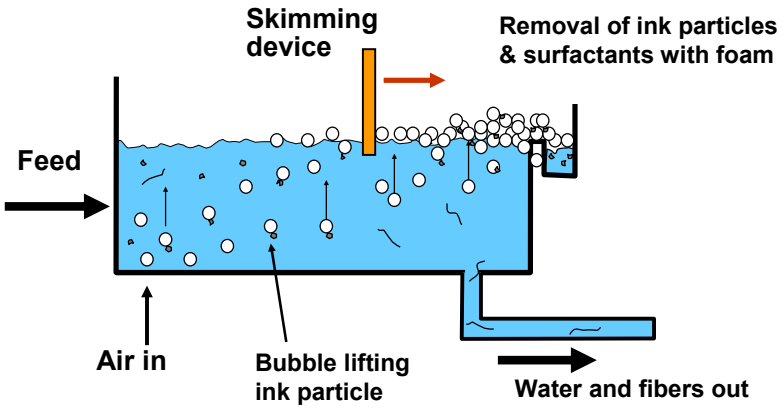

Fig. 8. Schematic diagram of dissolved air floating (DAF) for removal of ink from process water after being released from the surfaces of recovered fibers from printing papers

In a DAF separation process, air is first dissolved in water at high pressure; when the same water is injected at the base of a DAF floatation unit, large numbers of tiny bubbles are released from the dissolved air. The hydrophobic nature of many kinds of ink particles, especially offset lithographic inks, causes them to cling to bubble surface and thereby become lifted to the surface of the water (Heindel 1999). The foamy froth that collects at the surface of the DAF unit becomes skimmed from the water surface, as shown schematically in Fig. 8.

Though the DAF process just described is expected to remove much of the surfactant as well as most of the hydrophobic ink particles from the process water, one can expect some of the surfactant to become recirculated into various operations within the paper mill. Two classes of surfactant are of concern, namely ionic and nonionic surfactants. Ionic surfactants that have been widely used in the past for deinking operations include fatty acid soaps and their calcium salts (Ferguson 1992; Theander and Pugh 2004; Costa and Rubio 2005). Such surfactants can cause complications due to their interactions with oppositely charged components in the system. For instance, an anionic surfactant such as sodium dodecyl sulfate (SDS) is expected to interfere with the performance of cationic additives, such as aluminum sulfate (papermaker's alum) and with cationic polymers such as some retention aids. In recent years it has become more common for papermakers to rely on nonionic surfactants for deinking. Although such surfactants, when they are present in paper machine systems, do not interfere with charged additives, they can act as wetting agents (Schmedding and Tatum 1998). It follows that they are expected to adversely affect the performance of hydrophobic sizing agents. The term sizing agents here refers to such additives as rosin, alkylketene dimer (AKD), and alkenylsuccinic anhydride (ASA), which cure during the industrial drying of paper and develop its resistance to wetting by aqueous fluids. In addition, all forms of deinking surfactants, to various degrees, can promote the stability of foam bubbles. As noted by Kulkarni *et al.* (1977a), because ionic surfactants carry a charge, one can expect that the bubbles will be ionically charged. This can cause them to remain separate from each other, especially in situations where the bubbles are entrained in a fiber suspension or otherwise immersed in the water phase. Such colloidal stability can be expected to work in opposition to some potential foam control measures. However, as was already noted by Miles and Ross (1944), the behavior of ionic surfactants can be affected also by such variables as pH, water hardness levels, and interactions with other charged materials.

Surfactants in additive formulations

Nonionic surfactants also are used in the formulations of certain additives for the papermaking process. In particular, acrylamide copolymer retention aids are routinely formulated as water-in-oil emulsions to accommodate their synthesis, transportation to paper mills, and storage at the mill prior to use. The nature of the surfactant is dictated by their intended role as stabilizers of water droplets within a continuous oil phase. A base level of surfactants can be expected to be present in typical papermaking furnish, due to the continuous addition of that kind of retention aid product during the operation of a high percentage of paper machines throughout the world. In some cases, there may be significant contributions to foam in the paper mill systems. Though it is possible to avoid such usage of surfactants by dispersion of dry-bead retention aid products at the paper mill, such practices are less used in comparison to water-in-oil emulsified retention aid formulations (Lu *et al.* 2002).

Dissolved Polymers

If there is a goal to prepare long-lasting bubbles – as in the case of party bubbles – then it is important to include a water-soluble polymer in the formulation. For example, polyvinyl alcohol (PVOH) is a common component in bubble-making kits. Studies have shown that the presence of the PVOH contributes to aqueous foam bubble durability (Gottberg *et al.* 2019; Wang *et al.* 2019; Dehdari *et al.* 2020; Xu *et al.* 2020). Likewise, if one observes troublesome and persistent foam in a pulp and paper manufacturing facility, it is likely that there are significant amounts of a water-soluble polymer or polymers present (Gottberg *et al.* 2019; Wang *et al.* 2019; Dehdari *et al.* 2020; Xu *et al.* 2020). Some of the types of soluble polymers that can play such a role in pulp and paper mill systems are described in the subjections that follow.

Hemicellulose

The wood itself can contribute significant amounts of hemicellulose to the process water in a typical pulp and paper mill system. In principle, a portion of the hemicellulose will become dissolved from the wood material in the course of chemical pulping, *e.g.* the kraft process (Henriksson *et al.* 2024), and during bleaching (Jiang *et al.* 2000). In brownstock washing operations, hemicellulose present in the water is expected to render the air bubbles more persistent due to steric stabilization (Patra *et al.* 2021). In addition, relatively concentrated solutions of hemicellulose can be used for the preparation of solid foam packaging products (Deng *et al.* 2015).

Papermaking additives

Perhaps the most important source of water-soluble polymers in paper machine process water is the size press. During normal operations, soluble starch is applied to the paper surface at a size press, and the main benefits can be increased paper stiffness, increased surface strength, less dusty paper, and therefore less contamination of printing operations (Hubbe 2024). But during periods in which the size-pressed paper does not meet product specifications (*e.g.* due to wrinkles, the wrong basis weight, or the wrong color, *etc.*), the defective paper becomes repulped and sent back into the papermaking process again. Because most of the starch applied at size presses is unmodified (*i.e.* "pearl") starch or oxidized starch, it does not tend to remain adsorbed onto the surfaces of cellulosic fibers in aqueous solution. Rather, it tends to stay in the water phase. For this reason, increased foam levels on paper machines that have size presses are sometimes correlated to the level of "broke" fibers that are being used currently. The dissolved starch's contribution to solution viscosity is expected to contribute to the stability of bubbles, thus hurting the performance of foam-control agents (Jha *et al.* 2000). The stabilization likely can be attributed to the higher viscosity within the bulk phase decreasing the rate of stretching of air-aqueous interfaces. The slower rate of stretching provides more time in which surfactant molecules can exchange between the bulk phase and the interface to maintain stability. Such a mechanism, known as the Marangoni effect, contributes to the stability of bubbles (Chen *et al.* 2015).

Positively charged polymer products, including cationic starch and cationic acrylamide retention aids, are intended to adsorb onto cellulosic fiber surfaces and therefore not build up in the process water. However, there is a limit beyond which the fiber surfaces will have the capacity to adsorb the added cationic polymer. In the case of cationic starch, that limit seems to lie in a range between about 1% and 1.5% on a dry weight basis (Moeller 1966). Two limiting aspects of the fiber surfaces are space and

charge density. Because cationic starch usually has a relatively low charge density (Hubbe 2014), it can be expected that limited space at fiber surfaces usually will determine how much of that product can be adsorbed onto the fibers during a papermaking process.

Often the most problematic water-soluble polymers present in paper machine process water, from the standpoint of foam, are wet-strength agents. These polymers, such as poly(amidoamine-epichlorohydrin) (PAAE), have the job of maintaining at least some of the paper strength after the paper has become completely wet, as in the case of a wet paper towel or paper banknotes unintentionally passing through a washing machine cycle. Difficulties can arise in cases where the PAAE or other cationic wet-strength product is not quite effective enough to reach the wet-strength specifications for the paper product. The natural inclination of the papermakers in such cases is to increase the dosage of the additive. But at some point, the fibers already will have a net positive charge at their surfaces, and any additional wet-strength agent will be repelled from the fiber surface and remain in the water.

Dissolved polymers vs. drainage of bubble walls and surface viscosity

In all of these cases just described, *i.e.* hemicellulose (if present), size-press starch recirculated in broke to the paper machine system, cationic starch used in excess, or sufficiently high levels of wet-strength agent to exceed the charge capacity of the fiber surfaces, the polymers can be expected to impede the drainage of water within the vertical segments of walls between adjacent bubbles (Wang *et al.* 2016). The situation is illustrated in Fig. 9. Note how, within the narrow confines of the liquid layer within a bubble wall, a relatively small amount of water-soluble polymer may effectively keep the bubble wall from draining. Gravity forces that otherwise would have tended to drain water within the bubbles that constitute banks of foam will be blocked, which is a recipe for troublesome foam.

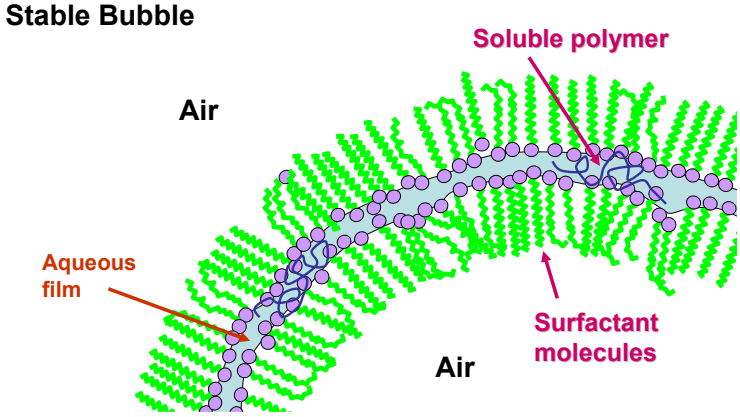

Fig. 9. Schematic illustration of the mechanism by which dissolved polymers that happen to be present in the film of water between adjacent bubbles will tend to hinder gravity-induced drainage, which otherwise would destabilize the foam

Dissolved polymers also contribute to viscosity, which can include the viscous effects associated with bubble surfaces. Brown *et al.* (1953) were the first to note that increased surface viscosity led to increased stability of foams. These concepts have been supported by more recent work (Kanner 1968; Kanicky *et al.* 2000; Wang *et al.* 2019; Choudhury *et al.* 2020). Dehdari *et al.* (2023) observed very stable foams in some systems

that contained both poly(vinyl alcohol) and various acidic nanoparticles, including Al_2O_3; the effects were attributed to the development of a protective layer. Such observations provide a connection to the next topic to be discussed, *i.e.* the likely involvement of particles in the stabilization of emulsions, as well as possible effects relative to foam.

Particulates and Droplets

The presence of various particles or emulsified droplets within process water can be expected to make foam-related phenomena more complicated. In particular, certain particles have been shown to function as stabilizers for emulsions in so-called Pickering systems (Lazaar and Hachem 2022; Deng *et al.* 2025; Marquez *et al.* 2025). It has been proposed that even emulsion droplets, if they get trapped within the walls separating pairs of bubbles, can block gravity drainage and thereby increase foam durability (Koczo *et al.* 1992). It follows that such particles are likely to alter the behavior of foams.

Lignin precipitation due to lower pH

A recent review article has brought attention to the fact that nano-spheres of lignin can serve as stabilizers for emulsions (Marquez *et al.* 2025). Such phenomena are relevant to foam in pulp and paper mills systems due to the fact that such lignin spheres may arise during the washing of unbleached kraft pulps, *i.e.* brownstock washing. As the highly alkaline medium is being displaced by near-neutral rinse water during brownstock washing, the pH value is lowered. This results in the protonation of phenolate groups ($pK_a \cong 10$) within the lignin, along with a substantial reduction in the amount of negative charge associated with the lignin. It has been shown that with the progressive lowering of pH, more and more lignin comes out of solution (Hubbe *et al.* 2019; Trovagunta *et al.* 2024). For instance, 90%-pure lignin can be obtained just by acidifying alkaline pulping liquor and heating it (Lynn *et al.* 2025). Micrographs of kraft fibers that have been collected after brownstock washing sometimes show the presence of granular particles at fiber surfaces (Koljonen *et al.* 2004), and these have been assumed to be lignin. Whether and how such particles might affect foaming behavior does not appear to have been studied in detail. It is possible that such particles may impede gravity drainage of films of water between pairs of bubbles (Koczo *et al.* 1992).

In the event that lignin particles become incorporated into foam in pulp and paper mill systems, there is reason to expect that such bubbles will have a more brittle character (Lazaar and Hachem 2022). The reason has to do with an absence of Marangoni-type effects, which explain the high stability of typical surfactant-stabilized foam system (Anazadehsayed *et al.* 2018). In other words, there is a smooth increase in interfacial tension when such ordinary foam bubbles are stretched, but such flexibility would not be found if particles were the main stabilizing component. Though brittle foam banks could possibly be beneficial from the standpoint of foam control, one needs to be concerned about adverse effects of deposits, as will be discussed next.

Deposit promotion

A further way that precipitation of lignin, especially in the presence of foam, can adversely affect pulp and paper operations is by contributing to deposits on the operating equipment. Foam bubbles can play a role in collecting relatively hydrophobic particles, using mechanisms related to those described earlier in the context of DAF units and removal of ink from process water (*i.e.* Fig. 7). Unintended foam banks can collect at multiple locations within pulp and paper mills, such as at the surface of tanks and within

air-padded headboxes. If and when such processes bring about the agglomeration of particles such as lignin, there is a danger that visible spots may appear in paper products.

MONITORING OF ENTRAINED AIR AND VISIBLE FOAM

In principle, there are several ways in which air bubbles within pulp and paper mill fiber suspensions can be monitored. These can be classified as (a) ways to monitor visible foam, (b) ways to quantify the relative volume of air bubbles within water specimens, and (c) ways to detect and characterize the presence of entrained air bubbles within water.

Monitoring Visible Foam

The monitoring of visible foam is highly dependent on the layout of process equipment. In a typical brownstock washing system, foam can be expected to develop in locations where water is cascading through a mesh screen. However, that location will be hostile for placement of camera equipment. Thus, a flow channel placed after the washer itself can be recommended. In order to provide a quantitative element, a digital camera system can be set up to quantify attributes of foam (Honkanen and Eloranta 2023).

Monitoring Entrained Air by Density

To monitor the quantity entrained air, a simple approach is to accurately weigh a specified volume of flowing process water at ambient pressure (May and Buckman 1975; Allen *et al.* 1993). In principle, in the absence of bubbles, a dilute aqueous solution will have a density of approximately 1.000 g/mL. If fibers are known to be present, this value might be different, but still rather steady and predictable. Thus, calibration values can be obtained by occasionally placing pure water in the device. Downward deviations from the calibrated density, after correcting for the effect of fiber content, can then be attributed to the volume occupied by bubbles.

More complete information can be obtained, starting with a similar known volume of process water or dilute fiber suspension, if the pressure can be varied in a systematic way (Allen *et al.* 1993). Thus, Dougherty (1989) describes the use of a piston to systematically change the volume of a rigid container system, with simultaneous evaluation of the pressure. In this way, it is possible to quantify entrained air by volume. Information obtained during automatic running of the devise can be used as the basis for controlling the flow of a foam-control agent. Ajersch *et al.* (1992) showed that superior results could be achieved when using a vibrating U-tube containing a flowing papermaking fiber suspension, in which results were being compared at two different applied pressures. The resulting values of dispersed air content were judged to be sufficiently accurate, and the tests could be carried out continuously at high speed.

Ultrasonic Monitoring of Entrained Air

The presence of bubbles in an aqueous sample is known to affect the transmission of ultrasound (Allen *et al.* 1993). By using such an approach, online equipment has been developed for online monitoring of entrained air in paper machine systems (Pietikainen 1992). As shown by Bamberger (2006), the ultrasonic waves are able to effectively quantify entrained air even in the presence of cellulosic fibers. Audible sound waves also have been used in laboratory work (Al-Masry *et al.* 2006). The cited work showed

interesting effects of foam-control agents on bubble size distributions depending on the flow rate of the water and in response to anti-foam treatments of the surfactant solutions.

Online Control of Foam

The next step after establishing an automated measurement of entrained air or visible foam in pulp and paper mills can be to close the loop and implement a controlled system of adding a foam-control agent (Sheppard *et al.* 2011). By this means, greater stability can be achieved with respect to such outcomes as the production rate, the steadiness of the operations, and the regularity of paper quality.

Defoamer testing

An effective basic system for laboratory evaluation of defoaming agents can be assembled with a graduated cylinder that is supplied with sparged air at the base (Allen *et al.* 1993). Lobo and Bolton (2013) and Bolton *et al.* (2014) describe a procedure in which the air is first sparged into a stirred container filled with the aqueous mixture of interest. The contents are then transferred to a graduated cylinder to measure the volume. The volumetric air content is determined by comparing the mass with a calibration amount obtained with an air-free reference specimen. The next step in the test uses vacuum to form a mat of pulp. The rate of drainage provides a measure of how much the foam bubbles are interfering with drainage. A somewhat more sophisticated arrangement can be set up with continuous pumping. By such means it is possible to measure not only the height of foam but also an indication of how long various foam-control agents can continue to be effective after their addition (Clas and Allen 1994). In addition, there is an ASTM method (D 3519, 1993) that employs a kitchen blender to generate the foam.

When running lab equipment such as that just described, it is critical to match aspects of the conditions within the pulp and paper manufacturing facility of interest as closely as practical. In particular, it is important to carry out tests at the same temperature as is prevalent in the industrial process. This is important because some of the most effective defoaming agents are likely to be formulated so that they will have greatest effectiveness within a selected range of temperature. The highest performance of such products is often just above the cloud point temperature of the surfactant contained in the foam-control product formulation (Pletnev *et al.* 1983; Nemeth *et al.* 1998; Chaisalee *et al.* 2003). As the temperature is raised to the cloud point, surfactants in the mixture become unstable, leading to the rapid development of emulsion droplets (Hinze and Pramauro 1993). Notably, at such conditions, a coacervate phase can essentially provide droplets of emulsion, which may play the role of foam-control agents. In view of the effects just described, there can be a strong incentive to carry out lab tests right at the industrial facility of interest. In that way, by taking quick samples from the actual process, not only can the temperature conditions be easily matched, but there may be various unknown impurities in the process that would be absent if tests were done elsewhere.

MECHANICAL DEAERATION TECHNOLOGY

Overview of Mechanical Deaeration Devices

In different paper machine systems, there are basically three kinds of approaches that are being used to mechanically remove air during continuous processing within pulp and paper mills. As described in the subsections that follow, these can be described as

inherent rising of bubbles to the surface of water, vacuum deaeration, and centrifugal deaeration.

Inherent Rising of Bubbles to the Surface in a Chest

Of all methods to be considered, the "inherent rising of bubbles" approach is both the most commonly practiced and the simplest, since it merely takes advantage of the existing layout of equipment in a typical paper machine system. On a Fourdrinier paper machine, when water drains through the forming fabric, it rains down onto a shallow pool of water held by a so-called "tray". At that location there is considerable opportunity for sufficiently large bubbles to float to the surface and perhaps pop, except that both of these events will depend on the size of the bubbles. According to the Stokes equation (Guazzelli 2011), a bubble as small as 1 μm in radius will require about four hours to rise 5 cm (perhaps the depth of water in a hypothetical pool in a tray) at a temperature of 40 °C, which is within the common range for paper machine operations. At that rate there will not be effective separation during the several seconds that it would likely take for the water to pass through the length of the tray. By contrast, if the bubbles have a radius of about 1 mm, then only about 0.015 seconds would be needed to escape to the surface of the same tray. In principle, such a growth of bubble size might be achieved by multiple coalescence events involving pairs of bubbles.

Escape of bubbles to the top of various chests, including the seal tanks and white water silo, are expected to be yet more challenging due to the depths of those units, and also the fact that there will be a downward flow in the white water silo, since the flow from the base of the silo goes back to dilute incoming thick-stock at the fan pump. Twin-wire forming sections lack the spacious tray systems, so there is even less opportunity for bubbles to be able to separate themselves by rising.

Vacuum Deaeration

Much more effective mechanical deaeration can be achieved, even removing both dissolved and entrained air from paper machine furnish, by using equipment that applies a vacuum (Allen *et al.* 1993; Matula and Kukkamäki 1998; Matula 2000).

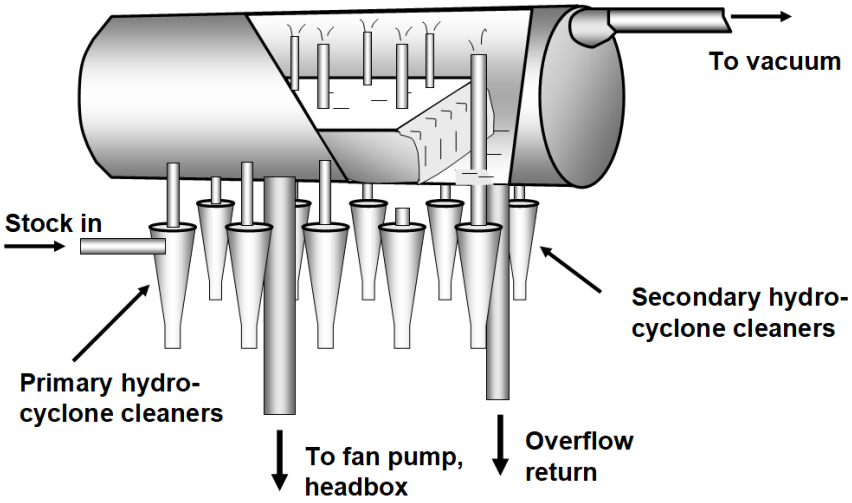

Fig. 10. Schematic diagram of vacuum-type deaerator equipment acting to remove air from the accepts flow of hydrocyclone cleaning devices in a paper machine system

To take advantage of gravity, such devices are typically located well above the main floor of the paper machine forming section. In this way, a hydrostatic head of water at least partly compensates for the inherent depressurization required for the vacuum operation. Figure 10 shows a schematic diagram of a vacuum deaeration device.

Note that this device has been set up to receive the accepts from a set of hydrocyclone cleaners, such as already has been depicted in Fig. 4. This is appropriate, since, as mentioned earlier, hydrocyclones can be an important source of air entrainment. As shown in Fig. 10, vacuum is applied at the top of the deaeration unit. The negative pressure causes much of the dissolved air present in the water to emerge as bubbles. The low pressure causes such bubbles to be much larger than they would have been at ambient pressure, which favors their rapid rising and separation from the bulk phase of the water. It is also being assumed that collisions among the bubbles will result in yet larger bubbles and that those bubbles will quickly pop (presumably due to the action of foam control agents, which are the subject of the next section). Thus, water that overflows a weir and continues on its journal towards the headbox and forming section of the paper machine will contain very little air. This situation is depicted in Fig. 11, which compares a modern Fourdrinier paper machine system without and with a vacuum deaerator of the type described above. Note the large contrast in the level of dissolved air after the deaerator in the right-hand part of the figure. Also note the lack of either kind of air in the headbox, as reported in the cited work for the system fitted with the vacuum deaeration system.

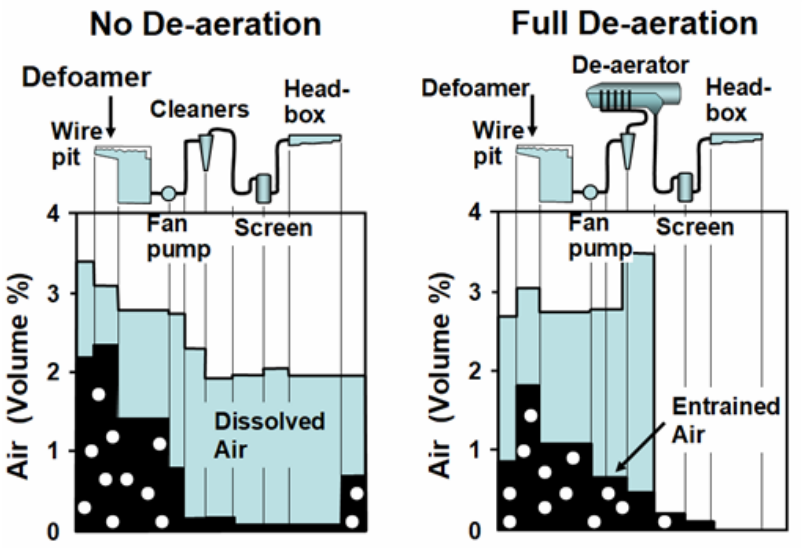

Fig. 11. Schematic diagram of expected levels of entrained (while bubbles with back background) and dissolved (blue background) air in a Fourdrinier paper machine system without and with a vacuum-type deaerator (figure redrawn based on an original by Matula and Kukkamäki 1998)

Centrifugal Deaeration

When using centrifugation rather than vacuum as a means of removing air from papermaking furnish, the goal is not to remove dissolved air (Meinander and Olsson 1999; Cutts 2004). Rather, mainly the dissolved air is the target for removal. Another key difference is the placement of the device. Centrifugal deaerators, as depicted in Fig. 12, are placed on the floor below where the forming section of the machine is located. Specifically, it will be placed between the base of the white water silo and the fan pump. Note that the

system needs to be actively controlled, *e.g.* by measuring the pressure of the air being drawn from the device, to maintain the "water wall" in a stable position for smooth operation. Again, in this case, users of centrifugal deaeration equipment don't expect to rely on it alone; rather they will probably also be running an optimized chemical foam control product or products, as will be described next.

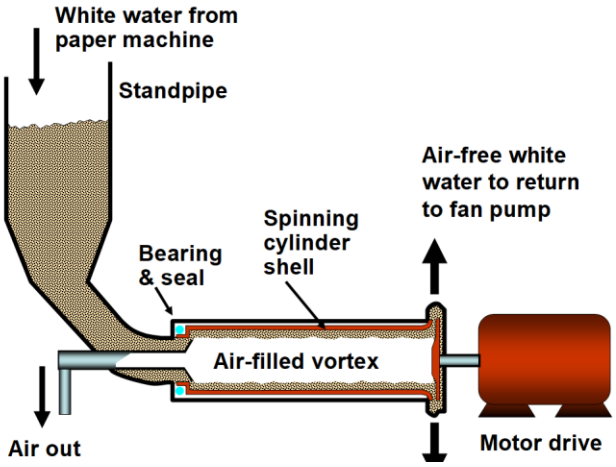

Fig. 12. Schematic diagram of a centrifugal-type deaerator intended to remove entrained air from papermaking process water soon after it has been released from the wet web in the forming section of the paper machine (figure redrawn based on an original from Meinander and Olsson 1999)

PRINCIPLES OF FOAM CONTROL

To shed light on current understanding of both foam stability and its control, this section starts with a historical overview of the development of foam-control products, then classical descriptions of the mechanisms of those agents, and then feeding strategies aimed at taking advantage of such mechanisms.

Foam-control Chemistry Historical Overview

The history of the development of foam control agents can provide some insight into how they work. Among the first known foam-control agents were simple oils (Allen *et al.* 1993). These had various bad effects, *e.g.* possible oily spots in paper products. One can envision such products as being able to scavenge a range of potential foam stabilizing substances, such as fatty acid soaps, from aqueous mixtures due to their generally hydrophobic nature. In addition, though it has not been much used as an industrial defoaming agent, it has long been appreciated that milk can be quite effective for control of foam in some instances (Allen *et al.* 1993). This fact can be regarded as a hint in the direction of modern foam-control agents for pulp and paper manufacturing applications, which mostly consist of emulsions. In the case of milk, the oil in the droplets will include triglyceride fats, and the surface-active agents include lecithin (Ho *et al.* 2023).

Foam control agents designed for paper machine applications have been known at least since the 1940s (Morehouse 1945; Robinson and Woods 1948). Early developers of foam control technology learned that better performance could be achieved by optimizing both the oil phase (the droplets) and the stabilizers (generally surface-active agents) (Allen

et al. 1993). There was a need for further developments when it was discovered that some aromatic components in petroleum-type oils could react with chlorine bleach using in some pulp and paper mills, with the production of highly toxic chlorinated aromatic compounds (Allen *et al.* 1993). One of the ensuing directions of development was to use aromatic-free petroleum oil, namely low-odor paraffin solvent (Clas and Allen 1994). Another developmental path was to abandon the usage of petroleum altogether and to rely on silicone-type components (Allen *et al.* 1993). Such an approach had the added advantage of usually not promoting deposition of fatty and resin acids in pulp and paper mill systems (Bradt *et al.* 1996). The reason is that the silicone-type compounds, though being hydrophobic, generally are not mutually soluble with the hydrophobic compounds that are released during the pulping of wood (Hansen 2007; Hoekstra 2007).

Surfactants as Components in Foam-control Formulations

Types of surfactants employed

Surfactants, which generally can be defined as molecules having a hydrophilic group connected to an oleophilic group, can be regarded as required ingredients of all fast-acting foam-control agents (Pelton 1989; Garrett 1993; Denkov *et al.* 2014). Their effectiveness in this role can be attributed to their tendency to form monolayer films at the air-water interfaces (Jha *et al.* 2000). The hydrophobic groups of such surfactants are often derived from vegetable oils, *e.g.* C18 alkyl chains. The goal is to select surfactants having a tendency to quickly form saturated monolayers, meaning that the hydrophobic portions of the molecules comprise a densely packed monolayer at the air-water interface (Jha *et al.* 2000). Continual exchange of surfactants from the water and micellar phases with the interface contribute to a two-dimensional film pressure, which can lead to film spreading. A diverse range of surfactants used in various foam control products have included fatty alcohols (Joshi *et al.* 2005), fatty alcohol ethoxylates (Sawicki 2005), and nonylphenols with C8 to C10 length ethylene oxide hydrophilic chains (Chaisalee *et al.* 2003). Jha *et al.* (2000) demonstrated effective foam control action with twelve highly diverse surfactants, including cationic, anionic, and nonionic varieties.

Table 2 lists a variety of surfactants that have been claimed in US patents as possible components of foam-control patents. Something worth noting in this tabulation is the very wide breadth of some of the patent claims, even including cationic and amphoteric surfactants as possibly being viable components of foam-control formulations. Such options may or may not be the preferred embodiments, which sometimes are spelled out in either examples or claims of the same patents. As a general rule, nonionic surfactants have been specified most frequently in US patents of foam-control formulations. A practical reason for this preference is the fact that such surfactant systems are less likely to be sensitive to such factors as pH, salt concentrations, and differences in colloidal charge of different industrial processes.

Table 2. Examples of Surfactants Listed in US Patents Describing Possible Foam Control Formulations

Class of Surfactant Claim in Patents	US Patent Citation
Nonionic emulsifiers such as condensation products of higher fatty alcohols and ethylene oxide, or with alkylphenols, *etc.*	Berg and Smalley 1977
Soaps of fatty acids containing 12 to 22 carbons. Also sulfonates and nonionic surfactants such as ethylene oxide glycol esters of long-chain fatty acids.	Shane and Schell 1978
Ethylene oxide condensate surfactants, *e.g.* octylphenol	Gammon 1980
Silicone surfactants, such as polysiloxane-polyakylene oxide copolymer, which may be combined with other surfactants	Schmidt & Gammon 1980
Anionic, cationic, or nonionic surfactants, such as having a fatty acid chains of 12 to 22 carbons and polyoxyethylene surfactants.	Elfers 1980
Anionic or nonionic surfactant, such as a fatty acid soap or polyoxyethylene chain attached to a long-chain fatty acid alkyl chain	Boylan 1981, 1982
Anionic surfactants that include ethylene oxide and alkyl chains	Abel *et al.* 1989
Nonionic polyether surfactant with a polyhydric alcohol fatty acid ester	Svarz 1990a,b
Anionic or nonionic surfactants or mixtures are preferred, including salts of higher fatty acids and alkoxylated alkylphenols	Deac *et al.* 1990
Polyethylene glycol, dimethylpolysiloxane, alkoxylated dimethylpolysiloxane, *etc.*	Furman 1992
Nonionic surfactants including polyethylene glycol esters	Nguyen 1994
Anionic, cationic, or nonionic surfactants or mixtures, including salts of fatty acids, oxyalkylated phenols, such as nonylphenol or isooctylphenol reacted with ethylene oxide, *etc.*	Wegner *et al.* 1994
Nonionic polyether surfactant with a polyhydric alcohol fatty acid ester	Nguyen 1995
Surfactants derived from polyethylene glycol, polypropylene glycol, polypropylene triol, alcoxylated dimethylpolysiloxane, *etc.*	Kim 1996
Nonionic polyether surfactant made by propoxylation of propylene glycol followed by ethoxylation	Hendriks 1996
Anionic, cationic, or nonionic surfactants	Wollenveber 1997
Anionic, cationic, or nonionic surfactants, as well as mixtures	Schumacher *et al.* 1997
Anionic surfactants such as alkylbenzenesulfonates or alkyl sulfonates	Moller *et al.* 1998
Anionic, cationic, and nonionic surfactants, including fatty acid soaps, amine salts, polyethylene oxide condensation products, *etc.*	Pichai and Breindel 2001
Combination of certain alkoxylated alcohol and anionic surfactants	Corbel *et al.* 2003
Nonionic surfactants including sorbitan fatty acid ester, glycerol fatty acid ester, fatty acid-poly(alkylene oxide), and silicone-based emulsifiers	Cheng *et al.* 2011a,b
Polyethylene glycol, alkyl-modified silanes, ethylene oxide/propylene oxide block copolymers, alkylpolyethylene oxides, fatty acid sorbitan esters, *etc.*	Martin *et al.* 2012
Nonionic surfactants such as ethoxylated alcohols, sorbitan esters with fatty alcohols, silicone polyethers, propylene oxide/ethylene oxide copolymers, anionic surfactants, *etc.*	Lobo *et al.* 2016
Nonionic: polyoxyalkylene-modified organopolysiloxane, as well as sorbitan fatty acid esters, polyethylene alkyl ethers, polyoxyethylene oxypropylene alkyl ethers, polyoxyethylene castor oils, *etc.*	Kobayashi *et al.* 2019
Nonionic, anionic, cationic, amphoteric, and mixtures of surfactants. Examples include polyoxyethylenelauryl alcohol.	Heebner *et al.* 2025

Hydrophilic-lipophilic balance (HLB) of the surfactants

As a general principle, a surfactant to be employed in a foam-control formulation will need to be able to displace and spread within existing monolayers of surfactants already present in a foamy mixture that requires treatment. A rule of thumb in selecting suitable surfactants for that role is called the hydrophilic-lipophilic balance (HLB) Griffin 1954). On the HLB scale, a higher number will correspond to longer or more influential hydrophilic groups compared to lipophilic groups. When studying a series of nonionic surfactants, Rodríguez-Abreu (2019) found a strong correlation between HLB values and the packing density of the ethylene oxide groups.

Based on Fig. 13, the surfactants used in foam-control would be expected to have hydrophile-lipophile balance (HLB) values in the range of about 2 to 3, meaning that they would be strongly lipophilic (Pasquali *et al.* 2008). Most studies of foam-control agents have reported higher values. For instance, Zhang *et al.* (2007) found good foam control results when using surfactant blends with HLB in the range of 8 to 9, and Gao *et al.* (2023) reported excellent defoaming results with use of a surfactant having an HLB of about 10.5. Qiao *et al.* (2022) found increasing effectiveness of foam control formulation with decreasing HLB values in the approximate range 12 to 10. Gao *et al.* (2024) reported strong foam control action with a polyether modified polysiloxane surfactant having an HLB of 10.5.

A possible reason for the apparent disagreement is that there is likely to be a very wide range of prevailing surface tensions in system requiring foam control. Christiano and Fey (2003) compared 11 widely available commercial surfactants having HLB values ranging from 3 to 21 as potential anti-foam agents. All were judged to be effective, though the amount of surfactant required was found to decrease with in increasing HLB value. In other words, surfactants with higher HLB values were more effective. A second possible reason is that particulate additives to such formulations (see later) are typically highly hydrophobic, and sometimes other components of the formulation can play related roles.

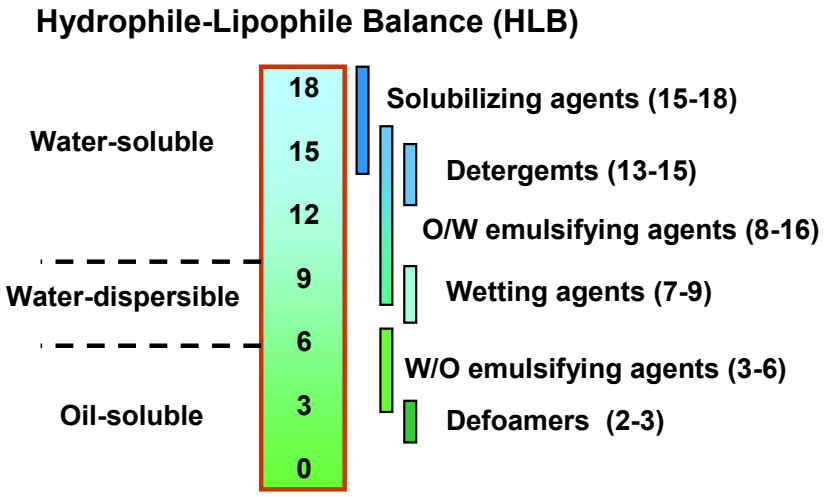

Fig. 13. Summary of hydrophile-lipophile balance (HLB) values associated with various common applications of surface-active agents (redrawn based on a Wikipedia figure)

Table 3 provides HLB-related "preferred ranges" or specifications that have been provided in US Patents having the words "antifoam" or "defoamer" in the title. While patents are not always based on statistically significant findings, they can provide insight into what corporations are placing emphasis on and investing in. Note that the Table is organized according to increasing value of HLB (or mid-point in a range of preferred HLB values). It is notable that the HLB values of such surfactants spanned a huge range from 0.1 to 12. Only one of the patents listed numbers in agreement with the HLB values of 2 to 3 listed in Fig. 13 for defoamers. A possible explanation for those low values is that such components might be playing the role analogous to hydrophobic particles in some foam-control formulations.

Table 3. Hydrophilic-Lipophilic Balance (HBL) 'Preferred Ranges' of Specified Values for Various Surfactants in 'Antifoam' and "Defoamer" Agents Described in US Patents

Component of Foam Control Formulation	HLB	Citation
Ethylene oxide/propylene oxide block copolymer	0.1 to 5	Hendriks 1996
Surfactants for brownstock washer siloxane copolymer defoamers	>5	Lobo *et al.* 2016
Surfactants such as long alkyl chain alcohols, carboxylic aids, and esters	>6	Wegner *et al.* 1994
Surfactants, such as sodium or ammonium salts of fatty acids of alkoxylated alkylphenols or oxyethylated oils	>6	Schuhmacher *et al.* 1997
Polyether surfactant with a polyhydric alcohol fatty acid ester	7 to 10	Svarz 1990a,b
Nonionic emulsifier, condensation products of higher fatty alcohols with ethylene oxide chains	8 to 12	Berg & Smalley 1977

Figure 14 describes a common observation, in the development of foam-control agents, that with increasing hydrophobic character, the surfactants contribute more and more to the stabilization of foam (Zarate-Muñoz *et al.* 2015). But after gradually raising the temperature and reaching a maximum in foaminess, known as the cloud point, an abrupt collapse of foam often is observed. The transition defines the point beyond which the surfactant has become slightly too hydrophobic or too insoluble for foam stabilization. Zarate-Muñoz *et al.* (2015) showed that the cloud point can be predicted based on the HLB value and other aspects of nonionic surfactants.

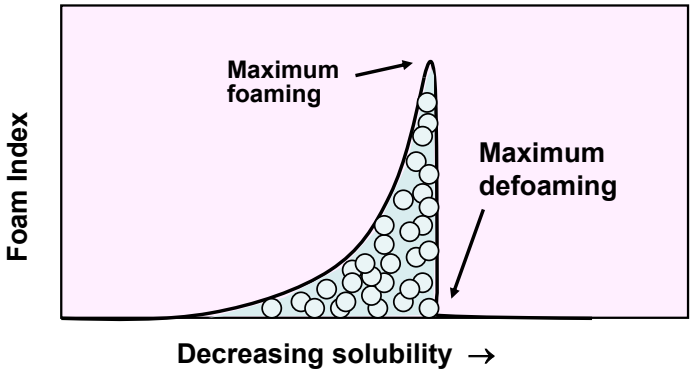

Fig. 14. Commonly observed dependency of foam characteristics of surfactants relative to their water solubility (figure adapted from TAPPI Introduction to Wet End Chemistry course)

Microemulsion-type formulating and the HLD_N concept

It can be hypothesized that optimal formulation of a foam-control agent might be governed by the same physical phenomena associated with optimization of detergent systems and microemulsions (Hubbe *et al.* 2022). The reason is that, just in the case of foam-control systems, microemulsions used in detergent systems tend to perform best when interfacial tensions become very low. In microemulsions systems, such as cold-water laundry detergents, it has been found that the hydrophilic-lipophilic difference or deviation (HLD_N) (Salager *et al.* 2000; Salager 2021) can be a key variable. This parameter represents the difference of a given surfactant system from its optimum formulation for emulsification, and it can be calculated based on physical parameters (Salager *et al.* 2000; Zarate-Muñoz *et al.* 2015; Salager 2021). Notably, some US patents contain references to the principles of microemulsions (Gammon 1980; Nguyen 1994; Furman 2002).

Spreading of oils and surfactants

Dating back at least to the time of Benjamin Franklin (1774), it has been appreciated that suitable hydrophobic oils can spread rapidly on water surfaces, forming very thin films. The extent of the spreading was such that 5 mL of the oil smoothed the waves of the pond over an area of several square meters. A requirement for such action is that the compounds need to have sufficiently large hydrophobic groups to render them insoluble in water, while at the same time having at least one hydrophilic group. Though a great deal of science has been learned since the days of Franklin, modern foam control agents generally contain at least one water-insoluble surfactant having a rapid-spreading tendency. These mixtures are often formulated by emulsification of an oil (Bergold *et al.* 1990; Ishida 2001). For instance, when formulating a food product, a defoaming effect can be achieved by including certain flavor oils (Qi *et al.* 2018).

Silicon-based products and oil-free options

Silicone-related oil products have become increasingly popular for control of foam (Sinka and Lightman 1977; Rekonen *et al.* 1990; Brandt *et al.* 1996; Campbell *et al.* 1997; Jha *et al.* 2000; Hoekstra 2007). The oil in such formulations can be poly(dimethylsiloxane) (PDMS), which is highly hydrophobic (Hill and Fey 1999; Owen 2010). However, the PDMS can optionally be omitted in formulations based on just the surface-active components. Nonionic surfactants have been combined with silicone-based formulations to fine-tune the performance (Christiano and Fey 2003). Another popular way to prepare commercial foam-control agents is to use water as a main component (Twoomey 1986, 1990); such formulations were said to be less expensive than similar products formulated with oils. The success of such products provides further support for strategies in which one is relying mainly upon just surface-active agents, along with optional hydrophobic particles, to carry out the defoaming action.

Hydrophobic Particle Additives

Another milestone was the discovery that foam-control products could be rendered more effective by their formulation with suitable particles (Allen *et al.* 1993; Ayeyard *et al.* 1994; Brandt *et al.* 1996; Spence 1997; Denkov 2004). These can include fumed silica that has been rendered hydrophobic. For instance, a trialkoxyalkylsilane can be reacted with the silica surfaces (Belyakova and Varvarin 1999; de Vos *et al.* 1999; Wang *et al.* 2013). Amide wax particles, such as ethylene-bis-stearamide (EBS), also have been widely used, especially in brownstock washing (Allen *et al.* 1993; Brandt *et al.* 1996). Best effects

are achieved when such particles are hydrophobic (Kulkarni *et al.* 1977b; Aveyard *et al.* 1993; Garrett *et al.* 1994; Denkov 2004; Joshi *et al.* 2009) and preferentially with an angular or jagged shape (Frye and Berg 1989; Pelton 1989; Wang *et al.* 2013, 2024). Here, the word "angular" implies that the particles include some acute angles and sharp edges. Aveyard *et al.* (1994) reported effective foam breakage with cylindrical particles, whereas the spherical particles they considered actually contributed to foam stability in some cases. In addition, the performance of the hydrophobic particles often increases with increasing particle size (Kosco *et al.* 1994; Joshi *et al.* 2005). Joshi *et al.* found maximum foam destruction when the hydrophobic particle size was about 3 μm. Direct observations by Tamura *et al.* (2000) showed that bubbles broke when the thickness of their surfactant bilayer wall had been decreased to match the size of hydrophobic particles. Wang *et al.* (1999) showed that hydrophobic silica particles tended to situate themselves at the interface between silicone oil and air, which is consistent with their apparent role in piercing the surfactant bilayer between adjacent bubbles.

Table 4 lists some attributes of hydrophobic particles that have been specified in US patents of foam-control formulations. Though a relatively wide range of particle sizes is represented within the list, it is notable that most of the cited ranges include particles at least as large as 1 μm in diameter or somewhat larger. Such particles would be sufficiently large to be able to bridge the aqueous films between adjacent bubbles. It is a common experience that rainbow colors can be seen when viewing airborne aqueous bubbles, and such observations provide evidence that the respective bubble-wall thicknesses were one or more factors of a wavelength of visible light, *i.e.* at least 400 to 700 nm. Bubbles that do not show colors are likely to have bubble walls that are thinner than this range.

Table 4. Attributes of Hydrophobic Particles for 'Antifoam' and "Defoamer" Formulations Described in US Patents

Attributes of Hydrophobic Particles to be Used in Foam-control Formulations	Particle size (μm)	Citation
Amides and hydrophobic silica particles	0.02 to 1	Michalski & Youngs 1975
Hydrophobic amide-type particles that have been finely ground	< 44	Suwala 1976
Hydrophobic silica particles, with conflicting descriptions of particle size	<1 or 15	Berg & Smalley 1977
Hydrophobic amide particles with sizes of 5 to 6 on the Hegman scale	25 to 38	Shane & Schell 1978
Almost any particle size of silica particles may be used, but finer particles preferred	"Finer"	Ihde 1978
Hydrophobic silica particles	0.02 to 1	Schmidt & Gammon 1980
Silica particles rendered hydrophobic by surface esterification with a fatty epoxide	14 to 22	Slovinsky & Masciaszek 1982
The presence of hydrophobic particles (fumed silica) within lenses of silicone oil was judged to be necessary by not sufficient to bring about bubble collapse at Plateau borders.	6 to 8	Wang *et al.* 1999
Hydrophobic amine particles such as ethylene bis-strearamide	< 100	Pichai & Breindel 2001
Kaolin, chalk, bentonite, talc, silica, urea-formaldehyde, *etc.*	0.1 to 10	Dyllick-Brezinger *et al.* 2005

Silica particles rendered hydrophobic by coating with poly (dimethylsiloxane)	-	Kremer 2008
Hydrophobic silica particles	< 10	Schneider *et al.* 2010
Hydrophobic silica particles or ethylene bis-strearamide	2 to 110	Cheng *et al.* 2011a,b
Hydrophobic particles can be silica, wax such as ethylene bis-strearamide, or other.	-	Lobo *et al.* 2016
Fumed silica, *etc.*, which may have been modified by silane compounds or other treatments	0.01 to 0.5	Heebner *et al.* 2025

Classic Descriptions of Foam-control Mechanisms

Cautionary note concerning mechanistic models

In the subsections that follow, it is important to bear in mind a note of caution from Wang *et al.* (2016). They pointed out that foam structures are complicated, and different mechanisms can be at work simultaneously. Even when there is excellent evidence to support a given mechanism, the real situation represented by a pulp and paper mill environment can be expected to pose challenges. In contrast to typical laboratory tests, the industrial system will contain such items as cellulosic fibers, changing levels of soluble polymers, a wide range of ions, different temperatures, and differences in the formulation of different foam-control agents. Thus, it will continue to be challenging to bridge the gap between the laboratory and the mill. Denkov *et al.* (2014) expressed an opposing, and therefore more optimistic view regarding foam-control mechanisms. In their view, although the formulations of foam-control agents are highly diverse, the effects of those agents often share a lot of similarities. Likewise, Pelton and Goddard (1994) and Garrett (1995) demonstrated that some effects of foam-control agents can be predicted based on dosage of the agent and other known factors.

Entering

There is widespread agreement in the literature that a droplet of foam-control agent must "enter" into the wall of a bubble as the first step in the mechanism of effective foam control (Robinson and Woods 1948; Ross 1950; Garrett 1993; Ayeyard *et al.* 1994; Ayeyard and Clint 1995; Chaisalee *et al.* 2003; Denkov 2004). In the discussion that follows, main attention will be directed toward a situation depicted earlier in Fig. 7, Parts (b) and (c), wherein three connected bubbles happened to be completely immersed in either air or an aqueous phase, respectively. The vulnerable locations in such assemblies of immersed bubbles appear to be (a) the relatively flat walls that separate each part of bubbles and (b) the junctions between such relatively flat areas in the bubble walls. These locations have become known as Plateau borders, in honor of one of the pioneers in learning about the structure of foam (Almgren and Taylor 1976). Figure 15 envisions a droplet of a foam control product that has been applied as a fine mist as it lands upon and enters the bubble wall. In general terms, for the entering to happen, there must be sufficient affinity between the components of the droplet and the surfactant layer that is stabilizing the foam.

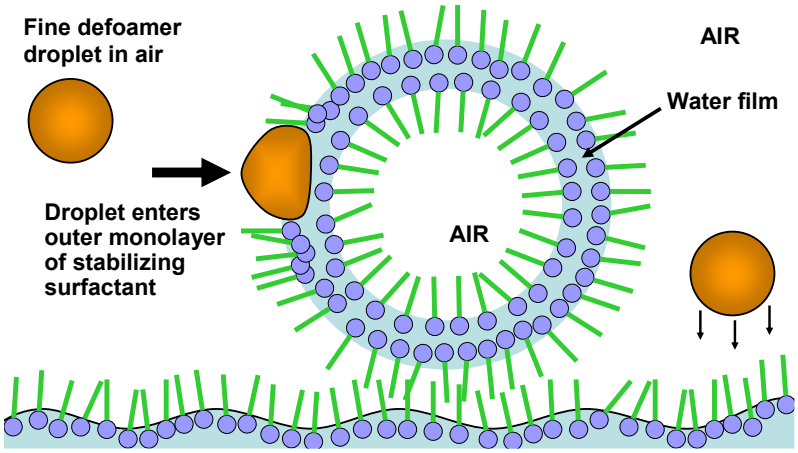

Fig. 15. Schematic diagram of a droplet of foam-control formulation, applied as a mist spray in the air phase, in the process of entering a surfactant monolayer at the wall of a bubble that is resting on the water surface

The next figure envisions a similar effect, except that in this case there are three bubbles, and they happen to be submerged in an aqueous phase. The "hydrophobic particle" depicted in this figure represents a widely employed formulation option (Pelton 1989). Because Fig. 16 represents a mechanism taking places in the water phase, it is required that the foam-control agent be formulated with suitable stabilizing agents, *i.e.* an optimized type and amount of surfactant. The emulsion droplet also may contain an oily component, such as silicone oil, *e.g.* poly(dimethylsiloxane) (Jha *et al.* 2000; Sawicki 2005; Owen 2010; Wang *et al.* 2024).

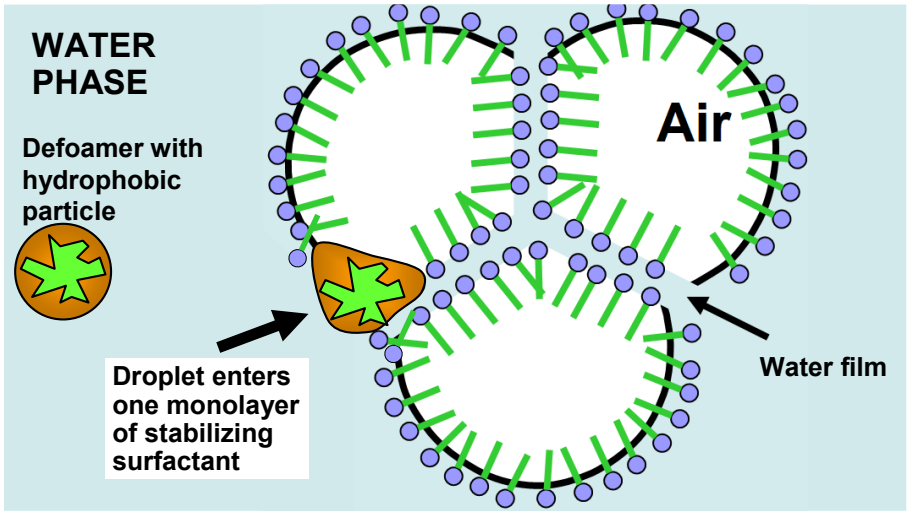

Fig. 16. Schematic diagram of a droplet of foam-control formulation, applied as a mist spray in the air phase, in the process of entering a surfactant monolayer at the wall of a bubble that is resting on the water surface

In order to have its intended effect, it is widely agreed that the emulsion droplet needs to be able to insert itself into a monolayer of surfactant that is acting as the main stabilizer for the foam that needs to be controlled. An "entering coefficient" providing the criterion for entry in the situation depicted in Fig. 16 can be expressed as (Robinson and Woods 1948),

$$E = \gamma_f + \gamma_{d,f} - \gamma_d \quad (1)$$

where γ_f is the interfacial tension (water-air interfaces) in the foamy mixture, the middle term is the interfacial tension in the mutually saturated mixture of "defoamer" and "foamy system", and the final term is the interfacial tension of the "defoamer" in pure water. Entering of the defoamer droplet into the bubble wall is expected when the value of E is greater than zero. In this equation, the word "defoamer" is being used to denote the surfactant in the foam-control agent. To meet this criterion, the value of γ_f needs to be smaller than the sum of the dominant surfactant combination that is serving as the stabilizer of bubbles in the system plus the corresponding term after the system has become fully equilibrated. As illustrated in Fig. 16, that inequality allows the defoamer droplet to enter into the first monolayer of surfactant that it encounters as it enters the bubble from the adjacent aqueous phase. The main take-away is that, to enable the "entering" step to take place, the key requirement that the interfacial tension resulting from the surfactant in the foam-control agent must be moderately low. For instance, according to Eq. 1, the value of γ_f may be higher than that of the foamy mixture itself, in some cases.

As a plausible alternative to directly entering a monolayer of surfactant layer, as was depicted in Fig. 16, another possibility is that a droplet of formulated emulsion diffuses within the Plateau border film of a group of bubbles. This possibility is illustrated in Fig. 17. In such an arrangement it is reasonable to expect that bridging between the adjacent monolayer films can take place later, for instance due to nano-scale wavelike motions within the films. Such a mechanism has been demonstrated by means of high-speed microphotography (Wang *et al.* 1999).

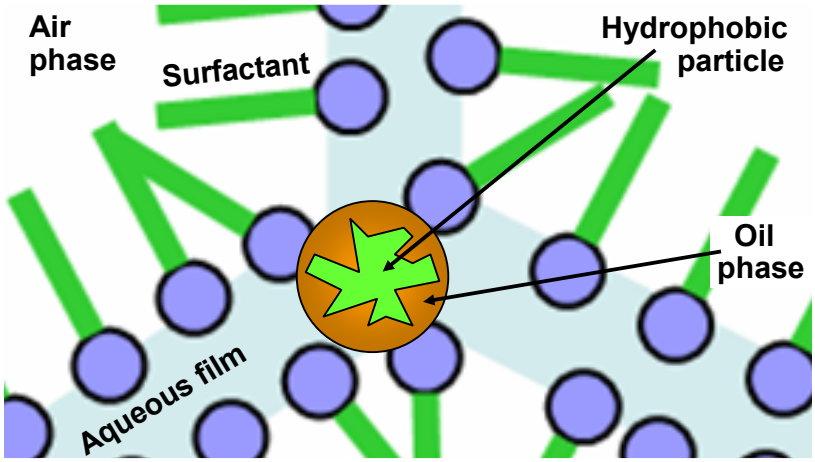

Fig. 17. Schematic diagram of a droplet of foam-control formulation, applied as a mist spray in the air phase, in the process of entering a surfactant monolayer at the wall of a bubble that is resting on the water surface

Spreading

Once a droplet of foam control agent has inserted itself into a bubble wall, the next pertinent question regards whether or not it will be able to spread (Kulkarni *et al.* 1977a; Garrett 1993; Avery-Edwards *et al.* 1994; Racz *et al.* 1996; Denkov 2004; Denkov *et al.* 2014; Pelton 1989; Yang *et al.* 2023). Jha *et al.* (2000) have presented some of the best evidence that the spreading of foam-control oils on bubble surfaces has a strong correlation with the effectiveness of foam-control products. The cited authors showed that a large

spreading tendency can be attributed to a two-dimensional spreading pressure embodied within a condensed monolayer of a well-chosen surfactant (Hubbe *et al.* 2020a). They also reported a strong positive correlation between spreading tendency and the effectiveness of foam control. It is often assumed that the emulsion particle initially is present within just one monolayer of surfactant, rather than spanning two layers of bubble wall (Garrett 1993; Chaisalee *et al.* 2003). The most interesting situation is when one of the foam control droplets happens to be situated right at the Plateau border. Considering that starting point, a spreading criterion can be written as follows (Harkins 1941),

$$S_{d/f} = \gamma_f - (\gamma_{d'} + \gamma_{fd'}) \quad (2)$$

where $S_{d/f}$ is the spreading coefficient, γ_f is the interfacial tension of the foamy system, $\gamma_{d'}$ is the interfacial tension the surfactant in the foam-control system in its present state of saturation with any other surfactants, and the final term is the interfacial tension of the whole system after equilibration.

Bubble wall thinning

Depending on how rapidly the foam-control agent is able to spread within a monolayer of surfactant at a bubble wall, one of the expected effects will be a thinning of the water film separating the two adjacent bubbles. This effect is illustrated in Fig. 18. Denkov *et al.* (2014) envision the walls between adjacent bubbles as having thinned to such an extent that droplets of foam-control agent in the intervening space cause bulges in the bubble's double-wall. As the area between the bubbles is momentarily increased by the spreading action, there will be less water per unit area between the bubbles. This makes the structure more vulnerable to breakage. Experimental work by Tamura *et al.* (2000) showed that such structures can be unstable, leading to bridging by droplets of foam-control agent and subsequent coalescence of pairs of bubbles. In addition, random wavelike motions within the film may result in an opening of a window between the bubbles, and that unstable intermediate structure is expected to rapidly lead to coalescence of the two bubbles into a larger bubble (Garrett 1993). As noted by Pelton (1989), such coalescence can be regarded as the central event which, if repeated very larger numbers of times, can effectively destroy foam in aqueous systems.

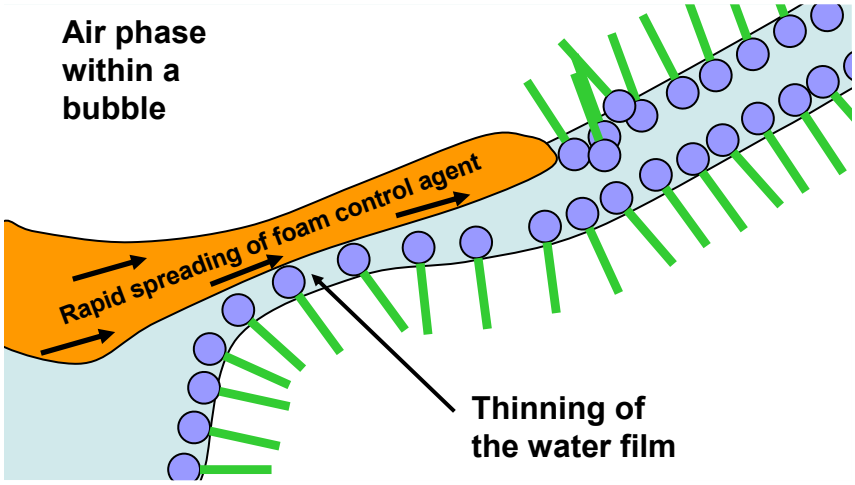

Fig. 18. Schematic diagram representing the hypothesized spreading of the foam-control agents within one of the monolayers in the film between two adjacent bubbles, causing a momentary thinning of the water film between them

The role of hydrophobic particles in piercing bubble bilayer walls

Hydrophobic particles that are used in the formulation of foam-control agents have been shown to increase the effectiveness of many such products (Dippenaar 1982a,b; Frye and Berg 1989; Aveyard *et al.* 1993; Garrett *et al.* 1994; Koczo *et a.* 1994; Ayeyard and Clint 1995; Denkov 2004). The spreading action induced by the foam control agent provides two different opportunities for involvement of hydrophobic particles in piercing the walls between adjacent bubbles. First, the thinning of the wall between adjacent bubbles, as just described, may allow a sufficiently large hydrophobic particle to bridge across both surfactant monolayers that define the bubble wall (Owen 2010). At that point, depending on some details related to contact angles, an opening between the adjacent bubbles may occur (Owen 2010). In other cases, the spreading action may allow the hydrophobic particle to essentially tear open a window between the adjacent bubbles (Pelton 1989; Racz *et al.* 1996). Figure 19 illustrates the mechanical part of the particles' apparent role in ripping apart the surfactant bilayer in the course of spreading of the foam control agent. Rapid spreading events associated with use of foam-control agents were apparently first observed experimentally by Dippenaar (1982a,b).

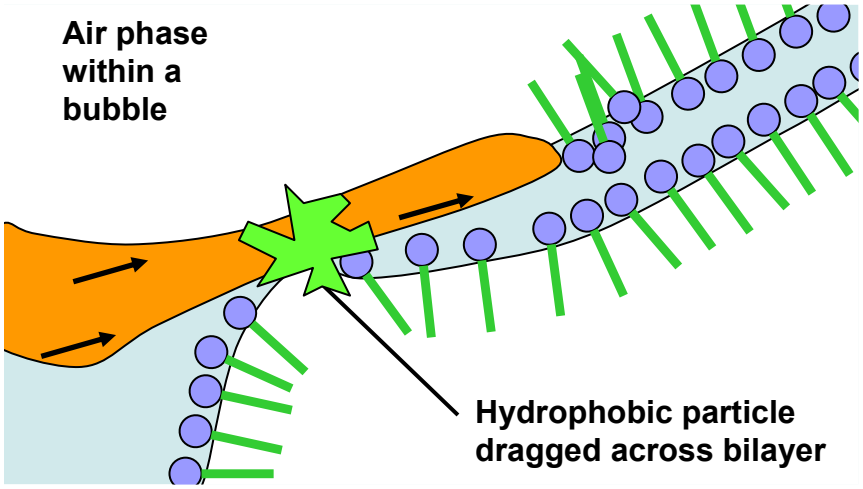

Fig. 19. Schematic diagram illustrating the concept of a hydrophobic particle being dragged rapidly across the bubble wall such that the thinned aqueous film becomes pierced

Another way that rapid spreading of a foam-control product potentially could lead to foam collapse is by rapid localized depletion of surface-active agent (Kulkarni *et al.* 1977b). The cited authors proposed that depletion could come about by rapid adsorption of surfactant onto hydrophobic particles. In view of the Marangoni effect (Pelton 1989; Garrett 1993; Anazadehsayed *et al.* 2018), such depletion could serve as an additional cause of spreading and thinning of the walls between pairs of bubbles.

Viscosity effects

In principle, a rapid spreading action will be favored by a low viscosity of the surfactant used in formulating the foam-control agent. Theoretical studies have identified increasing two-dimensional viscosity at water-air interfaces as an important factor in predicting instances of stable foam (Brown *et al.* 1953; Kanner 1968). Work by Wang *et al.* (2019) and Chowdhury *et al.* (2020) showed that higher surface viscosity (*i.e.* two-dimensional viscosity) tends to render foams more stable. Foam-control formulations with intermediate alkyl chain lengths of the surfactant (*e.g.* eight carbons) are sometimes found

to be more effective than longer lengths (Garrett 1993). At the optimum length, the alkyl chain length may be sufficient to achieve a strong surface-active effects while at the same time contributing relatively little to surface viscosity. In support of these concepts, Jha *et al.* (2000) found that the relative antifoaming efficiency increased with decreasing surface viscosity of the surfactant monolayer.

Bridging

Bridging is widely believed to be a key milestone in the breakage of foam. The bridging agent may be either the foam control emulsion droplets themselves or in many cases the hydrophobic particles in the formulation. The bridges span across the two surfactant monolayers that compose the walls between bubbles (Frye and Berg 1989; Pelton 1989; Aveyard *et al.* 1993; Garrett *et al.* 1994; Koczo *et al.* 1994; Nemeth *et al.* 1998; Denkov 2004; Joshi *et al.* 2009; Yang *et al.* 2023).

A bridging coefficient has been defined in an effort to predict whether or not bridging will occur in a given system (Aveyard *et al.* 1993). The cited authors express such a coefficient as follows,

$$B = \gamma_{aw}^2 + \gamma_{ow}^2 - \gamma_{oa}^2 \quad (3)$$

where γ_{aw} is the air-water interfacial tension, γ_{ow} is the oil-water interfacial tension, and γ_{oa} is the oil-air interfacial tension. Bridging is expected when $B > 0$.

In foam-control formulations that do not contain solid particles, the role of bridging sometimes can be served by an oil component. Such an effect was demonstrated by Georgiev *et al.* (2023). For foamy systems stabilized by various surfactants in combination with poly(vinyl alcohol), they found that foam-control action would be described by a two-step process. First, the foam-control emulsion droplets became situated between adjacent bubbles. Second, the emulsion films at the bubble surfaces became ruptured by the foam-control material.

Pinch-off at surface of hydrophobic particles

The term “pinch-off” will be used in this article to describe an event in which the surface of a hydrophobic particle becomes dewetted due to coming together of lines of three-way contact between the particle, air, and an aqueous phase (Pelton 1989; Aveyard and Clint 1995; Denkov 2004; Owen 2010; Denkov *et al.* 2014; Yang *et al.* 2023). The process is diagramed schematically in Fig. 20. According to Kruglyakov (1994), the onset of film rupture is an indication that three-phase contact (involving air, water, and the solid surface) is not possible due to the contact angles and other factors.

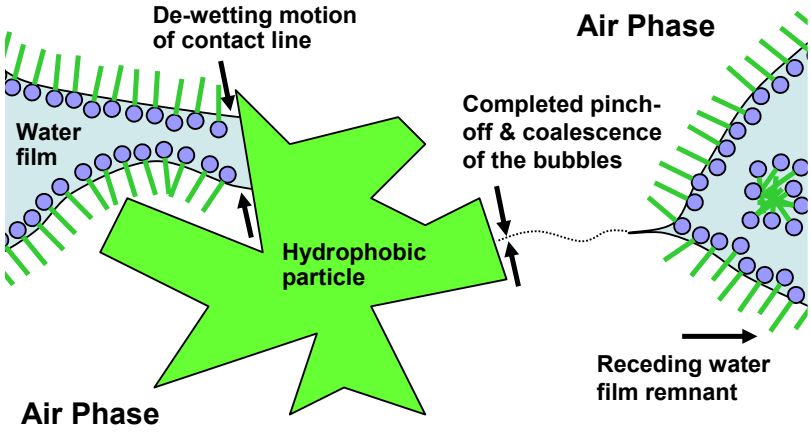

Fig. 20. Schematic diagram illustrating the concept of "pinch-off" due to movement of the meniscus lines of contact at the surfaces of a hydrophobic particle that is used to enhance foam-breaking effects

Onset of bubble coalescence

When focusing on quasi-equilibrium conditions, *i.e.* excluding what might happen during a rapid spreading event, it has been proposed that ultimate collapse of foam, at least at one point, can be predicted based on interfacial thermodynamics (Kruglyakov 1994). Specifically, any three-way contact between water, air, and a third phase needs to conform to relationships that can be determined by experimentation. Thus, whether or not the hydrophobic particle will succeed in opening up a window between adjacent bubbles, especially as a result of relatively slow thinning of a bubble wall, will depend on angles of contact with the hydrophobic particle. The key to success is expected to lie in having a sufficiently low surface free energy of the hydrophobic particle (Belyakova and Varvarin 1999; de Vos *et al.* 1999; Wang *et al.* 2013). In addition, as discussed next, angular particles, containing acute angles and sharp edges, are likely to be more effective in both bridging between the two monolayers of surfactant defining the bubble wall and in enabling the pinch-off process.

Shape of the hydrophobic particles

Particle shape appears to be important relative to the completion of the pinch-off event (Pelton 1989; Garrett 1993; Tamura *et al.* 2000; Wang *et al.* 2024). Frye and Berg (1989) noted that the spherical shape of an emulsion droplet of foam control agent tended to be not as effective as the non-spherical shapes of hydrophobic solid particles. Likewise, though hydrophobic spheres of silica were found to be effective in such products, better effects could be achieved following grinding of such spheres, essentially making micro-shards of glass. The latter particles achieved almost 100% removal of foam. The cited authors proposed that the angular hydrophobic particles were able to achieve easier movement of the lines of three-phase content, leading to more effective bridging, and thereby leading to effective pinch-off. Related work by Joshi *et al.* (2005) showed that the particle must be solid to achieve superior foam-control effects; this is consistent with the necessarily round shape of completely melted particles. Pelton (1989) added a further stipulation that the particles should also be smooth on their faces, thus facilitating rapid movement of contact lines across their surfaces. Yang *et al.* (2023) added the stipulation of "having sharp edges" to the list of desired features in the particles.

Implications of bubble size distribution

It has been shown that treatment of an entrained air suspension with a foam-control agent resulted in heterogeneity of bubble sizes (Al-Masry *et al.* 2006). This situation seems consistent with the non-equilibrium processes described in previous subsections, along with a possibility that the foam-control agent might have a non-uniform distribution in the system, at least initially. Al-Masry *et al.* (2006) employed a sparging system to provide a relatively uniform distribution. Addition of foam-control agent at increasing amounts led to an increased average bubble size, especially at relative low flow rates, which is consistent with the pairwise coalescence of bubbles.

Specifications of surfactants for foam-control products

When developing the formulation for a new foam-control product, there are some general expectations concerning selection of the surface-active agent or agents. There are different ranges for the hydrophile-lipophile balance (HLB) values that have been found to work well for different applications of surfactants. Low values of HLB are representative of compounds in which the hydrophobic end of the molecule is somehow larger or longer than the hydrophilic end, and *vice versa*. Due to the diversity of categories and structures of such compounds, the HLB values can be regarded as guides rather than accurate descriptors. A research question to consider is whether or not desired foam-control effects can be fine-tuned or rendered more robust by using a calibrated ratio of two surfactants having somewhat different HLB values. There is some evidence that pure surfactants have been more successful agents of foam control in some instances (Jha *et al.* 2000).

HLB difference

As was noted earlier, foam-control systems share some common features with modern detergent formulations for laundering (Salager *et al.* 2000; Hubbe *et al.* 2022). In both cases, formulations are optimized in such a way as to achieve very low values of interfacial tension, either briefly or over an extended time. One of the parameters that has been utilized for the optimization of cold-water detergent system is the hydrophilic-lipophilic difference (HLD_N) (Salager *et al.* 2022). The value of this parameter can be calculated based on a salinity term, the alkane carbon number, and some factors that do not change in the course of numerical integration. In principle, the lowest value of interfacial tension is expected when the value of HLD_N approaches zero. However, because the goals of foam control are quite different from those of laundry detergents, it is not yet known whether the HLD_N are equally applicable to foam-control applications. On the positive side, it can be hypothesized that a microemulsion system is likely to be effective for encapsulating surface-active substances present in aqueous mixtures. However, as unfavorable aspect, the long-term persistence of very low interfacial tensions provided by such detergent systems would be expected to adversely affect the development of inter-fiber bonding in paper as it is being formed and dried (Hubbe 2006).

Another point of reference, in selection of a surfactant for a foam-control product, is the cloud point. As mentioned earlier, it is often found that foam-control agents are most effective when they are applied at a temperature near to but above the point at which their pure solution in water becomes cloudy, as the temperature is increased (Pletnev *et al.* 1983; Chaisalee *et al.* 2003). From a mechanistic standpoint, it appears that one should aim for a condition in which the surfactant has developed an unstable tendency due to its insolubility in the water phase.

Loss in effectiveness over time

Once a foam-control agent has been added to an industrial process, one can envision a strong immediate effect on foam, followed by a gradual process of equilibration over the course of time. Such an effect is shown in Fig. 21, which was redrawn in simpler form based on the work of Clas and Allen (1994). As shown, injection of air into a solution of 20% synthetic black liquor caused a rapid build-up to a foam height of about 300 mm. The plotted green triangles corresponded to an oil-based foam control agent, which had a steady effect at preventing the foam level to rise above its initial level. This behavior caused the cited authors to classify the product as an anti-foam agent, since it was effective in preventing foam from developing. In theory, the petroleum-based oil in the formulation could be expected to act as a reservoir for various surface-active compounds, thus reducing their effects as foam stabilizers. The plotted orange circles correspond to a water-based defoamer, which knocked down the foam almost completely for the first 20 minutes or so, but then became progressively less effective. The quick and strong suppression of foam means that the agent would generally be classed as a defoamer. The observed loss of effectiveness, in the latter case, can be attributed to a mixing of materials, eventually tending toward an equilibrated mixture of all the surfactants present in the system. In addition, Racz *et al.* (1996) suggested that the foam-control surfactant soon becomes incorporated into small, stable emulsion droplets, which have lost any defoaming activity. Since the surfactants that would be used in the foam-control product would have a lower interfacial tension than initially present in the system, one can expect that the system's prevailing interfacial tension will end up somewhat lower than it was initially. If such a treatment were carried to extremes, the expected outcome would be such a low prevailing interfacial tension as to make the system resistant to further usage of foam-control agents. In addition, over-use of foam-control products may eventually result in stabilization of foam (Reinhardt *et al.* 1998).

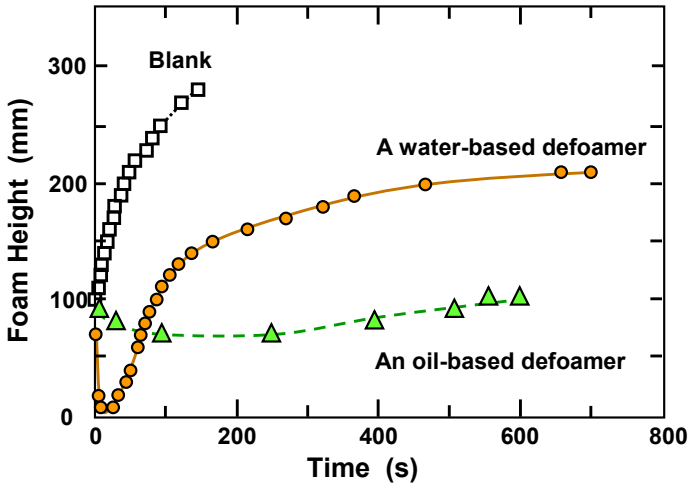

Fig. 21. Example of loss of effectiveness of different foam-control agents as a function of the duration of time since their addition to papermaking furnish (redrawn and simplified from Clas and Allen 1994)

Based on the literature search results, there has been relatively little attention paid to the modeling of kinetic aspects of foam control. An exception was the work of Pelton (1996). The reported model calculated the likely rates of collisions between foam control

emulsion particles and air bubbles in the liquid phase. The model correctly predicted effects of such variables as the dosage of foam-control agent, the initial characteristic bubble size, and changes in the height of floating foam layers in the test equipment as a function of time. The success of the modeling can likely be attributed to the focus on well-defined laboratory conditions.

Deposit problems related to foam

A further reason to avoid adding an overdose of foam-control product is to minimize contributing to unintended deposits of material onto the wetted parts of process equipment. As already has been noted, both the surfactants and any particles comprising the foam-control product can be assumed to be relatively hydrophobic. Based on thermodynamics, one can expect there to be a tendency for such components to associate themselves with other hydrophobic matter, such as wood pitch, lithographic inks, or hydrophobic sizing agents being added to the fiber suspension. Such material can precipitate from the aqueous phase and build up on various surfaces, including stainless steel or plastic. There have been reports identifying foam-control agents as being present in deposits collected at various points within paper machine systems (Dorris *et al.* 1985; Hoekstra 2007; Sithole and Watanabe 2013).

Foam Control Feeding Strategies

Most operations that take place within modern pulp and paper facilities can be classed as continuous processes. Some exceptions include batch kraft pulping, batch-wise pulping of recycled fibers, and preparation of certain chemical additives, can be described as continuous. Thus, most feeding strategies for foam control agents will be set up to deliver relatively steady, continuous metering of flows to the system. Turbulent flow, offering relatively rapid dispersement of the foam-control agent, is recommended as a means to achieve high effectiveness throughout the treated process stream. Positive displacement pumps, such as diaphragm-type piston pumps, can be used to meter the as-received emulsified product to the point of addition to the process (Jackson *et al.* 2018).

To determine a favorable rate of injection, it is recommended to carry out the kind of test that is illustrated in Fig. 22 (Hubbe and King 2009). In the example shown, the rate of addition was decreased in a stepwise, systematic way over a sufficiently long time (*e.g.* holding each level for 15 minutes or more) to allow the system to approach a relatively stable level of foam or entrained air, based on an online test. As the dosage of foam-control agent was being decreased, the measured level of entrained air increased. The delay effects shown in the figure are consistent with the lingering effects previously added foam-control agent at the higher dosage. Then, when the dosage was returned to its initial level, the level of entrained air soon fell back to its initial level. This example can be regarded as evidence of successful usage of a foam-control agent at a favorable level of addition. If the initial dosage of foam-control agent had been greatly in excess of the needed amount, then there would have been no increase in entrained air following a modest decrease in the addition rate.

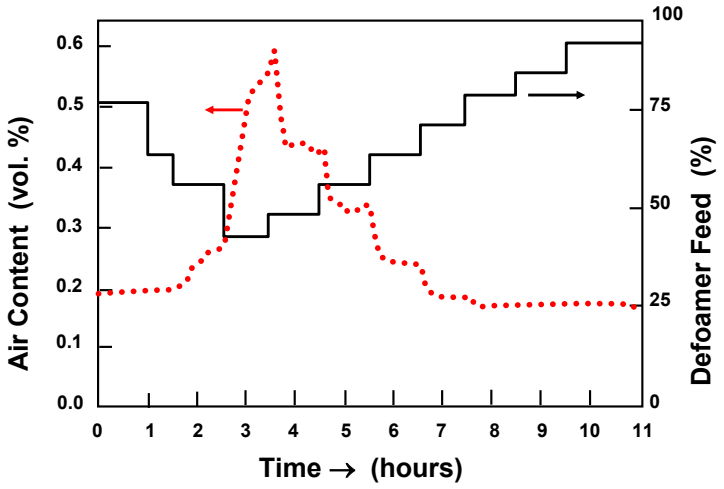

Fig. 22. Schematic diagram of a routine dosage-response test at a paper mill to determine whether a foam-control agent is being applied at a suitable level. This figure is a redrawn version of a figure included in TAPPI's Introduction to Wet End Chemistry course.

Multi-point addition

Given the transient nature of foam-control treatments, it is reasonable to consider strategies of multi-point addition to both brownstock washing systems and paper machines. Such procedures have been recommended as a way to achieve better overall control of the foam (Bandekar *et al.* 2014; Brandt *et al.* 1996). In some cases, there may be more than one location in a process where the operators have observed a need for control. For instance, one addition point may be intended to decrease entrained air before a filtering operation, and another addition point (and maybe even a different foam-control product) may be added such as to break down banks of foam at the top of a seal chest. In the latter case, one might consider application of a fine, low-volume spray of diluted foam-control agent at the top of the bank of foam (Garrett 1993). Bandekar *et al.* (2014) demonstrated the addition of foam control product to the process water (not the shower water) of a brownstock washing system at multiple points. According to Brant *et al.* (1996), at least two addition points for foam control additives are commonly used in brownstock washing systems.

FOAM CONTROL IN THE PULP AND PAPER MILL

This section has four areas of focus. The two primary focus areas are brownstock washing and the wet end of the paper machine. Briefer discussion is then provided related to foam control at the size press and during the preparation of aqueous coatings for paper.

Brownstock Washing

As stated in the Introduction, two priorities with respect to brownstock washing are to maintain sufficiently rapid flow of rinse water through the fiber mat and to achieve efficient displacement of lignin-rich water from that mat. As a first step in understanding such effects, the components tending to stabilize foam in such washing systems will be considered.

Composition of brownstock filtrate

The composition of the process water entering the brownstock washers can be regarded as challenging from the perspective of foam control. The term "weak black liquor" is often used to denote the liquid entering the washer system. A pH value higher than about 10 at that point will be maintaining both phenolic and carboxylic acids present in the water in their negatively charged ionic states. As shown in detail by Zhang *et al.* (2021), kraft lignin has abundant phenolic groups. Because the pK_a value of these groups is about 10, this means that lignin that has been released from the fibers during pulping will be present as negatively charged macromolecules. These tend to be repelled from the surfaces of fibers, which have a negative charge throughout the ranges of pH most commonly used in pulping and papermaking. Hemicellulose is expected to be the most prominent water-soluble polymer type that will be responsible for the persistent nature of foam present in brownstock system (Wallberg *et al.* 2006; Wallmo *et al.* 2009). The fatty acids, as well as any triglyceride fats originally present in the wood can be expected to have become transformed into their soap form (Niemela 1990), along with resin acid soaps when pulping involves softwood species. Typical compositions of such mixtures of carboxylic acid soaps have been reported (Käkölä *et al.* 2007). As is evident in the name "soap," these substances largely account for the stabilization of foam in brownstock washing systems. According to Kanicky *et al.* (2000), Kanicky and Shah (2003), and Douliez and Gaillard (2014) favorable self-association among adjacent fatty acid chains in a monolayer can lead to highly stable foams at certain pH values.

High solubility of the hemicellulose in the aqueous phase can be expected due to the presence of carboxylic acid groups, which confer a negative charge throughout the pH range encountered in brownstock washers. Though much of the hemicellulose will remain part of the fibers after kraft pulping, that portion that becomes dissolved will be repelled from the fiber surfaces by like charges. Zhu *et al.* (2015) quantified xylans and glucomannan hemicelluloses in lignin specimens that have been precipitated at different pH values.

Operators of brownstock washing systems need to manage some tricky issues related to pH during a typical washing operation. Ultimately, the goal will be to displace almost all of the weak black liquor from the fiber mat by the time the final washing stage has been completed. The reason for using a counter-current washing system is that such a practice will minimize the extent of dilution of the weak black liquor from the fibers. The unavoidable changes in pH and composition of the filtrate during washing implies that it can be difficult to achieve an optimized foam control program that can encompass the whole washing process. As shown in Fig. 23, as the pH is lowered, more and more of the kraft lignin can be expected to precipitate out of solution (Uloth and Waring 1989).

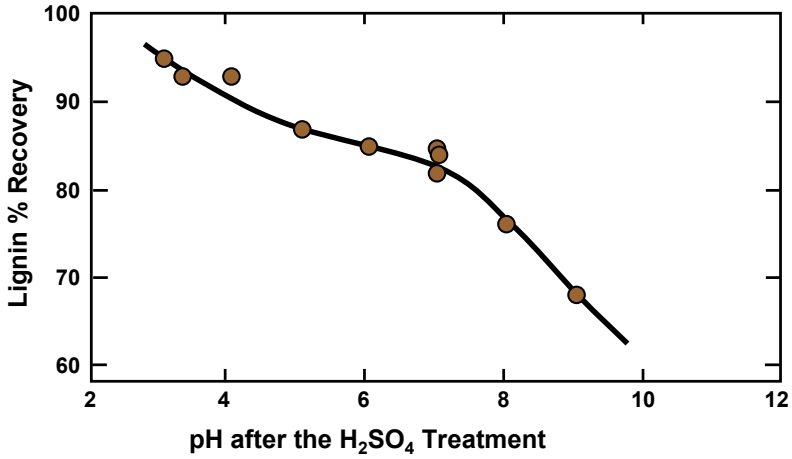

Fig. 23. Increasing precipitation of kraft lignin (going from right to left) in response to gradual addition of strong acid (figure redrawn from original data by Uloth and Wearing, 1989)

The effects shown in Fig. 23 can be understood based on expected changes in the protonation of kraft lignin as a function of pH. The initial increase in precipitation of lignin from the solution phase, as the pH is reduced in the vicinity of 10, can be attributed to protonation of the phenolic -OH groups, which have a pK_a value of about 10. The pH relationships are shown in Fig. 24 for a hypothetical simple fragment of lignin.

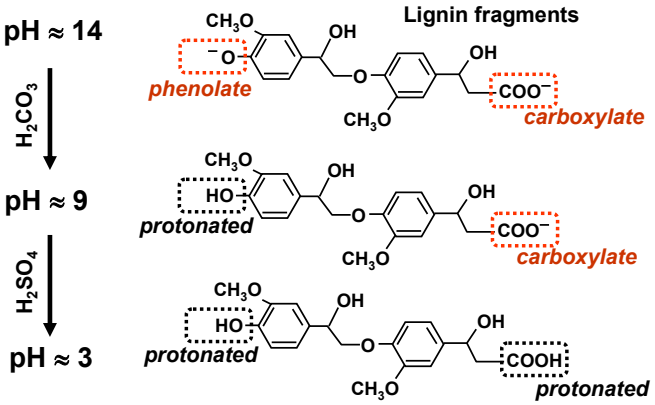

Fig. 24. Expected states of dissociation (with negative ionic charge) *vs.* protonation (with neutral charge) of two kinds of acidic species with a hypothetical fragment of lignin that is being progressively reduced in pH from kraft cooking conditions, first to pH near to 9 and then near to 3

However, in order to protonate carboxylate groups, which may be present on the aliphatic groups of lignin or remaining hemicellulose fragments remaining bound to the lignin, a much lower pH would be needed (Hubbe *et al.* 2019). Carboxylic acids on those entities often have pK_a values of about 3.3 (Laine 1997).

Consistent with these principles, Allen and LaPointe (2003) found that reprecipitation of extracted materials back onto the fibers in the course of brownstock washing could be reduced by raising the pH and temperature of the rinse water. The cited study was mainly concerned with such compounds as resin acids and fatty acids. However, it is reasonable to expect that NaOH addition to wash water in later stages of washing may delay or minimize reprecipitation of lignin back onto the fibers.

As a combined treatment, along with the usage of defoamers, Pelton and associates showed that brownstock washing efficiency could be further improved by taking steps to overcome channeling effects (Pelton and Grosse 1994; De *et al.* 1997; Lappan *et al.* 1997). This effect was achieved by adding a cationic polymer to the wash water. Such treatment resulted in polyelectrolyte complex formation between the cationic polymer and solubilized lignin byproducts. These complexes preferentially blocked just the larger channels of flow within the mat, thereby forcing more of the flow to take place through smaller channels. The effects were demonstrated using packed beds composed of clear solid glass beads of different sizes. Technical feasibility was also demonstrated at production scale in a pulp mill (Lappan *et al.* 1996).

Points of addition in brownstock washing systems

It has been proposed that a multi-point addition strategy be adopted for feeding foam-control additives (Bandekar *et al.* 2014). Such practices can be justified based on several grounds. First, as explained earlier, there is often a rapid decline in effectiveness with the passage of time after a foam-control agent has been added. Second, typical brownstock washing systems are comprised of separate units, and issues related to dewatering rate and displacement efficiency may need to be optimized separately in each case. And third, multiple treatment locations opens the possibility of using different foam-control formulations in different parts of the process. In addition to providing a strategy to achieve more uniform flow in a nonuniform pulp mat, the findings also confirmed the importance of pulp mat uniformity in general, relative to achieving efficient displacement of lignin during brownstock washing.

Bleaching stage washers

Foaming issues also can be encountered during the washing operations following different stages of bleaching, especially following the alkaline extraction stages (Dragan 1989). The alkaline conditions in those stages are expected to release remaining fatty acids and some of the remaining hemicellulose, both of which will contribute to stabilization of foam.

Paper Machine Foam Control

Entrained air has the potential to slow down the production of a main product from a paper mill. In addition, large bubbles in severe cases can adversely affect product quality. Subsections that follow will consider findings related to how various foam-control products may promote dewatering, affect the quality of paper products, and how they have some reported side-effects. Some particular issues related to foam can arise when a paper mill team is practicing acidic papermaking (rosin-alum systems). Likewise, some aspects of alkaline papermaking, especially when there is unintended dissolution of calcium carbonate fillers, can lead to foam problems.

Drainage issues

As has been widely reported, entrained air bubbles in a papermaking furnish tend to slow the rate of dewatering (Brecht and Kirchner 1959; Gertjejansen and Hossfeld 1967; Karras and Springer 1989; Rauch and Sangl 2000; Pelton *et al.* 2002; Helle and Paulapuro 2004; Martorana and Kleemann 2006). These observed effects can generally be explained as due to a tendency of the bubbles to block drainage channels within the wet web of paper (Hubbe and Heitmann 2007).

While reduced drainage due to air bubbles in papermaking fiber suspensions has been widely reported, as shown above, there also have be reports showing positive effects of surfactant addition on drainage rates. Touchette and Jenness (1960) showed that the addition of between 1 and 2% surfactant, based on dry pulp mass, increased the water removal by about 12 to 35% in laboratory tests, when considering seven commercially available surfactants representing different chemical classes. More recently, Lehmonen *et al.* (2020) showed that addition of sodium dodecyl sulfate at the level of 3 g/L to papermaking furnish resulted in higher dryness after forming of refined bleached softwood pulp (18 degrees Schopper-Riegler). Such results, though helping to show that the surfactant itself was not the direct cause of reduced drainage, should not be taken as a recommendation to add such high amounts of surfactant to a paper machine system, depending on the grade of paper being considered. Touchette and Jenness (1960) observed decreases of as much as 40% in tensile strength and burst strength, when individually adding the same diverse group of surfactants at the 1% and 2% levels, though some of the surfactants gave a slight positive effect on strength. Notably, the highest strength results were achieved with anionic or nonionic surfactants, *i.e.* those having low affinity for the cellulosic surfaces, which typically bear a negative ionic charge.

Product quality issues

As reported by Mudaly (2007), entrained air in the wet web is often given as a main cause for pinholes in paper products. The mechanism appears to involve the forceful sucking of bubbles through the wet web as it passes over suction boxes.

Campbell *et al.* (1997) found that foam control agents tended to render newsprint paper more water-wettable, which was undesirable. The effect was attributed to the agent's necessary content of surface activity. In other words, the surfactants in the formulations were opposing the intended effects of rosin-alum sizing by acting as wetting agents.

Deposit issues

When foam bubbles are able to rise, form a floating layer of froth, and then the bubbles eventually break at some point in a papermaking process, such a cycle may serve as an unintentional concentrating process for relatively hydrophobic contaminants, including pitch and stickies. These may then become entrained back into the papermaking furnish, such that they contribute to spots in the paper product (Allen *et al.* 1993). In addition, the hydrophobic nature of components of foam control products raises a danger that efforts to control foam can sometimes contribute to deposit problems (Brandt *et al.*1996). In particular, ethylene-bis-stearamide, which is often used as a hydrophobic particle to enhance the effectiveness of brownstock washer defoamer products, is often implicated in deposit problems in paper mills (Brandt *et al.* 1996). Likewise, Dorris *et al.* (1985) reported finding amide-type defoamer products in pitch deposits in paper machine systems. Dunlop Jones and Allen (1989) found that such deposits tended to increase with increasing addition of the defoamer products. According to Hoekstra (2007) such problems are often dependent on the composition of the foam-control product, with some oil-based foam control products having a tendency of contributing to pitch deposition problems. Silicone products have been reported to decrease problems associated with pitch deposits (Twoomey 1990; Brandt *et al.*1996; Hoekstra 2007). Though silicone-based foam control products have largely displaced the oil-based products, they too are known to contribute to deposits of hydrophobic materials in some paper machine systems (Sithole and Watanabe 2013).

Acidic papermaking issues related to foam

The term "acidic papermaking" usually can be taken as an indication that the papermaking operation involves usage of a rosin product for hydrophobic sizing. The highly acidic compound aluminum sulfate (papermaker's alum) is often used in such systems to anchor the rosin to the fibers. Background information regarding rosin-alum sizing systems has been described in more detail elsewhere (Strazdins 1981; Ekhtera *et al.* 2008; Xu *et al.* 2016). Briefly stated, most rosin purchased and used by papermakers has its origins in the kraft pulping process. However, most of it has been chemically modified by means of a Diels-Alder reaction with fumaric anhydride, giving rise to a product called fortified rosin size. The fortification reaction renders the rosin more storage-stable, easier to emulsify, and more securely anchored to fiber surfaces following interaction with alum. Some of the rosin is supplied to the paper industry as a rosin soap. The other main option is as an emulsion of the protonated form of rosin, except that a minor portion of the rosin likely will be present in its soap form, so as to serve as a stabilizer for the emulsion. The emulsion form of rosin is most often stabilized with a cationic polymer.

Episodes of excessive foam from rosin-alum papermaking operations often can be traced to an imbalance of chemical additives. In particular, foam can be expected when an insufficient amount of alum has been used to fully interact with the rosin. In the case of rosin soap, one can calculate the estimated amount of aluminum that will be needed to form the aluminum precipitate of abietic acid or levopimaric acid, which together will account for most of the material present (Nyren and Back 1958). It has been estimated that a ratio of alum to rosin (as hydrated alum solid *vs.* rosin solids) in the range 1:1 or 1.5:1 will be sufficient to interact with the carboxyl groups of the rosin (Strazdins 1981). The calculation can be tricker in the case of emulsified rosin, since the reaction with aluminum does not take place until the paper is passing through the dryer section of the paper machine. Another complication is the fact that some of the alum may be effectively consumed by other tasks, such as charge neutralization and reducing the pH of the process water. A further complication arises when some papermakers attempt to achieve rosin sizing above the usual acidic range. For instance, when the pH is raised above about 5, the added alum becomes progressively less effective, which favors the development of persistent foam.

Another set of problems involves the protonated form of rosin sizing products. Although only a minor portion of the rosin in such products is expected to be in its soap form, there can be a gradual deprotonation during the time that the rosin emulsion is present in the fiber suspension, especially if the pH is higher than about 5. Papermakers generally don't start out planning to implement rosin under high pH conditions, but the pH may be forced to higher levels due to calcium carbonate, which often is present in recovered fibers from used printing paper. Thus, relatively long residence of a rosin emulsion products at relatively high temperature and relatively high pH all will be expected to increase the observed levels of foam (Marton 1989).

Alkaline papermaking issues related to foam

When calcium carbonate particles are being used as a filler, mainly to provide brightness, opacity, and reduced cost to printing papers, the pH will likely be in a range between about 8 and 8.5 (Crouse and Wimer 1991). Though rosin soap is avoided in paper mills operating under such conditions, some other kinds of surfactants may be present. For instance, the hydrophobic sizing agent alkenyl succinic anhydride (ASA) will start to undergo hydrolysis as soon as it comes into contact with the furnish. Hydrolyzed ASA, a dicarboxylic acid, will then be present in the system to an extent that will depend on such

factors as the effectiveness of a retention aid system. The ASA hydrolysate can be described as a sticky, sparingly soluble surfactant that is prone to forming complexes with divalent metal ions such as calcium and magnesium (Stitt 1997). The latter can lead to deposits on the wetted surfaces paper machine equipment.

Another potential stabilizer of foam will include deinking surfactants, as mentioned earlier.

Something else that is important to know about calcium carbonate is that its dissolution, upon contact with acidic media, will cause the release of carbon dioxide, which is quite soluble in water. Thus, when the pressurized stock experiences a rapid drop in pressure, upon its emergence from the slice of a headbox, the amount of entrained air has the potential to be especially high (Duan and Sun 2003). Thus, papermakers are advised to clearly select either acidic papermaking (with an alum-buffered system) or an alkaline system (in which nothing is added that will tend to reduce the pH below about 7). Intermediate conditions can be expected to give rise to objectional amounts of foam.

Points of defoamer addition on the paper machine

Addition points for foam control agents on paper machines can be selected depending on the priorities of the operating team. Often the highest priority is placed on enhancing the dewatering rate and on avoiding pin-hole features in the paper. Both of these goals can be addressed by minimizing the amount of entrained air in the jet of stock that emerges from the headbox. As mentioned earlier, adding the foam-control agent just before the hydrocyclone clearers has the advantages of intensive mixing with the furnish, as well as the likelihood that some air will be able to be drawn from the system at the accepts from primary hydrocyclones. In cases where a paper machine has been fitted with vacuum deaeration equipment (as shown earlier in Fig. 10), there is an even stronger incentive to choose the inlet to the hydrocyclones as a preferred addition point.

Another location where problematic foam tends to collect is at the surface of seal chests, which are typically on the floor below where the forming section is located. In particular, the siphons from low-vacuum suction boxes can be expected to be discharged into such chests (Hubbe *et al.* 2020b), with the development of foam. In such applications there can be a preference to use mist sprays of fast-acting defoamer products that are effective in breaking existing banks of foam that has risen to the surfaces of such chests.

The Size Press and Foam Issues

The size press can be an especially challenging operation in terms of foam control. Because the size press is routinely used to apply starch solutions to the paper surface, there is an inherent polymeric water-soluble stabilizer always present in the form of dissolved starch. The relatively high viscosity can be expected to suppress rapid spreading of foam control products due to the presence of the viscous starch polymers throughout the water phase. In addition, the size press operation involves agitation and even splashing, especially if there is an overflow of starch that is directed back to a run tank.

Yet more challenging foam problems sometimes are associated with the usage of hydrophobic copolymers, which can be added at the size press together with starch as a means of developing resistance to water penetration into the paper. The chemistry and behavior of such additives has been considered in another review article (Bildik Dal and Hubbe 2021). These copolymers, which can include styrene maleic anhydride (SMA) and styrene acrylate (SA) products, are sensitive to the pH of the system; to avoid conditions leading to excessive foam, the pH may need to be monitored and adjusted, following the

recommendations of the supplier. Furthermore, it may be challenging to find a foam control agent that has minimum adverse effect on the intended effect of the added copolymer in developing hydrophobicity of the paper.

Formulation of Aqueous Coatings and Foam Issues

Foam control issues can pose challenges during preparation and application of aqueous coatings for paper products (Hudson 1968; Berger and Gast 1976; Reinhardt *et al.* 1998). A typical coating formulation consists of pigment (*e.g.* clay or calcium carbonate particles of ~1 to 5 μm diameter), binder (usually latex, starch, or a combination of the two), and various additives (Lehtinen 2000). The solids content is often higher than 50%. Especially in cases where starch products play a major role as the binder, they have the potential to serve as stabilizers for foam by contributing to solution viscosity. Coating formulations can be quite viscous, though this depends on both the application equipment and the formulation. A further issue is that coating formulations are subjected to extensive hydrodynamic shear during their preparation in order to achieve a high uniformity of the mixture.

Air entrainment during coating preparation often can be minimized by adjustment of mixing conditions. In particular, the physical arrangement of an impeller, as well as its speed, can be adjusted to avoid the occurrences of vortex flow that could draw air into the mixture (Motamedvaziri and Armenante 2012).

MECHANISTIC IMPLICATIONS OF REPORTED FINDINGS

Though there appears to be sound experimental and theoretical support for the main mechanisms of foam-control action presented in articles considered in this review, some of the experimental findings suggest that at least one additional mechanistic step should be considered. As was in the foregoing discussion of paper machine applications of foam-control agents, there is a need to explain the observed enhancements in drainage rates (Hakamäki and Kovasin 1985; Twoomey 1990; Allen *et al.* 1993; Pelton *et al.* 2002; Hoekstra 2007; Mudaly 2007; Lobo and Bolton 2013; Bolton *et al.* 2014; Santos and Hart 2014). As was noted earlier, especially in the paper machine applications, the mechanism needs to account for the fact that only a fraction of a second may have passed between the moment of depressurization of the furnish as it emerges from the headbox and when most of the water has been removed from the wet web. Such a short time is not sufficient for very small entrained air bubbles to move by gravity, regardless of whether they have been converted into larger bubbles by the action of a foam control agent. In addition, it is worth taking seriously the early findings of Poschmann (1962), who noted that the presence of fibers tends to hold individual entrained are bubbles apart from each other, thus calling into question any drainage-promoting mechanism that requires coalescence between adjacent bubbles.

A clue to the resolution of the dilemma just described can be found in the early work of Touchette and Jenness (1960). These authors found that addition of various surface-active agents to papermaking furnish tended to increase the dewatering rates, according to laboratory tests. A further key to unraveling the mechanism can be drawn from a method that has been used for determining the characteristic size of pores in textiles (Miller and Tyomkin 1986, 1994). The test takes advantage of the following relationship

between the maximum value of vacuum that can be applied before a pore of radius R will be drained,

$$R = 2\ \gamma_{aw} \cos\ \theta / (\Delta P) \quad (4)$$

In Eq. 4, the term γ_{aw} is the interfacial tension, θ is the contact angle, and ΔP is the applied pressure (or vacuum) that is just sufficient to draw the meniscus through the material. The physical situation is illustrated in Fig. 25, which envisions a single pore through the textile product and models that pore as a uniform cylinder. Note that according to this model, the flow is initially resisted by the maximum capillary forces at a meniscus at the top entrance to the pore, just before the value of ΔP exceeds the capillary pressure.

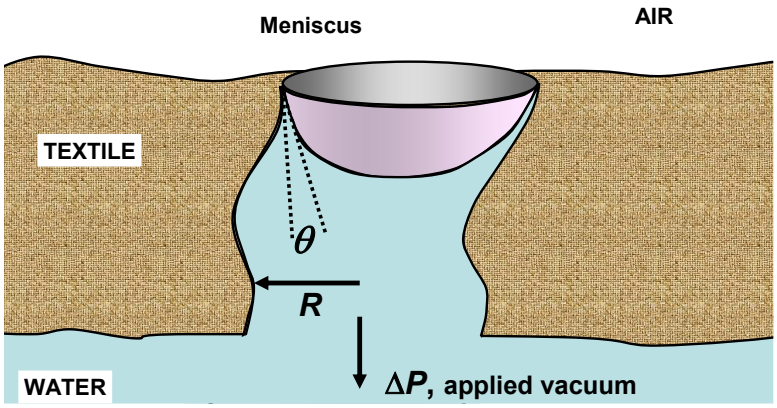

Fig. 25. Model corresponding to the derivation of the equation for estimating the predominant sizes of pores in textile fabrics

In order to fully apply the concept of capillary resistance to entrained air bubbles present in a wet web, there can be some modifications to governing equation and also to the diagram describing the effect. For instance, where Fig. 25 shows just a single meniscus impeding drainage within an idealized channel in a wet web, it is possible to imagine that there could be multiple bubbles, even in one channel. This could, in principle, add to the resistance to dewatering.

Ordinarily, during the test to estimate the predominant pore size, the analyst would use pure water, for which the parameter γ_{aw} will equal 72 mN/m. However, as was noted earlier, the most effective foam control agents are designed in such a way as to quickly and temporarily lower the values of γ_{aw} to fractions of that amount. It is proposed here that such effects can make it possible for any bubbles of air, which otherwise might have blocked the passage of water from the paper web (or fiber mat in a brownstock washer) to be quickly pulled through, with only minor capillary resistance. It follows from Eq. 4 that a strong decrease in interfacial tension, due to the actional of a foam-control agent, will greatly decrease the force needed to pull the air through the wet web of paper. It is proposed that such effects allow such devices as hydrofoils, forming blades, and suction boxes to more effectively pull filtrate through the fiber mat, thus overcoming the tendency of such bubbles to block drainage channels (Hubbe *et al.* 2020b). In addition, by reducing the interfacial tension temporarily to a very low level, the foam control treatment would allow the bubbles to easily change their shape, allowing them to be pulled through tiny openings without creating problematic pinholes. This concept is illustrated schematically in Fig. 26. Such

considerations also would be relevant for drainage through mats of fibers in brownstock washing.

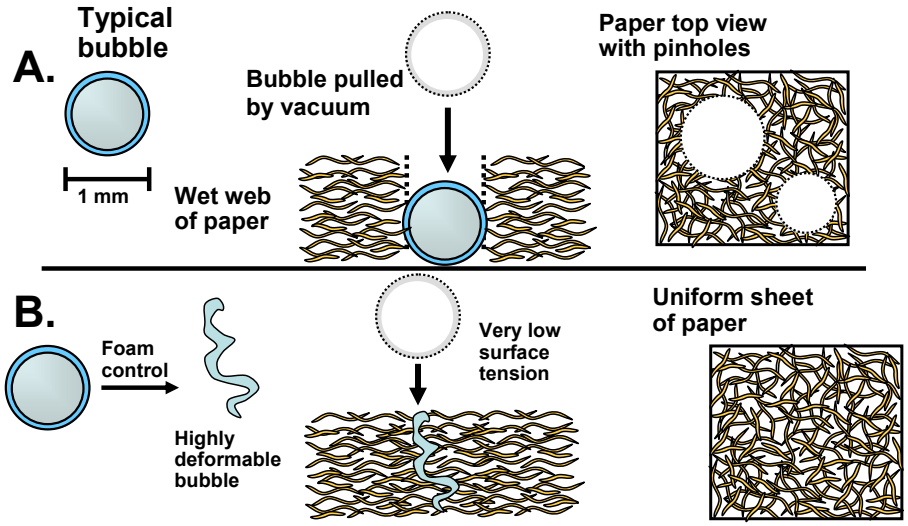

Fig. 26. Concept by high temporarily very low interfacial tension may facilitate high deformation of bubbles such that they fail to create significant pinholes; A: Effect of typical entrained air bubble in paper wet web as it passes over suction box; B: Proposed lack of pinhole creation when bubbles are rendered very highly deformable by foam control treatment

CONCLUDING STATEMENTS

Due to the complexities of different industrial operations, including differences in equipment, raw materials, pulping conditions, various impurities, and different kinds of paper being made, and different operating temperatures, it is inherently difficult to predict levels of foam or entrained air or to be able to forecast what will be the best-performing foam-control product. Rather, the mechanistic principles outlined in this article may serve as guideposts in combination with empirical testing. Nevertheless, based on this review of the literature related to foam control in pulp and paper mill systems, several conclusions and recommendations appear to be justified:

1. Problematic levels of foam present in pulp and paper mills systems usually can be traced to a combination of factors, which include the following:
   (a) Presence of an aqueous solution
   (b) Presence of an air phase
   (c) Some form of agitation, sucking, raining, or splashing
   (d) At least one surface-active agent
   (e) At least one water-soluble polymer

2. When looking for a cost-effective long-term solution to excessive entrained air or visible foam in pulp and paper mill systems, it makes sense to place priority on minimizing any of the factors mentioned in the previous item that are at least partly under the control of the operating team. For example, known sources of surfactants to the system can be scrutinized and reduced, as in the case of excessive use of deinking surfactants. In addition, adequate

washing of pulp after pulping or bleaching stages is important in order to minimize carry-over of surfactants such as fatty acid soaps. Likewise, papermakers should avoid levels of polymeric additives that exceed the adsorption capacity of the fiber surfaces.

3. Foam control agents can be formulated in ways that avoid the possibility of generation of toxic chlorinated organic compounds. Options include (a) using petroleum oils in the formulation that are free of aromatic content, (b) using silicone-based oils, such as polydimethylsilane (PDMS), or (c) formulating the foam-control agent primarily with a surfactant and optional hydrophobic particles.

4. The efficacy and cost-efficiency of foam-control treatment often can be improved by such measures as

(a) Adding fresh foam-control agent at a point of good mixing just ahead of the point where it needs to have its intended effect
(b) Using optimized smaller dosages at more than one addition point
(c) Selecting a product that is formulated for application at the temperature range prevailing in the mill application

5. Foam-control products can be enhanced by adding solid particles having the following attributes:

(a) Solid nature
(b) Hydrophobic surfaces
(c) Size large enough to span a surfactant bilayer bubble wall
(d) Angular shape
(e) Smooth surfaces

6. A generalized mechanism to describe the broad range of foam control effects, based on the published literature, can include the following:

(a) Emulsions droplets that are able to enter bubbles walls due to a sufficiently low interfacial tension
(b) Sufficiently low viscosity of the formulation, so as to allow rapid spreading on bubble walls
(c) Thinning of bi-layer type bubble walls, followed by bridging and pinch-off effects to bring about coalescence between pairs of adjacent bubbles
(d) Optional use of optimized hydrophobic particles, which can play roles in bridging of surfactant bilayers and inducing pinch-off of bubble walls.
(e) Temporary lowering of air-water interfacial tensions in the system, thereby allowing air bubbles to be easily drawn through the wet web of paper with minimal capillary resistance and enhancing the rate of dewatering

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REFERENCES CITED

Abel, H., Guth, C., and Berendt, H.-U. (1989). "Antifoams for aqueous systems and their use," US Patent 4880564 A, Ciba-Geigy assignee.

Ajersch, M., and Pelton, R. H. (1994). "Growth of bubbles on pulp fibers and on carbon black dispersed in supersaturated carbon dioxide solutions," *Nordic Pulp & Paper Research Journal* 9(2), 129-133, 135. https://doi.org/10.3183/npprj-1994-09-02-p129-133

Ajersch, M. J., Pelton, R. H., and Chan, A.K. T. (1992). "Measuring dispersed air in newsprint pulp suspensions," *TAPPI J.* 75(2), 125-129.

Alimadadi, M., and Uesaka, T. (2016). "3D-oriented fiber networks made by foam forming," *Cellulose* 23(1), 661-671. https://doi.org/10.1007/s10570-015-0811-z

Allen, L. H., and Lapointe, C. L. (2003). "Temperature and pH: Important variables for deresination in kraft brownstock washing," *Pulp Paper Can.* 104(12), 59-62.

Allen, S. L., Allen, L. H., and Flaherty, T. H. (1993). "Defoaming in the pulp and paper industry," in: Garrett, P. R. (1993). *Defoaming: Theory and Industrial Applications*, Marcel Dekker, New York, Ch. 3, pp. 151-175.

Al-Masry, W. A., Ali, E. M., and Aqeel, Y. M. (2006). "Effect of antifoam agents on bubble characteristics in bubble columns based on acoustic sound measurements," *Chem. Eng. Sci.* 61(11), 3610-3622. https://doi.org/10.1016/j.ces.2006.01.009

Almgren, F. J., and Taylor, J. E. (1976). "Geometry of soap films and soap bubbles," *Sci. Amer.* 235(1), 82-93. https://doi.org/10.1038/scientificamerican0776-82

Anazadehsayed, A., Rezaee, N., Naser, J., and Nguyen, A. V. (2018). "A review of aqueous foam in microscale," *Adv. Colloid. Interface Sci.* 256, 203-229. https://doi.org/10.1016/j.cis.2018.04.004

ASTM D 3519 – 88 (1993). "Standard test method for foam in aqueous media (blender test)."

Avery-Edwards, D., Elms, R., and Buckingham, A. (1994). "Silicone antifoams for nonwoven applications," *TAPPI J.* 77(8), 235-238.

Aveyard, R., Binks, B. P., Fletcher, P. D. I., Peck, T. G., and Rutherford, C. E. (1994). "Aspects of aqueous foam stability in the presence of hydrocarbon oils and solid particles," *Adv. Colloid Interface Sci*. 48. 93-120. https://doi.org/10.1016/0001-8686(94)80005-7

Aveyard, R., and Clint, J. H. (1995). "Liquid droplets and solid particles at surfactant solution interfaces," *J. Chem. Soc. Faraday Trans*. 91, 2681-2697. https://doi.org/10.1039/ft9959102681

Aveyard, R., Cooper, P., Fletcher, P. D., and Rutherford, C. E. (1993). "Foam breakdown by hydrophobic particles and nonpolar oil," *Langmuir* 9, 604-613. https://doi.org/10.1021/la00026a041

Bamberger, J. A. (2006). "Using ultrasound to characterize pulp slurries with entrained air," in: Proceedings of the ASME Fluids Engineering Division Summer Conference, Vol. 2, pp. 463-465. https://doi.org/10.1115/FEDSM2006-98325

Bandekar, R., Ni, J. P., Zhang, H. J., Liu, H. B., and Ni, Y. H. (2014). "A case study: Optimization of defoamer addition with new multiple addition points at an eastern Canadian mill," *J-FOR – J. Sci. Technol. For. Prod. Proc.* 4(3), 6-10.

Belyakova, L. A., and Varvarin, A. M. (1999). "Surfaces properties of silica gels modified with hydrophobic groups," *Colloids Surf. A – Physicochem. Eng. Aspects.* 154(3), 285-294. https://doi.org/10.1016/S0927-7757(98)00650-5

Berg, R. K., and Smalley, D. S. (1977). "Water-based defoamer compositions," US Patent 4032473 A, Associated Chemists assignee.

Berger, P. D., and Gast, J. A. (1976). "Analysis and measurement of foaming phenomena in water-based coating systems," *J. Coating Technol.* 48(621), 55-59.

Bergold, W., Degen, H.-J., and Melzer, J. (1990). "Antifoam based on oil-in-water emulsion," US Patent 4976888 A, BASF assignee.

Bildik Dal, A. E., and Hubbe, M. A. (2021). "Hydrophobic copolymers added with starch at the size press of a paper machine: A review of findings and likely mechanisms," *BioResources* 16(1), 2138-2180. https://doi.org/10.15376/biores.16.1.BildikDal

Bliss, T. (1994). "Centrifugal cleaners and their applications in stock preparation systems," TAPPI 1994 Stock Preparation Short Course, TAPPI Press, Atlanta.

Bolton, T. S., Lobo, L. A., Nicholson, D., and McClary, A. W. (2014). "Brownstock washing fundamentals: Enhancing drainage through chemistry – Part 2," *TAPPI J.* 13(3), 55-62. https://doi.org/10.32964/TJ13.3.55

Boylan, F. J. (1981). "Liquid defoamer and defoaming process," US Patent 4303549 A, Drew Chem. assignee.

Boylan, F. J. (1982). "Liquid defoamer and process of use thereof," US Patent 4340500 A, Drew Chem. assignee.

Brandt, C. S., Teasley, J. G., and Anderson-Norris, A. (1996). "Water based silicone defoamers: A new generation of defoamers," *PaperAge* 112(10), 24-24.

Brecht, W., and Kirchner, U. (1959). "Air content of pulp suspensions," *Wochenbl. Papierfabr.* 87(8), 295-305.

Brondi, C., Mosciatti, T., and Di Maio, E. (2022). "Ostwald ripening modulation by organofluorine additives in rigid polyurethane foams," *Ind. Eng. Chem. Res.* 61(40), 14868-14880. https://doi.org/10.1021/acs.iecr.2c01829

Brown, A, G., Thuman, W. C., and McBain, J. W. (1953). "The surface viscosity of detergent solutions as a factor in foam stability," *J. Colloid Sci.* 8(5) 491-507. https://doi.org/10.1016/0095-8522(53)90055-5

Campbell, S., Ness, J., and Hodgson, K. (1997). "Defoamer performance and its effect on the water sensitivity of newsprint," 1997 TAPPI-PPERA Student Conference Poster Session and 1997 TAPPI Joint Engineering/Papermakers SuperConference, pp. 149-162.

Chaisalee, R., Soontravanich, S., Yanumet, N., and Scamehorn, J. F. (2003). "Mechanism of antifoam behavior of solutions of nonionic surfactants above the cloud point," *J. Surfactants Deterg.* 6(4), 345-351. https://doi.org/10.1007/s11743-003-0280-3

Chen, J., Yang, C., and Mao, Z. S. (2015). "The interphase mass transfer in liquid-liquid systems with Marangoni effect," *Eur. Phys. J. – Special Topics* 224(2), 389-399. https://doi.org/10.1140/epjst/e2015-02368-0

Cheng, H. N., Fernandez, E. O., and Sheepy, J. M. (2011a). "Defoamers for pulp and papermaking applications," US Patent 7879917, Hercules assignee.

Cheng, H. N., Fernandez, E. O., and Sheepy, J. M. (2011b). "Defoamer emulsion for pulp mill applications," US Patent 7893115, Hercules assignee.

Choudhury, A., Paidi, V. K., and Kalpathy, S. K., and Dixit, H, N, (2020). "Enhanced stability of free viscous films due to surface viscosity," *Phys. Fluids* 32(8), article 082108. https://doi.org/10.1063/5.0016282

Christiano, S. P., and Fey, K. C. (2003). "Silicone antifoam performance enhancement by nonionic surfactants in potato medium," *J. Indust. Microbiol. Biotech.* 30(1), 13-21. https://doi.org/10.1007/s10295-002-0003-3

Clas, S. D., and Allen, L. H. (1994). "Comparison of the performances of water-based and oil-based defoamers," *Pulp Paper Can.* 95(1), 33-36.

Corbel, G., Svarz, J. J., and Smith, A. (2003). "Aqueous defoamer composition," US Patent 6562875 B1, Ondeo Nalco assignee.

Costa, C. A., and Rubio, J. (2005). "Deinking flotation: Influence of calcium soap and surface-active substances," *Minerals Eng.* 18(1), 59-64. https://doi.org/10.1016/j.mineng.2004.05.014

Crouse, B. W., and Wimer D. G. (1991). "Alkaline papermaking – An overview," *TAPPI J.* 74(7), 152-159.

Cutts (2004). "Compact wet end systems for superior papermaking," *Pulp Paper Canada* 105(4), 28-30; T83-T85.

De, D., Hrymak, A. N., and Pelton, R. (1997). "Polyelectrolyte precipitate formation during miscible displacement in porous media," *AICHE J.* 43(10), 2415-2423. https://doi.org/10.1002/aic.690431005

Deac, Y. D., Popa, C. A., Dumitru, L., Nedelcu, M., Krutsch, G., Pachtinger, L. H., De Clercq, A., Bergold, W., Degen, H.-J., and Melzer, J. (1990). "Antifoam based on oil-in-water emulsion," US Patent 4976888, BASF assignee.

Dehdari, B., Parsaei, R., Riazi, M., Rezaei, N., and Zendehboudi, S. (2020). "New insight into foam stability enhancement mechanism, using polyvinyl alcohol (PVA) and nano-particles," *J. Molec. Liquids* 307, article 112755. https://doi.org/10.1016/j.molliq.2020.112755

Deng, P. P., Liu, X. P., Zhang, T., Li, Y. W., Wu, K., Chen, K., Kuang, Y., Chen, J. J., and Jiang, F. T. (2025). "Konjac glucomannan-based foams incorporating cellulose phase change microcapsules for efficient thermal energy regulation," *Carbohyd. Polym.* 352, article 123191. https://doi.org/10.1016/j.carbpol.2024.123191

Denkov, N. D. (2004). "Mechanisms of foam destruction by oil-based antifoams," *Langmuir* 20, 9463-9505. https://doi.org/10.1021/la049676o

Denkov, N. D., Marinova, K. G., and Tcholakova, S. S. (2014). "Mechanistic understanding of the modes of action of foam control agents," *Adv. Colloid Interface Sci.* 206, 57-67. https://doi.org/10.1016/j.cis.2013.08.004

Denkov, N., Tcholakova, S., and Politova-Brinkova, N. (2020). "Physicochemical control of foam properties," *Curr. Opin. Colloid Interf. Sci.* 50, article 101376. https://doi.org/10.1016/j.cocis.2020.08.001

de Vos, R. M., Maier, W. F., and Verweij, H. (1999). "Hydrophobic silica membranes for gas separation," *J. Membrane Sci.* 158(1-2), 277-288. https://doi.org/10.1016/S0376-7388(99)00035-6

Dippenaar, A. (1982a). "The destabilization of froths by solids. 1. The mechanism of film rupture," *Int. J. Mineral Processing* 9, 1-14. https://doi.org/10.1016/0301-7516(82)90002-3

Dippenaar, A. (1982b). "The destabilization of froth by solids. 2. The rate determining step," *Int. J. Mineral Processing* 9, 15-22. https://doi.org/10.1016/0301-7516(82)90003-5

Dorris, G. M., Douek, M., and Allen, L. H. (1985). "Analysis of amide defoamers in kraft mill pitch deposits," *J. Pulp Paper Sci.* 11(5), J149-J154.

Dougherty, S. J. (1989). "Online entrained-air measurement for brownstock-washer defoamer control," *TAPPI J.* 72(1), 50-54.

Douliez, J. P., and Gaillard, C. (2014). "Self-assembly of fatty acids: From foams to protocell vesicles," *New J. Chem.* 38(11), 5142-5148. https://doi.org/10.1039/c4nj00914b

Dragan, R. (1989). "Use of antifoaming agents in the pulp and paper industry. (4). Combatting foam during the manufacture of bleached hardwood pulp," *Celuloza si Hartie* 38(3), 105-106.

Duan, Z. H., and Sun, R. (2003). "An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar," *Chem. Geol.* 193(3-4), 257-271. https://doi.org/10.1016/S0009-2541(02)00263-2

Dunlop Jones, N., and Allen, L. H. (1989). "The influences of washing, defoamers and dispersants on pitch deposition from unbleached kraft pulps," *J. Pulp Paper Sci.* 15(6), J235-J241.

Dyllick-Brezinger, R., Guenther, E., Lorencak, P., Glas, G., and Bonn, J. (2005). "Defoamer and/or deaerator on the basis of oil-in-water dispersions," US Patent 6864292, BASF assignee.

Ekhtera, M. H., Charani, P. R., Ramezani, O., and Azadfallah, M. (2008). "Effects of poly-aluminum chloride, starch, alum, and rosin on the rosin sizing, strength, and microscopic appearance of paper prepared from old corrugated container (OCC) pulp," *BioResources* 3(2), 383-402. https://doi.org/10.15376/biores.3.2.383-402

Elfers, G. H. (1980). "Process of inhibiting foaming utilizing maleic ester copolymer based defoamers and defoamed compositions," US Patent 4230599 A, Diversey assignee.

Ferguson, L. D. (1992). "Deinking chemistry" (Parts 1 & 2), *TAPPI J.* 75(7), 75-83; (8), 49-58.

Franklin, B. (1774). "Of the stilling of waves by means of oil," *Phil. Trans.* 64, 445-460: 448. https://doi.org/10.1098/rstl.1774.0044

Frye, G. C., and Berg, J. C. (1989). "Mechanisms for the synergistic antifoam action by hydrophobic solid particles in insoluble liquids," *J. Colloid Interface Sci.* 130(1), 54-59. https://doi.org/10.1016/0021-9797(89)90077-5

Furman, R. (1992). "Polymeric defoamer compositions," US Patent 5152925 A, Exxon Chem. assignee.

Furman, R. (2002). "Polyester water-based defoamer," US Patent 6464828 B1.

Gammon, C. T. (1980). "Microemulsion defoamer compositions and processes for their production and use," US Patent 4208301 A, Diamond Shamrock, assignee.

Gao, Y.-F., Wang, J., Xu., D.-H., Lin, Y.-X., Song, W.-B., Wong, Y.-B., Xu, F., and Gong, C. (2024). "Preparation and performance evaluation of CNF-enhanced polyether-modified polysiloxane defoamer," *J. Surfact. Deterg.* 28(2), 363-372. https://doi.org/10.1002/jsde.12808

Garrett, P. R. (1993). "The mode of action of antifoams," in: *Defoaming: Theory and Industrial Applications*, P. R. Garrett (ed.), Marcel Dekker, New York.

Garrett, P. R. (1995). "A simple statistical theory for the effect of changes in antifoam concentration on foamability," *Langmuir* 11(9), 3576-3584. https://doi.org/10.1021/la00009a048

Garrett, P. R., Davis, J., and Rendall, H. M. (1994). "An experimental study of the antifoam behavior of mixtures of a hydrocarbon oil and hydrophobic particles," *Colloids Surf. A – Physicochem. Eng. Aspects* 85(2-3), 159-197. https://doi.org/10.1016/0927-7757(93)02678-8

Georgiev, V., Mitrinova, Z., Gers-Barlag, A., Denkov, N., and Tcholakova, S. (2023). "Role of hydrodynamic conditions and type of foam stabilizer for antifoam efficiency," *Colloids Surf. A – Physicochem. Eng. Aspects* 681, article 132838. https://doi.org/10.1016/j.colsurfa.2023.132838

Gertjejansen, R., and Hossfeld, R. (1967). "Gas-liquid relationships and their effect upon the permeability of wood pulp pads to water," *TAPPI* 50(4), 204-208.

Gottberg, J. M., Lappalainen, T., and Salminen, K. (2019). "Polyvinyl alcohol as foaming agent in foam formed paper," *TAPPI J.* 18(8), 475-485. https://doi.org/10.32964/TJ18.8.475

Griffin, W. C. (1954). "Calculation of HBL values of non-ionic surfactants," *J. Soc. Cosmetic Chem.* 5, 259-259.

Guazzelli, E. (ed.) (2011). *A Physical Introduction to Suspension Dynamics*, Cambridge University Press, Cambridge, UK. https://doi.org/10.1017/CBO9780511894671

Gülich, J. F. (2020). *Centrifugal Pumps*, 4th Ed., Springer. https://doi.org/10.1007/978-3-030-14788-4

Hakamäki, H., and Kovasin, K. (1985). "The effect of some parameters on brown stock washing: A study made with a pulp tester," *Pulp Paper Can*. 86(9), 45-52.

Hansen, C. M. (2007). *Hansen Solubility Parameters: A User's Handbook*, 2nd Ed., CRC Press, Boca Raton, FL, USA. https://doi.org/10.1201/9781420006834

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. https://doi.org/10.1063/1.1750953

Heebner, G., Bulanov, M., van Waes, P., and Krutzer, B. (2025). "Biobased defoamer compositions and methods of preparation thereof," US Patent 12246270, Kraton Chem., assignee.

Heindel, T. J. (1999). "Fundamentals of flotation deinking," *TAPPI J.* 82(3), 115-124.

Helle, T.-M., and Paulapuro, H. (2004). "Effect of precipitated gas bubbles in papermaking," *Appita J.* 57(6), 444-447.

Hendriks, W. A. (1996). "Antifoam composition for aqueous starch and paper coating systems," US Patent 5538668 A, Betz PaperChem assignee.

Henriksson, G., Germgård, U., and Lindstroem, M. E. (2024). "A review on chemical mechanisms of kraft pulping," *Nordic Pulp Paper Res. J.* 39(3), 297-311. https://doi.org/10.1515/npprj-2023-0015

Hill, R. M., and Fey, K. C. (1999). "Silicone polymers for foam control," in: *Silicone Surfactants*, Surfactant Science Series, R. M. Hill (ed.), Marcel Dekker, New York, Vol. 86, pp. 159-180. https://doi.org/10.1201/9780203739754-6

Hinze, W. L., and Pramauro, E. (1993). "A critical-review of surfactant-mediated phase separations (cloud-point extractions) – Theory and applications," *Crit. Rev. Anal. Chem.* 24(2), 133-177. https://doi.org/10.1080/10408349308048821

Hjelt, T., Ketoja, J. A., Kiiskinen, H., Koponen, A. I., and Pääkkönen, E. (2022). "Foam forming of fiber products: A review," *J. Dispersion Sci. Technol.* 43(10), 1462-1497. https://doi.org/10.1080/01932691.2020.1869035

Ho, T. M., Tanzil, A., Bhandari, B. R., and Bansal, N. (2023). "Effect of surfactant type on foaming properties of milk," *Food Bioproc. Technol.* 16(8), 1781-1793. https://doi.org/10.1007/s11947-023-03012-5

Hoekstra, P. M. (2007). "Improving washing efficiencies in the kraft pulp mill with new defoamer technology," Engineering, Pulping and Environmental Conference 2007, TAPPI, Vol. 4, pp. 2600-2635.

Honkanen, M., and Eloranta, H. (2023). "Advanced real-time digital microscopy of foaming processes," *TAPPI J.* 22(1), 21-31. https://doi.org/10.32964/TJ22.1.21

Hubbe, M. A. (2006). "Bonding between cellulosic fibers in the absence and presence of dry-strength agents – A review," *BioResources* 1(2), 281-318. https://doi.org/10.15376/biores.1.2.281-318

Hubbe, M. A. (2014). "Prospects for maintaining strength of paper and paperboard products while using less forest resources: A Review," *BioResources* 9(1), 1634-1763. https://doi.org/10.15376/biores.9.1.1634-1763

Hubbe, M. A. (2021). "Energy efficiency challenges in pulp and paper manufacture: A tutorial review," *BioResources* 16(4), 8567-8639. https://doi.org/10.15376/biores.16.4.8567-8639

Hubbe, M. A. (2024). "Size press practices and formulations affecting paper properties and process efficiency: A Review," *BioResources* 19(1), 1925-2002. https://doi.org/10.15376/biores.19.1.Hubbe

Hubbe, M. A. (2026). "Stickies in recovered paper fiber suspensions: A tutorial review," *BioResources* 21(3), 8932-8999. https://doi.org/10.15376/biores.21.3.Hubbe

Hubbe, M., Alén, R., Paleologou, M., Kannangara, M., and Kihlman, J. (2019). "Lignin recovery from spent alkaline pulping liquors using acidification, membrane separation, and related processing steps: A review," *BioResources* 14(1), 2300-2351. https://doi.org/10.15376/biores.14.1.2300-2351

Hubbe, M. A., and King, K. (2009). *Cost-Saving Strategies in Papermaking Chemistry,* TAPPI Press, Atlanta, 237 pp.

Hubbe, M. A., McLean, D. S., Stack, K. R., Lu, X. M., Strand, A., and Sundberg, A. (2020a). "Self-assembly of alkyl chains of fatty acids in papermaking systems: A review of related pitch issues, hydrophobic sizing, and pH effects," *BioResources* 15(2), 4591-4635. https://doi.org/10.15376/biores.15.2.4591-4635

Hubbe, M. A., Sjöstrand, B., Nilsson, L., Kopponen, A., and McDonald, J. D. (2020b). "Rate-limiting mechanisms of water removal during the formation, vacuum dewatering, and wet-pressing of paper webs: A review," *BioResources* 15(4), 9672-9755. https://doi.org/10.15376/biores.15.4.Hubbe

Hubbe, M. A., Szlek, D. B., and Vera, R. E. (2022). "Detergency mechanisms and cellulosic surfaces: A review," *BioResources* 17(4), 7167-7249. https://doi.org/10.15376/biores.17.4.Hubbe

Hudson, P. S. (1968). "Foam control in paper coating," *Paper Technol. Ind.* 9(3), 185-186.

Hutchinson, G. H. (1995). "A review of progress in the technology and applications of offset lithographic inks," *JOCCA – Surf. Coat. Int.* 78(5), 188-194.

Ihde, F. J. (1978). "Silica based defoamer compositions having improved stability," US Patent 4123383 A, Diamond Shamrock, assignee.

Ishida, T. (2001). "New emulsion type defoamer for paper making process," *Kami Pa Gikyoshi/Japan Tappi Journal* 55(2), 34-38. https://doi.org/10.2524/jtappij.55.188

Jackson, L, Chen, J., Hubbe, M. A., and Rosencrance, S. (2018). "Handling, dilution, and pumping of papermaking additives," in: *Advances in Papermaking Wet End Chemistry Applications Technologies*, M. A. Hubbe and S. Rosencrance (eds.), TAPPI Press, Atlanta, pp. 7-42.

Jha, B. K., Christiano, S. P., and Shah, D. O. (2000). "Silicone antifoam performance: Correlation with spreading and surfactant monolayer packing," *Langmuir* 16(26), 9947-9954. https://doi.org/10.1021/la990600f

Jiang, Z. H., Van Lierop, B., and Berry, R. (2000). "Hexenuronic acid groups in pulping and bleaching chemistry," *TAPPI J.* 83(1), 167-175.

Johnson, K. A. (1985). "Great Lakes achieves improved brown stock washing, substantial bod load reduction and significant savings in defoamer use with Kamyr pressure diffusion washer," *Paper Age* 101(2), 22, 30.

Joshi, K. S., Baumann, A., Jeelani, S. A. K., Blickenstorfer, C., Naegeli, I., and Windhab, E. J. (2009). "Mechanism of bubble coalescence induced by surfactant covered antifoam particles," *J. Colloid Interface Sci.* 339(2), 446-453. https://doi.org/10.1016/j.jcis.2009.07.072

Joshi, K. S., Jeelani, S. A. K., Blickenstorfer, C., Naegeli, I., and Windhab, E. J. (2005). "Influence of fatty alcohol antifoam suspensions on foam stability," *Colloids Surf. A – Physicochem. Eng. Aspects* 263, 239-249. https://doi.org/10.1016/j.colsurfa.2005.01.004

Käkölä, J., Alén, R., Pakkanen, H., Matilainen, R., and Lahti, K. (2007). "Quantitative determination of the main aliphatic carboxylic acids in wood kraft black liquors by high-performance liquid chromatography-mass spectrometry," *J. Chromatog. A* 1139(2), 263-270. https://doi.org/10.1016/j.chroma.2006.11.033

Kanicky, J. R., Poniatowski, A. F., Mehta, N. R., and Shah, D. O. (2000). "Cooperativity among molecules at interfaces in relation to various technological processes: Effect of chain length on the pKa of fatty acid salt solutions," *Langmuir* 16(1), 172-177. https://doi.org/10.1021/la990719o

Kanicky, J. R., and Shah, D. O. (2003). "Effect of premicellar aggregation on the pKa of fatty acid soap solutions," *Langmuir* 19(6), 2034-2038. https://doi.org/10.1021/la020672y

Kanner, B. (1968). "Surface viscosity – Factor in foam stability," *Indust. Eng. Chem.* 60(5), 6-7.

Karras, M., and Springer, A. M. (1989). "Influence of aeration and polymer on drainage of pine kraft slurries," *Tappi J.* 72(2), 155-159.

Kim, S. H. (1996). "Defoamer composition," US Patent 5523019 A, Houghton assignee.

Kobayashi, A., Matsui, C., Sakurai, T., and Aoki, S. (2019). "Defoamer oil compound, production method therefor, and defoamer composition," US Patent 102322288 B2, Shen-Etsu Chem. Co., assignee.

Koczo, K., Koczone, J. K, and Wasan, D. (1994). "Mechanisms for antifoaming action in aqueous systems by hydrophobic particles and insoluble liquids," *J. Colloid Interface Sci.* 166, 225-238. https://doi.org/10.1006/jcis.1994.1288

Koczo, K., Lobo, L., and Wasan, D. T. (1992). "Effect of oils on foam stability: Aqueous foams stabilized by emulsions," *J. Colloid Interface Sci*. 150, article 492. https://doi.org/10.1016/0021-9797(92)90218-B

Koljonen, K., Österberg, M., Kleen, M., Fuhrmann, A., and Stenius, P. (2004). "Precipitation of lignin and extractives on kraft pulp: Effect on surface chemistry, surface morphology and paper strength," *Cellulose* 11(2), 209-224. https://doi.org/10.1023/B:CELL.0000025424.90845.c3

Kremer, L. N. (2008). "Silicone defoamer to better control hydrocarbon foam and reduce silicon content of liquid hydrocarbon products," US Patent 7427350 B2, Baker Hughes assignee.

Kruglyakov, P. M. (1994). "Mechanisms of antifoam action," *Uspekhi Khimii* 63(6), 493-505. https://doi.org/10.1070/RC1994v063n06ABEH000098

Kulkarni, R. D., Goddard, E. D., and Kanner, B. (1977a). "Mechanism of antifoam action," *J. Colloid Interface Sci*. 59, 468-471. https://doi.org/10.1016/0021-9797(77)90042-X

Kulkarni, R. D., Goddard, E. D., and Kanner, B. (1977b). "Mechanism of antifoaming: Role of filler particle," *Ind. Eng. Chem. Fundam.* 16, 472-474. https://doi.org/10.1021/i160064a014

Laine, J. (1997). "Effect of ECF and TCF bleaching on the charge properties of kraft pulp," *Paperi Puu* 79(8), 551-559.

Langevin, D. (2008). "Aqueous foams: A field of investigation at the frontier between chemistry and physics," *ChemPhysChem* 9, 510-522. https://doi.org/10.1002/cphc.200700675

Lappan, R. E., Hrymak, A. N., and Pelton, R. (1996). "Polymer enhanced brownstock washing: Mill trial," *TAPPI J.* 79(1), 170-178.

Lappan, R. E., Hrymak, A. N., and Pelton, R. (1997). "Dependence of in situ precipitate deposition on flow characteristics in multipermeability porous media," *Chem. Eng. Sci.* 52(17), 2963-2975. https://doi.org/10.1016/S0009-2509(97)00099-7

Lazaar, O., and Hachem, E. (2022). "Review on the study of Pickering emulsions: Theory and simulation," in*: 2022 2nd International Conference on Innovative Research in Applied Science, Engineering and Technology* (IRASET'2022), B. Benhala, K. Mansouri, A. Raihani, and M. Qbadou (eds.), IEEE, pp. 2022. https://doi.org/10.1109/IRASET52964.2022.9738128

Lehmonen, J., Retulainen, E., Paltakari, J., Kinnunen-Raudaskoski, K., and Koponen, A. (2020). "Dewatering of foam-laid and water-laid structures and the formed web properties," *Cellulose* 27, 1127-1146. https://doi.org/10.1007/s10570-019-02842-x

Lehtinen, E. (ed.) (2000). *Pigment Coating and Surface Sizing of Paper*, Fapet Oy.

Lobo, L. A., and Bolton, T. S. (2013). "Brownstock washing fundamentals: Enhancing drainage through chemistry – Part 1," *TAPPI J.* 12(2), 69-78. https://doi.org/10.32964/TJ12.2.69

Lobo, L. A., Bolton, T. S., and Mitchell, M. (2016). "On-site emulsification of defoamer for brownstock washing of pulp," US Patent 9371613 B1.

Lu, S. J., Liu, R. X., and Sun, X. M. (2002). "A study on the synthesis and application of an inverse emulsion of amphoteric polyacrylamide as a retention aid in papermaking," *J. Appl. Polym. Sci.* 84(2), 343-350. https://doi.org/10.1002/app.10340

Lunkenheimer, K., and Wantke, K. D. (1981). "Determination of the surface-tension of surfactant solutions applying the method of Lecomte-du-Nouy (ring tensiometer)," *Colloid Polym. Sci.* 259(3), 354-366. https://doi.org/10.1007/BF01524716

Lynn, B., Lowery, R., Pamukcoglu, Z., and Thies, M. C. (2025). "Recovering lignin from agricultural alkaline liquors via heat-induced flotation of a self-forming lignin cake," *Separ. Purif. Technol.* 360(1), article 130825. https://doi.org/10.1016/j.seppur.2024.130825

Martin, J., Wilson, R., Rosencrance, S., and Previs, D. (2012). "Polymeric defoamer additive," US Patent 8236889, Kemira Chem. assignee.

Marton, J. (1989). "Mechanistic differences between acid and soap sizing," *Nordic Pulp Paper Res. J.* 4(2), 77-80. https://doi.org/10.3183/npprj-1989-04-02-p077-080

Martorana, E., and Kleemann, S. (2006). "Influence of de-foamers and de-aerators on paper properties and process parameters," *International Paperworld IPW* (11-12), 22-23.

Marquez, R., Aguado, R. J., Tarrés, Q., Tolosa, L., Tardy, B. L., Hubbe, M. A., and Aguilar, M. D. (2025). "Lignin nanoparticles as stabilizers in Pickering emulsions," *Adv. Colloid Interface Sci*. 349, article 103752. https://doi.org/10.1016/j.cis.2025.103752

Matula, J. (2000). "ShortFlow™ - A new paper machine approach system and mill concept," *Paperi Puu* 82(3), 174-178.

Matula, J., and Kukkamäki, E. (1998). "New findings of entrained air and dissolved gases in PM wet end – Mill case study," *Wochenbl. Papierfabr.* 126(17), 814-820.

May, O. W., and Buckman, S. J. (1975). "Practical effects of air in papermaking," *TAPPI* 58(2), 90-94.

Meinander, P. O., and Olsson, L.-H. (1999). "Compact, airless wet end system," in: TAPPI 99 Proceedings, TAPPI Press, Atlanta, pp. 1213-1218.

Melzer, J., and Poschman, F. (1973). "Defoaming and deaeration of pulp suspension," *Papier* 27, 229-231.

Michalski, R. J., and Youngs, R. W. (1975). "Amides and hydrophobic silica as antifoams," US Patent 3923683 A, Nalco Chem. assignee.

Miles, G. D., and Ross, J. (1944). "Foam stability of solutions of soaps of pure fatty acids," *J. Phys. Chem.* 48(5), 280-290. https://doi.org/10.1021/j150437a006

Miller, B., and Tyomkin, I. (1986). "An extended range liquid extrusion method for determining pore size distributions," *Textile Res. J.* 56(1), 35-40. https://doi.org/10.1177/004051758605600105

Miller, B., and Tyomkin, I. (1994). "Liquid porosimetry – New methodology and applications," *J. Colloid Interface Sci.* 162, 163-170. https://doi.org/10.1006/jcis.1994.1021

Moeller, H. W. (1966). "Cationic starch as a wet-end strength additive," *TAPPI* 49(5), 211-214.

Moller, T., Eicken, J., Fischer, H., Wollweber, H.-W., Gress, W., de Haut, C., Mahler, J., Gorzinski, M., and Sladek, H.-J. (1998). "Block polymers containing ester groups as defoamers for aqueous systems," US Patent 5710207 A, Henkel assignee.

Morehouse, W. B. (1945). "Chemical defoamers in the manufacture of pulp and paper," *Technical Association Papers* (earlier title of *TAPPI Journal*) 28, 91-92.

Motamedvaziri, S., and Armenante, P. M. (2012). "Flow regimes and surface air entrainment in partially filled stirred vessels for different fill ratios," *Chem. Eng. Sci.* 81, 231-250. https://doi.org/10.1016/j.ces.2012.05.050

Mudaly, G. (2007). "Atlantic packaging Whitby reduces defoamer costs with new water based technology," Annual Meeting of the Pulp and Paper Technical Association of Canada (PAPTAC), Vol. C, pp. C61-C64, 2007

Nechita, P., and Nastac, S. M. (2022). "Overview on foam forming cellulose materials for cushioning packaging applications," *Polymers* 14(10), article 1963. https://doi.org/10.3390/polym14101963

Nemeth, Z., Racz, G., and Koczo, K. (1998). "Foam control by silicone polyethers – Mechanisms of 'cloud point antifoaming'," *J. Colloid Interface Sci.* 207(2), 386-394. https://doi.org/10.1006/jcis.1998.5777

Nguyen, D. T. (1994). "Antifoam/defoamer composition and method of use thereof in aqueous system," US Patent 5283002 A, Betz Laboratories assignee.

Nguyen, D. T. (1995). "Antifoam composition for aqueous systems," US Patent, Betz Laboratories assignee.

Niemela, K. (1990). "Conversion of xylan, starch, and chitin into carboxylic-acids by treatment with alkali," *Carbohyd. Res.* 204, 37-49. https://doi.org/10.1016/0008-6215(90)84019-Q

Nyren, V., and Back, E. (1958). "The ionization constant, solubility product and solubility of abietic and dehydroabietic acid," *Acta Chem. Scand.* 12(7), 1516-1530. https://doi.org/10.3891/acta.chem.scand.12-1516

Owen, M. J. (2010). "Foam control," in: *Advances in Silicones and Silicone-Modified Materials*, S. J. Clarson, M. J. Owen, S. D. Smith, and M. E. VanDyke (eds.), ACS Symp. Ser., Vol 1051, pp. 269-283. https://doi.org/10.1021/bk-2010-1051.ch020

Pasquali, R. C., Taurozzi, M. P., and Bregni, C. (2008). "Some considerations about the hydrophilic-lipophilic balance system," *Int. J. Pharmaceutics* 356, 44-51. https://doi.org/10.1016/j.ijpharm.2007.12.034

Patra, T., Rinnan, Å., and Olsen, K. (2021). "The physical stability of plant-based drinks and the analysis methods thereof," *Food Hydrocolloids* 118, article 106770. https://doi.org/10.1016/j.foodhyd.2021.106770

Pelton, R. (1989). "A review of brownstock defoamer fundamentals," *Pulp Paper Can.* 90(2), 61-68.

Pelton, R. (1996). "A model of foam growth in the presence of antifoam emulsion," *Chem. Eng. Sci.* 51(19), 4437-4442. https://doi.org/10.1016/0009-2509(96)81675-7

Pelton, R., Flaherty, T., Hrymak, A., and Shawafaty, N. (2002). "Video observation of pulp pad formation and properties in brownstock washing – Defoamers primarily help speed up drainage," *Pulp Paper Can.*103(11), 23-27.

Pelton, R. H., and Goddard, E. D. (1986). "A theory for foam growth-kinetics in the presence of antifoam emulsion," *Colloids Surf.* 21, 167-178. https://doi.org/10.1016/0166-6622(86)80089-0

Pelton, R., and Grosse, B. (1994). "Polymer-enhanced displacement of lignin solution from model packed-beds," *J. Pulp Paper Sci.* 20(3), J91-J95.

Pichai, P., and Breindel, K. (2001). "Defoamer process," US Patent 6251958, Henkel assignee.

Pietikainen, T. (1992). "Online air entrainment tests on paper machines," *TAPPI J.* 75(11), 185-191.

Pletnev, M. Y., Eremina, L. D., and Vlasenko, I. G. (1983). "Problem of thermally controlled foaming in solutions of surface-active agents," *Journal of Applied Chemistry of the USSR* 56(9), 2058-2065.

Poschmann, F. (1962). "Defoaming agents in the paper industry," *Das Papier* 15(7), 295-301.

Prosser, A. J., and Franses, E. I. (2001). "Adsorption and surface tension of ionic surfactants at the air-water interface: Review and evaluation of equilibrium models," *Colloids Surf. A – Physicochem. Eng. Aspects* 178, 1-40. https://doi.org/10.1016/S0927-7757(00)00706-8

Qi, N., Sun, H. Y., Zhao, H., and Li, Y. (2018), "Achieving foaming control smartly: Pre-solubilized flavor oil serves as an in situ homogeneous defoamer," *Soft Matter* 14(11), 2059-2067. https://doi.org/10.1039/c7sm02266b

Qiao, M., Chen, J., Gao, N. X., Shan, G. C., Wu, J. Z., and Ran, Q. P. (2022). "Synthesis and properties of different alkyl alcohol polyethers as the defoamers for concrete," *Colloids Surf. A – Physicochem. Eng. Aspects* 646, article 128998. https://doi.org/10.1016/j.colsurfa.2022.128998

Racz, G., Koczo, K., and Wasan, D. T. (1996). "Mechanisms of antifoam deactivation," *J. Colloid Interface Sci.* 18(1), 124-135. https://doi.org/10.1006/jcis.1996.0363

Rauch, R., and Sangl, R. (2000). "Latest findings on entrained air and dissolved gases in pulp suspensions," *Proc. TAPPI 2000 Papermakers Conf.*, TAPPI Press, Atlanta, 159-175.

Reinhardt, R. A., Heilen, W., Walhorn, E., Silber, S., and Adams, J. W. (1998). "Defoamer selection in waterborne coatings," *J. Coatings Technol.* 70(885), 157-160. https://doi.org/10.1007/BF02730086

Rekonen, O., Korpio, E., and Hovi, R. (1990). "A new generation of antifoam agents for pulp mills," *Paperi ja Puu* 72(7), 692-697.

Robinson, J. W., and Woods, W. W. (1948). "A method of selecting foam inhibitors," *J. Soc. Chem. Ind*. 67, 361-365. https://doi.org/10.1002/jctb.5000670908

Rodríguez-Abreu, C. (2019). "On the relationships between the hydrophilic-lipophilic balance and the nanoarchitecture of nonionic surfactant systems," *J. Surfact. Deterg.* 22(5), 1001-1010. https://doi.org/10.1002/jsde.12258

Ross, S. (1950). "Inhibition of foaming. II. A mechanism for the rupture of liquid films by antifoam agents," *J. Phys. Colloid Chem*. 54, article 429. https://doi.org/10.1021/j150477a018

Saint-Jalmes, A. (2006). "Physical chemistry in foam drainage and coarsening," *Soft Matter* 2, 836-849. https://doi.org/10.1039/b606780h

Salager, J. L. (2021). "Surfactant-oil-water systems," *J. Surfact. Deterg.* 24(5), 731-748. https://doi.org/10.1002/jsde.12518

Salager, J. L., Marquez, R., Bullon, J., and Forgiarini, A. (2022). "Formulation in surfactant systems: From Windsor to HLD_N," *Encyclopedia* 2022(2), 778-839. https://doi.org/10.3390/encyclopedia2020054

Salager, J. L., Marquez, N., Graciaa, A., and Lachaise, J. (2000). "Partitioning of ethoxylated octylphenol surfactants in microemulsion-oil-water systems: Influence of temperature and relation between partitioning coefficient and physicochemical formulation," *Langmuir* 16(13), 5534-5539. https://doi.org/10.1021/la9905517

Santos, R. B., and Hart, P. W. (2014). "Brownstock washing – A review of the literature," *TAPPI J.* 13(1), 9-19. https://doi.org/10.32964/TJ13.1.9

Sawicki, G. C. (2005). "Impact of surfactant composition and surfactant structure on foam control performance," *Colloids Surf. A – Physicochem. Eng. Aspects* 263, 226-232. https://doi.org/10.1016/j.colsurfa.2004.12.026

Schmedding, D., and Tatum, V. L. (1998). "Alkylphenol ethoxylate surfactants: A critical review of the science," in: *Int. Environ. Conf. Exhib.*, TAPPI Press, pp. 461-471.

Schmidt, W. T, and Gammon, C. T. (1980). "Water-in-oil emulsion defoamer compositions, their preparation and use," US Patent 4225456, Diamond Schamrock assignee.

Schneider, O., Burger, W., and Rautschek, H. (2010). "Method for the production of defoamer formulations," US Patent 7776929 B2, Wacher Chem. assignee.

Schuhmacher, R., Dralle-Voss, G., Oppenlaender, K., Wegner, B., and Hohmann, A. (1997). "Antifoams based on oil-in-water emulsions for the paper industry," US Patent 5700351 A, BASF assignee.

Shane, H. J. S., and Schell, F. S. (1978). "Water-emulsifiable defoamer composition," US Patent 4088601 A, Hart Chem. assignee.

Sheppard, P., Kent, K. R., and Molter, M. (2011). "Closed loop defoamer control stabilizes paper machine operations and reduces costs," in: *Paper Conference and Trade Show 2011, PaperCon* 2011, Vol. 2, pp. 899-908.
Shrinath, A., Szewczak, J. T., and Bowen, I. J. (1991). "A review of ink-removal techniques in current deinking technology," *TAPPI J.* 74(7), article 85-93.
Sinka, J. V., and Lightman, I. A. (1977). "Silica-base defoamer compositions with improved stability," *US Patent* 326570 (1973/01/24 AP).
Sithole, B., and Watanabe, C. (2013). "Using Py-GC/MS to detect and measure silicone defoamers in pulp fibres and mill deposits," *J. Anal. Appl. Pyrol.* 103, 8-16. https://doi.org/10.1016/j.jaap.2012.08.013
Sjökvist, T., Wålinder, M. E. P., and Blom, Å. (2018). "Liquid sorption characterisation of Norway spruce heartwood and sapwood using a multicycle Wilhelmy plate method," *Int. Wood Prod. J.* 9(2), 58-65. https://doi.org/10.1080/20426445.2018.1467602
Slovinsky, M., and Maciaszek, J. A. (1982). "Fatty epoxide hydrophobized silica as antifoams in brownstock washing aids," US Patent 4332696, Nalco Chem., assignee.
Spence, G. G. (1997). "Defoamers for brown stock washers," TAPPI 1997 Pulping Conf., pp. 207-210.
Stitt, J. B. (1997). "Slime and deposit control: Alkaline challenge," *PIMA's North American Papermaker* 79(9), 54-56.
Strazdins, E. (1981). "Chemistry of rosin sizing," *TAPPI* 64(1), 31-34.
Suwala, D. W. (1976). "Defoamer composition," US Patent 3951853, Diamond Shamrock assignee.
Svarz, J. J. (1990a). "Antifoam/defoamer composition," US Patent 4950420 A, Nalco assignee.
Svarz, J. J. (1990b). "Antifoam/defoamer composition," US Patent 4968448 A, Nalco assignee.
Tamura, T., Kageyama, M., Kaneko, Y., and Nikaido, M. (2000). "Preparation of novel silicone-based antifoams having a high defoaming performance," in: *Emulsions, Foams, and Thin Films*, K. L. Mittal and P. Kumar (eds.), pp. 161-175.
Theander, K., and Pugh, R. J. (2004). "Surface chemicals concepts of flotation de-inking," *Colloids Surf. A – Physicochem. Eng. Aspects* 240, 111-130. https://doi.org/10.1016/j.colsurfa.2003.12.014
Touchette, R. V., and Jenness, L. C. (1960). "Effect of surface active agents on drainage and physical strength properties of sulfate pulp," *TAPPI* 43(5), 484-489.
Trovagunta, R., Marquez, R., Tolosa, L., Barrios, N., Zambrano, F., Suarez, A., Pal, L., Gonzalez, R., and Hubbe, M. A. (2024). "Lignin self-assembly phenomena and valorization strategies for pulping, biorefining, and materials development: Part 1. The physical chemistry of lignin self-assembly," *Adv. Colloid Interface Sci*. 332, article 103247. https://doi.org/10.1016/j.cis.2024.103247
Twoomey, L. F. (1986). "Water-based antifoams boost profits, runnability," *Southern Pulp and Paper* 49(5), 33-34.
Twoomey, L. F. (1990). "New oil-free brownstock washer defoamer can help mills reduce dioxin-related problems," in: *1990 Pulping Conference, TAPPI Proceedings*, Tech. Assoc. Pulp Paper Ind., pp. 984-987.
Uloth, V., and Wearing, J. T. (1989a). "Kraft lignin recovery. Acid precipitation versus ultrafiltration," *Pulp Paper Can.* 90, 67-71. T357-T360; 34-37, T310-T314

Vines, S. M., Gratton, R., Raymond, L., and Gauthier, C. (1997). "Control of foaming at the size press," 83rd Annual Meeting, Technical Section CPPA, Canadian Pulp and Paper Association, B377-B382.

Wallberg, O., Linde, M., and Jönsson, A. S. (2006). "Extraction of lignin and hemicelluloses from kraft black liquor," *Desalination* 1999, 413-414. https://doi.org/10.1016/j.desal.2006.03.094

Wallmo, H., Theliander, H., Jönsson, A. S., Wallberg, O., and Lindgren, K. (2009). "The influence of hemicelluloses during the precipitation of lignin in kraft black liquor," *Nordic Pulp Paper Res. J.* 24(2), 165-171. https://doi.org/10.3183/npprj-2009-24-02-p165-171

Wang, G., Pelton, R., Hrymak, A., Shawafaty, N., and Heng, Y. M. (1999). "On the role of hydrophobic particles and surfactants in defoaming," *Langmuir* 15, 2202-2208. https://doi.org/10.1021/la980618a

Wang, H. T., Wei, X. B., Du, Y. H., and Wang, D. M. (2019). "Effect of water-soluble polymers on the performance of dust-suppression foams: Wettability, surface viscosity and stability," *Colloids Surf. A – Physicochem. Eng. Aspects* 568, 92-98. https://doi.org/10.1016/j.colsurfa.2019.01.062

Wang, J.-L., Nguyen, A. V., and Farrokhpay, S. (2016). "A critical review of the growth, drainage, and collapse of foams," *Adv. Colloid Interface Sci.* 228, 55-70. https://doi.org/10.1016/j.cis.2015.11.009

Wang, L., Wang, H., Rong, M., Li, W., Li, N., Liu, P., Li, X., and Zhang, Z. (2024). "Preparation of hyperbranched hydrophobic nano-silica and its superior needling-effect in PDMS defoam agent," *Journal of Colloid and Interface Science* 670, 698-708. https://doi.org/10.1016/j.jcis.2024.05.111

Wang, X. Q., Chai, Y. B., and Liu, J. L. (2013). "Formation of highly hydrophobic wood surfaces using silica nanoparticles modified with long-chain alkylsilane," *Holzforschung* 67(6), 667-672. https://doi.org/10.1515/hf-2012-0153

Wegner, B. S., Oppenlaender, K., Schuhmacher, R., Hohmann, A., and Dralle-Vos, G. (1994). "Antifoams for the paper industry based on oil-in-water emulsions," US Patent 5326499 A, BASF assignee.

Wollenveber, H.-S. (1997). "Aqueous dispersions of antifoam agents," US Patent 5679286 A, Henkel assignee.

Xu, C. H., Wang, H. T., Wang, D. M., Zhu, X. L., Zhu, Y. F., Bai, X., and Yang, Q. L. (2020). "Improvement of foaming ability of surfactant solutions by water-soluble polymers: experiment and molecular dynamics simulation," *Polymers* 12(3), article 571. https://doi.org/10.3390/polym12030571

Xu, L. B., Myers, J., and Hart, P. W. (2016). "How to use alum with cationic dispersed rosin size," *TAPPI J.* 15(5), 331-335. https://doi.org/10.32964/TJ15.5.331

Yang, P.-J., Li, L., Qin, S., Wu, D., Peng, Y., Liu, H.-Y., and Peng, X.-Y. (2023). "Effects and mechanisms of foam suppression in food waste anaerobic digester using defoaming agents," *Fuel* 342, article 1279290. https://doi.org/10.1016/j.fuel.2023.127920

Zarate-Muñoz, S., Troncoso, A. B., and Acosta, E. (2015). "The cloud point of alkyl ethoxylates and its prediction with the hydrophilic-lipophilic difference (HLD) Framework," *Langmuir* 31(44), 12000-12008. https://doi.org/10.1021/acs.langmuir.5b03064

Zhang, G.-Y., Liu, Y.-T., and Wei, C.-B. (2007). "Preparation of TS emulsion type organic silicon defoamer," *China Surfactant Detergent & Cosmetics* 37(2), 128-130.

Zhang, H. N., Ren, H., and Zhai, H. M. (2021). "Analysis of phenolation potential of spruce kraft lignin and construction of its molecular structure model," *Indust. Crops Prod.* 167, article 113506. https://doi.org/10.1016/j.indcrop.2021.113506

Zhu, W. Z., Westman, G., and Theliander, H. (2015). "The molecular properties and carbohydrate content of lignins precipitated from black liquor," *Holzforschung* 69(2), 143-152. https://doi.org/10.1515/hf-2014-0062