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FUNDAMENTALS OF FOAM AND DEFOAMING

1.   WHAT IS FOAM

Foam is a gas dispersed in a liquid. The gas is usually air or liberated carbon dioxide, and the liquid usually water.

The presence of gas and a pure liquid alone is not sufficient to produce foam, since pure liquids do not foam. The third component required to form foam, in addition to the gas and liquid, is a surfactant that is soluble in the liquid.

Surfactants are composed of molecules having both water-soluble and water-insoluble portions within the same molecule. An example of a surfactant is sodium palmitate:

FIGURE I

SURFACTANT (SODIUM PALMITATE)

$$Na^+ \; OOC^- \; - \; (CH_2)_{14} \; CH_3$$

Water-soluble   Water-insoluble
(hydrophilic)   (hydrophobic)
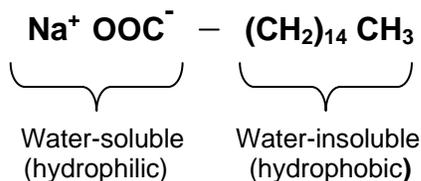
The molecules are named surfactants because they concentrate at the surface or air-water interface. The reason these molecules concentrate at the surface is to satisfy both the tendency of the water-soluble portion to be in water and the tendency of the water-insoluble portion to be away from the water. For example:

FIGURE II

ORIENTATION OF SURFACE ACTIVE MOLECULES AT AIR WATER INTERFACE

(SODIUM PALMITATE)

AIR $(CH_2)_{14} \; CH_3$ $(CH_2)_{14} \; CH_3$ $(CH_2)_{14} \; CH_3$

WATER   COO -   COO -   COO -
Na^+ Na^+ Na^+
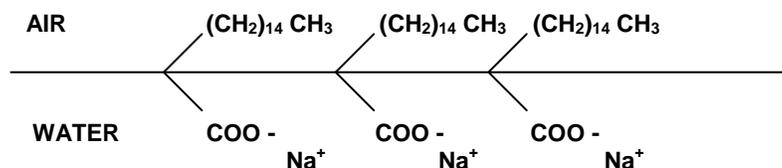
By orienting at the air-liquid interface, both of these tendencies are satisfied.

II: FOAM STABILITY

Foam manifests itself as bubbles or air cells separated by thin liquid films. In the case of a film between two air cells or bubbles, the surfactant molecules can concentrate at both surfaces of the film as shown in Figure III.

FIGURE III

Surfactant Molecules Concentrated at Both Surfaces of
a Liquid Film
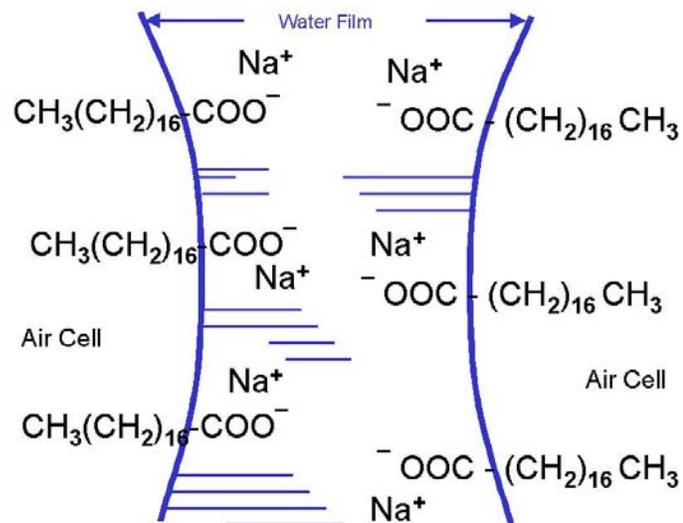
This liquid film is now self-supporting for four main reasons:

> (1)   Thinning of the film is prevented by the electrical repulsion of the like-charged surfaces. (The ionized COO $^-$ groups impart a negative charge to each surface) In order for the film to break, it must thin down until the walls meet. However, as the walls or surfaces of the film approach each other due to water drainage from the film, strong electrical repulsive forces are set up between the two surfaces, thereby preventing, or at least slowing down, their coalescence.

> (2)   Draining of the film is prevented because of its high viscosity. The COO $^-$ groups have high affinity for water molecules and form thick layers of tightly bound water at each surface. One effect of the formation of this bound water is an increase in viscosity of the thin

films that make up the walls of the bubble. Van der Waals' forces and electro-viscous effects combine with the above and result in films of very high viscosity.

(3)   Rupture of the film is retarded because of the ability of a film to heal itself. Any disturbance at the surface of a film (a falling dust particle or air motion) which displaces the surface molecules around the disturbance exposing water, which has a higher surface tension. Immediately, surfactant molecules will reorient themselves at the point of disturbance carrying underlying water with them that tends to heal the disruption as shown in Figure IV.

FIGURE IV

EFFECT OF DEFOAMER ON SURFACTANT ORIENTATION
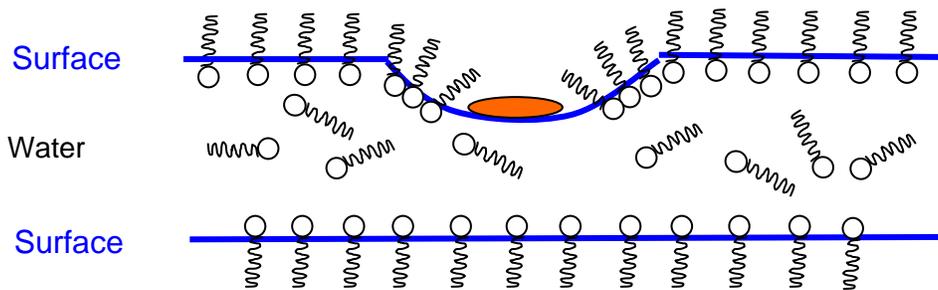
(4)   Rupture of the film is minimized because of the plasticity of the film. The presence of surfactant molecules at the surface of a film imparts a certain degree of plasticity or elasticity to the film. This property greatly decreases the possibility of rupture when ever-present external forces act on the exposed film.

Thus far our discussion of foam stability has been limited to two-phase foams which consist of a gas dispersed in a liquid containing a surfactant. There is a second type of foam which is even more stable, namely, a three-phase foam in which finely divided solid particles prevent foam bubbles from coalescing as shown below:

FIGURE V

Solid Stabilized Foam
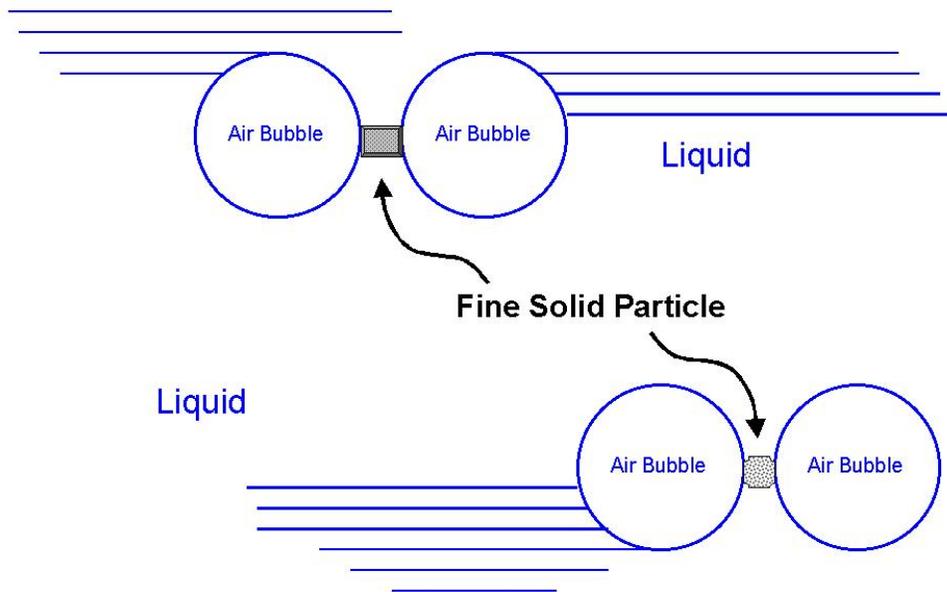
Solid-stabilized foam is the type generally found in a paper mill system, where filler materials, pigments, precipitates, other additives, and impurities act as stabilizing agents in the presence of a small amount of soluble surfactants.

For a solid particle to be stable at the air-liquid interface, its contact angle (measure of ease of wetting) should be 90° or less, depending on the shape of the solid. If the solid particle has a contact angle of 0° or 180°, it cannot stabilize foam since it will not concentrate at the interface.

The contact angle of a particle is dependent in part on the degree to which the surfactant is absorbed by the particle. In some cases, solid particles may have the proper contact angle without absorbing a surfactant. The effect of this relationship is shown below:

FIGURE VI

Effect of Contact Angle of Solid Particle at Air-Water Interface
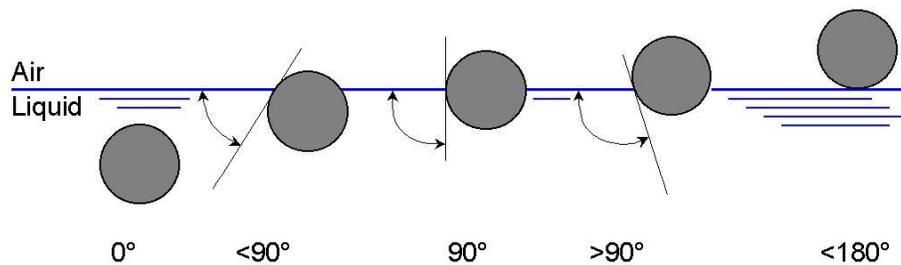
III.   PRODUCTION FOAM

Besides stabilizing the water films between air cells, the presence of a surfactant in the water also causes any air brought into the liquid to enter as finely divided bubbles. The reason for this is the lower surface tension of the surfactant solution which allows the formation of a much larger surface area when the same amount of work is done to bring air into the system. (A large number of small bubbles has a much larger surface area than the same volume of air present as a few large bubbles.)

The relationship of surface tension to the surface area produced is expressed by the equation:

FIGURE VII

$$A = \frac{W}{\gamma}$$ where

A = surface area of bubbles

W = work introduced into the system through agitation or other means

γ =   surface tension

Assuming the amount of work or agitation introduced into the system to be constant, the area will be an inverse formation of the surface tension. Therefore, the introduction of a surfactant lowers the surface tension, resulting in a larger area and, therefore, smaller bubbles.

Small air bubbles rise through liquid more slowly than large bubbles because of their lower buoyancy. (The rate of ascent of a bubble through a liquid varies as the cube of the radius). In their slower ascent, the small bubbles have more time to allow surfactant molecules to orient on their surface. As the bubble approaches the liquid surface, it pushes up a thin film of liquid and oriented surfactant which forms the outer skin of the bubble. This causes the bubble to be very stable at the liquid surface.

When bubbles do coalesce for any reason and become larger, they not only rise to the surface faster, but become less stable by providing a greater surface area subject to rupture.

Foam can be caused in three general ways: mechanical, chemical, and bacterial.

Mechanical entrainment:

Vigorous or incorrect agitation
Splashing or cascading of stock
Churning or air leakage in pumps
Internal aeration

Chemical introduction:

Type and condition of wood
Water conditions
Improperly washed pulp
Insufficient removal of bleaching
    solutions and colloidally dispersed
    products of bleaching reactions
Addition of chemical additives such as
    Rosin size, excess defoamer, fillers
    dyestuffs, resins, pitch control agents,
    slimicides, retention aids, strength
    additives, etc.
Poorly washed deinked or wastepaper
    furnishes
Excessive alkalinity

Liberation of gas in the aqueous medium
by acidification of a system containing
carbonates

Bacterial formation:

Fermentation of some types of stock on aging
Decomposition of certain additives
Presence of microorganisms in the system.

Troublesome foam is found in several different locations in pulp and paper mills. Generally speaking, the following are the most common areas of foam problems:

Pulp Mill

Primary stock washers
Dilute stock screens
Deckers and thickeners
Bleach plant washers
Black liquor filtrate tanks
Oxidizing towers
Evaporators

Paper Machine – Wet End

Centrifugal stock cleaners
Fourdrinier
Fan Pump, screens, headbox, wire pit, wire

Board Machine – Wet End

Centrifugal stock cleaners
Headbox
Screens
Vats

Paper and Board Machines

Size press
Coater
Calender

Obviously, each of the above represents a separate and unique foaming system; however, the function of drainage through a fibrous medium is common to several.

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Drainage is critical to washers and deckers for efficiency and production, and to sheet forming operations for strength, quality and efficiency of equipment.

IV: <u>EFFECTS OF FOAM</u>

The rate of drainage of a sheet can be affected by the presence of entrapped air in a wet web of fiber. The amount of air is less critical than the distribution of air. When a mat has a large number of bubbles entrapped, the drainage rate is slowed because the water passing through the sheet or mat can only pass through the films between the bubbles as shown below:

<u>**FIGURE VIII**</u>

Effect of Entrained Air on Drainage
Through a Fibrous Mat
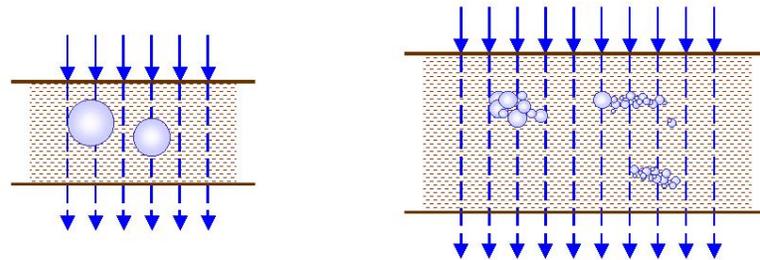
Brown stock washers represent a fiber-surfactant condition that illustrates the detrimental effect of entrapped air on drainage. (See Figure VIII.) Fatty acid and resin soaps and other surfactants are present in relatively high concentration and result in the air present being in a finely divided state. Since the purpose of this operation is to remove, by washing, the cooking liquors and other products formed during digestion, a high rate of liquid filtration is essential. Maximum washing efficiency cannot be achieved as long as air remains finely dispersed in the system; in fact, only the addition of a drainage aid can help once this condition exists. The use of a drainage aid or certain

defoamers can effectively cause the coalescence of these bubbles and increase the drainage rate of liquor through the stock.

The importance of high efficiency in the washing operation is best illustrated by considering some of the harmful and costly conditions that can result when the maximum amount of black liquor is not removed.

1.   Poor washer operation
2.   Lower production rate
3.   Loss of cooking chemicals
4.   High consumption of bleaching chemicals
5.   Excessive defoamer cost in subsequent operations

Brown stock washing is typically a high consistency system where the problem is to remove liquid from a solid (fiber) phase. Another problem somewhat the reverse of the above is the removal of air from a liquid phase in a low consistency system. This is typified by the release of air from a dilute stock solution on a paper or board machine.

As mentioned previously, with a high surfactant concentration in a given system, the number of bubbles will be greater because of the lower surface tension. The smaller the bubble, the less the buoyancy, resulting in less escape of air from the liquid medium. When a larger number of bubbles are present, there is less drainage area and the result is a "slow" sheet.

The physical make-up of a fibrous mat inherently results in poor drainage. Because the buoyancy of the bubble is not great enough to overcome the forces attracting the bubble to the fiber, the bubble will remain adjacent to the fiber, and can result in floating stock or air voids. Floating stock is troublesome because of wet web breaks that usually occur when these islands of stock are released. Air voids can cause poor formation, low sheet strength, nonuniform application of surface treating materials, and rejection of a sheet because of poor appearance.

Some of the other detrimental effects of foam in pulp and paper mill operations are as follows:

1.   Reduction in screening efficiency
2.   Carryover of acceptable fibers to secondary screens
3.   Low decker efficiency
4.   Stock flotation
5.   Pump binding
6.   Flotation of wet end additives.

In addition to these internal effects of foam, there is one external effect, namely, in the application of surface coatings to paper and board. This includes size press, calender, and coating operations. Foam is detrimental in these applications because it caused blemishes in the finished sheet characterized as "craters" or "volcanoes".

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Craters are the result of finely entrapped air in the coating that breaks at the surface after application. This leaves a "pit" which will fill with ink during printing and cause a distortion of the printed character.

Foam is caused in coating solutions by the presence of polymeric emulsions, dispersants, and other components. The pigment solids tend to stabilize this foam and also increase the viscosity of the coating color. These two effects tend to retard the release of air resulting in the above surface blemishes.

V.   CONTROL OF FOAM

Foam in pulp and paper mills may be either visible or invisible. Visible foam cannot be present without invisible foam having been generated, but invisible foam can be present without any outward indications of bubbles. Visible foam is normally the less harmful of the two and can frequently be eliminated mechanically. Invisible foam causes the more serious problems.

Considering the three ingredients required for the formation of foam – liquid, gas, and surfactant – it is quite understandable why foam is a problem in pulp and paper mills. It is obviously not practical to operate without water or in a vacuum. It is very necessary in most operations to introduce materials containing surfactants. In fact, surfactants are present in wood sugars, hemicellulose and lignin derivatives.

The first consideration toward minimizing a foam problem is to make the proper choice in selecting component ingredients and to use all additives at the minimum amounts consistent with good operation and quality. Secondly, certain mechanical corrections should be made, such as tighten up pump packing glands, extend all pipe lines to the bottom of the vessels into which they discharge, minimize free fall of stock over weirs, dams, and out of screens; eliminate the use of pumps with capacities larger than necessary; and install water showers at locations where foam might accumulate. The use of mechanical pulp mill foam breakers or paper machine headbox evacuation systems might be justified in certain cases.

Lower consistency, slower speeds, and longer wires can help overcome air entrainment on Fourdrinier wires because the release of air will be greater if stock concentration is less. Also, if the length of time the web remains fluid is extended either by slower speed or longer wires, the chance of more air being released is increased. Commercial defoamers can frequently eliminate the need for such drastic steps.

Heated stock will frequently release dissolved gases in the liquid medium. These minute bubbles will attach themselves directly to the fiber and will act as a nucleus for bubble growth. This sort of air is very difficult, if not impossible, to remove.

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Steam showers on the other hand sometime reduce surface foam by causing excessive stresses on the bubble wall due to sudden expansion of the film. It would seem reasonable that the greater the differential of temperature between steam and wet web, the greater the effectiveness of the steam shower.

In recent years some foam problems have become aggravated by operation of pulp and paper mill equipment beyond designed capacity. In such cases small mechanical changes have little effect, so chemical defoamers have been employed in increasing amounts.

The main function of a chemical defoamer is to cause coalescence of small bubbles before they rise to the surface of the bulk liquid medium. The method by which this occurs might be illustrated as follows:

FIGURE IX

Effect of Defoamer on Coalescence
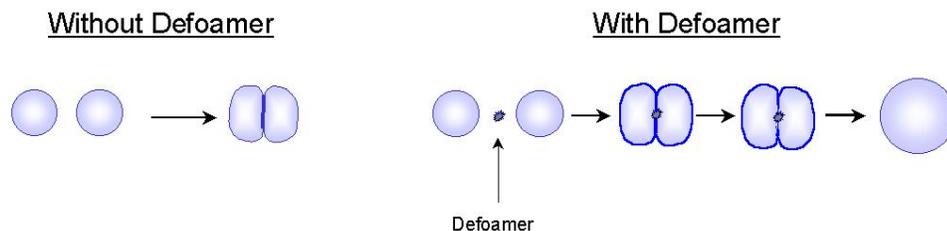
If sufficient coalescence has taken place, a large unstable bubble will appear at the air-liquid surface and collapse immediately.

A defoamer added to the bulk liquid system should come in contact with the bubble by diffusion, thermal agitation or random collision, and have the ability to prevent the formation of a stable surfactant layer on the bubble wall. If an elastic film of surfactant has already been formed, the defoamer should have the ability to break

through the surface of this film and spread rapidly forcing the deorientation of the surfactant layer and causing a weak thin spot in the film. When a system containing finely entrapped air is treated in this way, coalescence of the small bubbles will follow.

Whether a defoamer droplet will spread at the film surface once it contacts a bubble is dependent upon the concentration of surfactants in the foaming solution. The defoamer has a certain "spreading pressure" which decreases with increasing surfactant concentration until, at high concentrations of surfactant, the defoamer is ineffective.

The above explains the reason why defoamer should be injected into the bulk liquid and not simply added to the surface of a foaming system. An exception to this might be the spraying of a defoamer on a Fourdrinier wire, headbox, or on the surface of a stream of effluent. In these cases the purpose is to break surface foam by a slightly different principle. Once the bubble is on the surface of a liquid, it is impossible to apply the foregoing principles; however, for elimination of foam, drainage of the film is still necessary. The addition of low surface tension materials is recommended as they will increase the rate of film drainage, resulting ultimately in a thin film structure that cannot support itself.

The point of addition of defoamer is critical. The defoamer must be added at the point where air is being introduced or where it is being finely dispersed because at this instant a minimum amount of surfactant will have penetrated the air-liquid interface of the newly created bubble.

The complexity of foaming systems is frequently under-estimated, and even this discussion of the problem is greatly simplified. Each "foam problem" is a case history and universal application of one defoamer or one technique will ultimately lead to failure. A thorough examination of all known influences should be made before any recommendations are considered, and preferably laboratory or small scale screening trials should be used to substantiate these recommendations.