Creating tomorrow’s solutions

SILICONE PRODUCTS FOR ANTIFOAM AGENTS IN THE DETERGENTS INDUSTRY

Foam is a normal side effect of machine washing with liquid or powder detergents. But it is not just the surfactants in the detergent formulations which are responsible for the foam. The movement of the laundry during the wash cycle, the temperature, water hardness, ionic strength, pH and machine load, type of laundry and degree of soiling are also contributory factors.

Foam is crucial to the quality of a laundry wash. In moderation, it protects the laundry. But too much of it can affect the machine’s performance and the washing process itself and, what is more, increases water consumption. SILFOAM® antifoam agents from WACKER are a highly efficient and reliable means of controlling foam in detergent formulations and of enhancing processes. Additionally, SILFOAM® meets the needs of modern consumers for ecologically sound products that give a good wash, are easy to handle and conserve water and energy.

How do silicone products in defoamers work? Which detergent formulations are they suitable for, and how are they used? You’ll find the answers here – and if you have questions, please contact us. Your direct link to us: info.silicones@wacker.com.

1. SILICONE PRODUCTS FOR FORMULATING LIQUID AND POWDER DETERGENTS

1.1 Foam Formation in Washing Machines

Different types of washing machines are used around the world. The Europeans mainly use front-loaders with a horizontal axis. These are renowned for their excellent wash performance. However, they generate too much foam during the wash. The problem is that, during the wash cycle, the laundry is continually projected upwards and out of the wash liquor inside the drum. When it falls back into the liquor, it entrains air with it — and that gives rise to foam. Foam control is therefore essential for this type of machine.

In top loaders, which have a vertical axis, the laundry remains in the wash liquor throughout the wash, being moved back and forth by an agitator. Much less foam is generated and there is no need to control the level of foaming by the detergents. In fact, detergents for these machines often require a foam booster to be added. Top loaders are most popular in the USA, Japan and South America. However, there is a growing trend toward front loaders in the USA, where they are called high-efficiency or “HE” machines. This trend has its roots in environmental considerations. Front loaders require much less water for washing and rinsing than top loaders. Consequently, “HE” detergents are becoming more and more widespread on the US market and they, in turn, contain a foam brake.

1.2 Surfactants in Detergent Formulations

Surfactants are one of the active agents contained in detergents. They lower the surface tension of the water, and so enable the wash liquor to readily wet the textile fibers. They also help the wash liquor to wet the dirt, which is often greasy. They remove the dirt from the fibers by means of the so-called roll-up mechanism. Finally, the surfactants help to emulsify the dirt so that it stays in the wash liquor and is not deposited on the fibers again.
One property of surfactants is an ability to foam. Children are very familiar with this property because they use it to blow bubbles: dipping a plastic ring into the surfactant and gently blowing the film of surfactant which has formed in the ring into a bubble. Surfactants accumulate at the interface between air and water. In so doing, they stabilize the so-called foam lamellae. Surfactants differ in their ability to induce foaming.

- The anionic surfactants based on linear alkylbenzene sulfonates mainly used in detergents have a high tendency to foam, especially at low temperatures.

- Nonionic, alcohol ethoxylate surfactants foam extensively at low temperatures. When solutions of them are heated above the cloud point of the constituent surfactants, they stop foaming and may even exhibit defoaming properties.

- Alkyl ether sulfates foam at high temperatures whereas alkyl polyglycosides foam extensively, producing very stable lamellae. Anybody who has used a shampoo will be familiar with this.

1.3 Foam in Laundry Washes
The amount of foam produced in a washing machine depends on several factors – first, the type of machine and the wash program. Different brands of washing machines generate different volumes of foam. A high-end washing machine, for example, generates much less foam than its low-end counterpart. Other contributory factors are the constituent surfactants, their concentration and the surface tension. The extent of foaming is also governed by the temperature, water hardness, ionic strength, pH and machine load, the type of laundry and how dirty it is.

Is foam really necessary for washing laundry? Foam does several important jobs in a wash. During the wash cycle, it acts like a “pillow” to protect the laundry from the mechanical forces involved. This effect is primarily exploited in high-foaming detergents for delicate fabrics. The drawback is that excessive foam reduces wetting of the fibers by the wash liquor and impairs the cleaning effect. This has been demonstrated in scientific studies.1 (Please click here to go to the literature references.) Foam also helps to float insoluble dirt out of the wash liquor.

How much foam is needed for a wash depends primarily on the user. People all around the world have different views on this. In general, though, a certain minimum amount is always needed because otherwise consumers think that the detergent formulation is not working properly.
1.4 What Is Foam?

Foam can be defined as a dispersion of a gas in a liquid. The dispersion has roughly the same density as the gas. Whereas pure liquids form bubbles, foaming requires the presence of a surfactant to lower the surface tension of the liquid.

Gas bubbles obey Stoke’s law, which states that large gas bubbles rise faster than small ones. Bubbles inside a liquid are spherical, but on a surface are polyhedral.

Gravity and the pressure difference between the bubble and the surrounding liquid soon cause the gas bubble to start drying out. The foam lamellae, which are 1–600 μm thick, become increasingly thinner, until finally the gas escapes and the bubble bursts.
2. HOW DOES DEFOAMING WORK?

To understand defoaming, it is necessary to understand how foam becomes stabilized in the first place. Foam is stabilized when the so-called Marangoni effect comes into play. This, in turn, is based on the “Gibb’s elasticity.” A foam lamella is elastic because the surface tension changes with change in surface area of the gas bubble.

In a foam lamella, the surfactant molecules tend to concentrate at the bottom. This gives rise to a gradient in surface tension, which causes surfactant molecules in the lamella to be drawn upward; as they do so, they carry liquid with them. This “wet” or “dynamic” foam is vulnerable to attack by chemical antifoam agents. One example of this is champagne bubbles – which are rapidly destroyed by the alcohol in the champagne.

There are several mechanisms by which silicone antifoam agents work:

- Spreading – Fluid Entrainment
- Bridging – Dewetting
- Bridging – Stretching

2.1 Spreading – Fluid Entrainment
In this mechanism, an antifoam droplet penetrates the foam lamella. The silicone fluid spreads over the film surface and, due to the Marangoni effect, the water drains away radially from the fluid droplets. The foam lamella in the vicinity of the fluid droplet becomes thinner and finally ruptures.

![Diagram of Spreading – Fluid Entrainment](image)

- a) – silicone antifoam droplet spreads onto and/or enters into the foam lamella
- b) – The spreading of the oil over the foam film surface leads to Marangoni – driven flow of water radially from the oil drop, resulting in a local film thinning and rupture.
- c) – the foam lamella becomes thinner and thinner
  - air moves out
  - the bubble collapses

2.2 Bridging – Dewetting
In this mechanism, a silicone antifoam fluid droplet penetrates the foam lamella. The surfactant molecules at the interfaces of the foam lamella migrate away from the silicone surface, thereby “dewetting” the vicinity of the silicone droplet. The foam lamella in the vicinity of the silicone droplet thus becomes thinner and eventually ruptures.

![Diagram of Bridging – Dewetting](image)

- a) – silicone antifoam droplet spreads onto and/or enters into the foam lamella
- b) – a dewetting of the antifoam droplet starts
  - the surfactants move away from the silicone droplet
- c) – the foam lamella becomes thinner and thinner
  - air moves out
  - the bubble collapses
2. 3 Bridging – Stretching

Here, the antifoam fluid droplet penetrates the foam as in the other mechanisms. The fluid droplet forms a bridge across the foam lamella. Because the capillary pressure at the fluid-water is different from that at the fluid-air interface, the droplet of silicone antifoam fluid stretches. If it stretches too much, the lamella at the thinnest part of the stretched antifoam fluid droplet ruptures. This also causes a reduction in the original size of the antifoam fluid droplet.

For an antifoam to work, several thermodynamic conditions must be met. These are described by the coefficients for spreading, penetration and bridging, as shown in the following equations:

\[ S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA} > 0 \] (necessary for spreading-fluid entrainment; advantageous for all mechanisms)

\[ E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA} > 0 \] (necessary for all mechanisms)

\[ B = \sigma_{AW}^2 + \sigma_{OW}^2 - \sigma_{OA}^2 > 0 \] (necessary for bridging-stretching)

\[ \sigma_{AW} = \text{surface tension of the foaming medium (air-water)} \]

\[ \sigma_{OA} = \text{surface tension of the antifoam agent (oil-air)} \]

\[ \sigma_{OW} = \text{interface tension between antifoam agent and foaming medium (oil-water)} \]

These parameters are difficult to estimate because, although they can be determined by measuring the interfacial tension, such measurements are usually made under equilibrium conditions. The formation and destruction of foam are dynamic processes, however. Thus, these parameters can be used only to estimate the properties of an antifoam.

2. 4 Kinetics of Defoaming

What determines the effectiveness of an antifoam agent under these dynamic conditions? First, the barrier preventing the silicone droplets from penetrating the foam lamella must be overcome. The nature of this barrier depends on the type and concentration of surfactant molecule at the interface of the foam lamella. Hydrophilic particles in the silicone droplets can lower the barrier. These particles, which could be silica particles, must not be totally hydrophilic, as otherwise they will not interact with the silicone. Rather, a balance has to be struck between the right degree of hydrophilicity of the silica particles and the optimal efficacy of the antifoam agent.

Also important is the rate at which the antifoam spreads out. The spreading efficiency is a function of the viscosity. Low-viscosity oils spread out much faster. A high spreading rate is particularly important when new foam lamellae keep being formed. Silicone antifoam agents can become deactivated if the silica and residual fluid phase separate. That leads to the formation of inactive silica and silica-free droplets. In addition, the thin silicone film formed by spreading on the surface of the foam lamella may be destroyed or, in a high-surfactant liquor, the antifoam agent may become emulsified.

2. 5 Important Parameters for Efficient Defoaming

In practice, the effectiveness of silicone antifoam agents at controlling foam in surfactant-rich systems is defined by several important parameters.

2. 5. 1 Type of Surfactant

The type of surfactant and its concentration determine both the foaming behavior in the liquor and the effectiveness of the antifoam agent. For, the surfactants used influence the spreading, penetration and bridging coefficients of the antifoam agent. Generally, the surface tension of the antifoam agent must be lower than that of the foaming liquid. The surfactant also affects the drainage rate of the foam lamella, and the emulsification of the silicone droplet.
2. 5. 2 Shear Forces
Shear forces also have a decisive influence on defoamer persistence. High shear forces reduce the size of the antifoam droplet, and renders it less effective. In addition, shear forces and air entrainment – such as occurs when the laundry falls back in the drum of a washing machine – cause new bubbles to form and, with them, new foam lamellae. These foam lamellae increase the consumption of the antifoam agent.

2. 5. 3 Components of the Silicone Antifoam Compound
The composition of the silicone antifoam compound has a very profound influence on its effectiveness in practice. A primary role here is played by the silica used in the formulation. It is essential for lowering the barrier that prevents the antifoam droplet from penetrating the foam lamella. The silica must not be completely hydrophobic, but rather only partly so. Studies by the working group of Denkov et al. have shown that there is an optimum degree of hydrophobizing at which the antifoam agent exhibits the greatest efficacy in an aqueous surfactant liquor.² (Please click here to go to the literature references.)

2. 5. 4 Particle Size of the Antifoam Droplets
Last but not least, the particle size of the antifoam droplets exerts an influence on the effectiveness of the antifoam agent. This must lie in the range of the diameter of the foam lamella. On the other hand, emulsions become fundamentally unstable with increase in particle size. Formulators of antifoam agent emulsions therefore need to be skilled at achieving the right ratio of efficacy <=> stability <=> compatibility of an antifoam agent in a surfactant-rich formulation.

2. 5. 5 Viscosity
The viscosity of the antifoam agent has more practical implications. It determines important processing parameters, such as ease of pumping and metering, and dispersibility in the customer's formulation.

3. REQUIREMENTS FOR ANTIFOAM AGENTS

For best results, an antifoam agent must meet the following requirements:

- lower surface tension than the foaming medium
- insoluability in the foaming liquid
- low barrier to penetration of the foam lamella by the antifoam droplet
- rapid, homogeneous dispersion in the foaming liquid

3. 1 Organic and Silicone Antifoam Agents – SILFOAM® Wins on Points
Why are SILFOAM® silicone antifoam agents eminently suitable here? They have a lower surface tension than most other materials. Therefore, the thermodynamic requirements – namely that the spreading, penetration and bridging coefficients are positive – are met in most cases. The partly hydrophobized pyrogenic silica supports foam destruction because it facilitates penetration of the foam lamella. The ideal spreading power of silicones causes them to spread out particularly well and homogeneously in aqueous liquids – particularly if they are present as antifoam emulsions.

Sustainable Thanks to Less Material Consumption
What is the difference between using SILFOAM® antifoam and organic antifoaming agents, such as soaps, in aqueous surfactant systems? First and foremost, the defoaming efficiency of a silicone-based antifoam is a multiple of that of an organic defoamer. As a result, the silicone defoamer can be used at a much lower dosage. Correspondingly less of it is used in the antifoam agent – and that protects the environment.

Sustainable Thanks to Less Energy Consumption
In addition, SILFOAM® products can be used over a wide temperature range. Organic defoamers such as paraffins are only active above their melting point and require a specific, elevated wash temperature. The effectiveness of organic soap-based defoamers depends very much on the water hardness of the wash liquor. Soaps need a certain amount of calcium and magnesium ions in order to precipitate as calcium and magnesium soaps, and to become effective in this form. Consequently, soaps are limited in their capacity to act as defoamers in soft water. The same applies to the use of highly effective builder systems to lower the water hardness of the wash liquor. Although silicone defoamers cost
more to produce than organic defoamers, their versatility and their high efficiency render them far superior to organic defoamers for foam control in detergents.

3.2 Applications of Silicone Antifoam Agents
Silicone antifoam agents have a wide range of applications in the detergents sector. They generally fall into two groups – defoamers as process auxiliaries, and defoamers foamers as foam brakes in the end products.

Spray Drying Production Scheme for Powder Detergents

3.2.1 Slurry Deaerator
One example of the use of antifoam agents as process auxiliaries for slurry deaeration is the manufacture of powder detergents which are made by spray drying. Here, adding the antifoam agent to the powder-detergent slurry ensures that spray-drying in the tower yields a powder of uniform density. Unless an antifoam agent is used, trapped air bubbles in the high-viscosity slurry mixture cause irregular spray-drying, giving rise to a washing powder of non-uniform density distribution or a reduced density.

3.2.2 Filling
Silicone antifoam agents are also compelling when it comes to dispensing liquid formulations: by reliably suppressing foam formation, they ensure that the necessary high dispensing speeds are reached.

3.2.3 Product Defoaming
Silicone antifoam agents have an important role to play in defoaming end products. Their versatility here is enormous. For example, they can be added as powder antifoams to powder detergents, and can also be sprayed as liquid antifoams onto the detergent granules. Silicone antifoam agents are also ideal for providing foam control for the full range of liquid laundry detergents available on the market as structured, non-structured products and gel products.

4. WACKER SILICONE – THE BETTER ALTERNATIVE

SILFOAM® silicone-based antifoam compounds and powders are tailored to the needs of manufacturers of powder and liquid detergents. We will gladly work with you to establish the silicone antifoam agent which best meets your requirements. We carry out preliminary tests on real washing machines in our applied laboratories to analyze foam profiles at different levels of water hardness and temperature levels. We also perform experiments to determine the storage stability of SILFOAM® antifoam agents in the customer’s own matrix. Once they have conducted extensive compatibility and functional testing, our experts will provide considered product recommendation that is tailored to your problem. So that you can count on having efficient processes and competitive end products.

Should you have any questions, our experts are at your disposal. Your direct link to us: info.silicones@wacker.com.
Literature reference:
1 M. Liphard, A. Giza, Tenside Surf. Det. 34 (1997) 410 (Please click here to return to the article.)
2 N. D. Denkov; Langmuir 2004, 20, 9463-9505 (Please click here to return to the article.)