3. Silicone in the Food Industries

J.P. Lecomte, Dow Corning Europe SA, Seneffe (Belgium)

In food-related processes, silicones are very much associated with foam control agents because of the low surface tension displayed by polydimethylsiloxanes, and because this is a key property for formulating an effective antifoam. Foam control is critical here as in many other industries, as excessive foaming slows processes and can reduce volume efficiency.

Polydimethylsiloxanes as Surface-Active Ingredients in Antifoams

Silicone oils, or in particular polydimethylsiloxane (PDMS) materials, combine many unusual properties because of their molecular characteristics, such as the flexibility of the Si-O-Si backbone and the very low cohesive energy existing between methyl groups. PDMS polymers have low surface tension, and most of them are nonvolatile and remain liquid even at quite high molecular weights. They are also highly insoluble in water.

Because of the extreme flexibility of the siloxane backbone and ease with which various polymer configurations can be adopted, and despite the siloxane backbone's considerable polarity, it is the polymer side groups that are the primary surface-active entities in the polymer structure.

The pendant groups in PDMS are methyl groups, which show the weakest intermolecular interactions known: the London dispersion forces. The low surface tension, which is a direct manifestation of low intermolecular forces, confirms that the interactions between two PDMS chains occur only through their methyl groups. The polymer backbone controls the organization of the side groups at the surface, and its flexibility has a major effect on the ease with which the pendant groups can adopt preferred configurations. Thus, from a surface tension standpoint, the more flexible the backbone, the more readily will the lowest surface energy configurations be adopted. PDMS is a particularly favored case of very low intermolecular force pendant groups anchored along the most flexible backbone, thus allowing the methyl groups to be ideally presented to the external world.

It is often observed that neat silicone oil shows low efficiency as antifoaming agent. But mixtures of such oils with hydrophobic particles such as treated silica or finely divided high melting point waxes are generally much more effective than the individual components [1-2-3-4]. In fact, the mixture performs well even if each component is ineffective when used alone. This synergy is observed for most combinations of oils and solids and in various types of foaming media. Effective foam control agents continue to be developed using such combinations to adjust for different types of foam problems.

Many foam control agents are added to the foaming medium after being predispersed in water, either as self-dispersible neat materials, oil-in-water emulsions, or self-dispersible mixtures or compounds. This is because it is critical to have small droplets of antifoam in the liquid medium to have antifoaming activity. To rupture a foam film, an oil/hydrophobic particle droplet must in a first step emerge from the aqueous phase into the air-water interface during a process called entering. After this entering, some oil from the droplet can spread on the solution-air interface in a second step.

Two coefficients measure the changes in the free energy of the system associated with these two steps.

When an oil drop enters the air-water interface, the change is measured by the entering coefficient, E:

$$E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA}$$

A positive E means the surface tension of the antifoam liquid (σ_{OA}) is lower than the sum of the surface tension of the foaming liquid (σ_{AW}) and the interfacial tension between the antifoam and the foaming liquid (σ_{OW}). This value is the opposite of the free energy associated with the entering step.

When an oil drop spreads over the air-water surface, change is measured by a spreading coefficient, S:

$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA}$$

In this step, the water surface is replaced by an oil surface. A positive S means the surface tension of the foaming liquid (σ_{AW}) is greater than the sum of the surface tension of the antifoam liquid (σ_{OA}) and the interfacial tension between the antifoam and the foaming liquid (σ_{OW}). The free energy associated with this change is the difference between the energy of the end result (the sum of the oil-water interfacial tension and the oil surface tension) and the starting point (the water surface tension). The spreading coefficient is the opposite of the free energy change associated with the spreading step.

Both the entering coefficient and the spreading coefficient must be positive for the corresponding processes to be energetically favorable.

Entering is obviously essential to foam rupture, and it is generally agreed that the entering coefficient must be positive for a particle or droplet to cause rupture of a foam film.

A recent study suggests that spreading of a layer of oil eases the foam breaking mechanism, suggesting that the ability to spread is an important property for an oil used in antifoam formulations [5].

For both the entering and spreading coefficient to be positive, it is important to have a liquid with a low surface tension, which is the case with silicone oils.

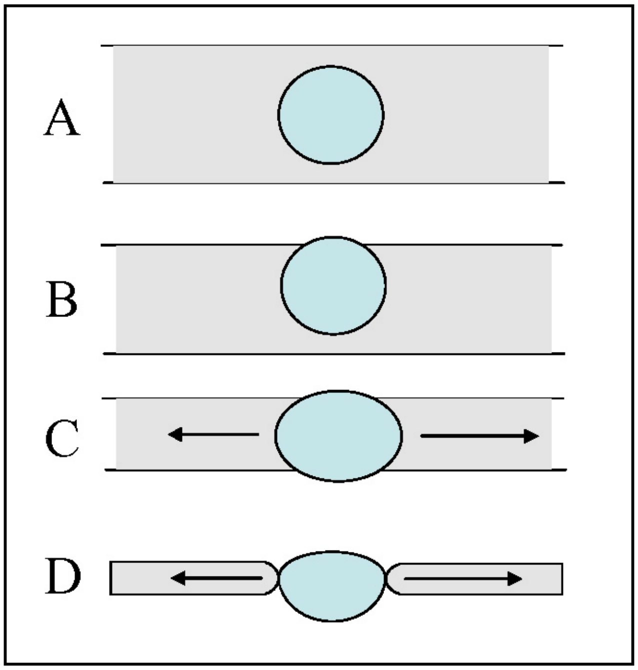

Figure 1. ***Schematic presentation of the bridging of a foam film by a spherical antifoam droplet. In A, the antifoam droplet is entirely in the liquid film. In B, the antifoam droplet has entered the surface. In C, the antifoam droplet bridges the film. In D, the process of bridge dewetting occurs, leading to destabilization of the foam film and eventually to foam rupture.***

It has been shown that hydrophobic particles ease entry of the antifoam droplet in the foam walls or film interfaces, explaining the benefit of their addition in antifoam formulation [2].

Once the silicone antifoam droplet has entered the two air-water interfaces (Figure 1), it forms an oil bridge between the two surfaces of the foam film. One of the mechanisms proposed in the literature involves at this stage the dewetting of the solution away from the antifoam droplets, because of the low surface tension of the oil, and leading eventually to the film rupture.

Although this is a simplified view of the mechanism of antifoam action, it helps explain why silicones are very effective for rupturing foam.

Food and Beverage

Foods are chemical mixtures consumed by humans for nourishment or pleasure. Most of the nutrients are provided by proteins, vitamins and minerals, whereas carbohydrates and fats provide energy. But any media containing such biomaterials and proteins with or without carbohydrates show high foaming tendencies. The proteins act as surfactants due to their amphiphilic structure. They can unfold and strongly adsorb at the interface, forming strong intermolecular interactions. This produces a viscoelastic, irreversibly adsorbed layer at the air-liquid surface, which stabilises the foam. These kinds of films are not easily broken.

This explains why foam is often encountered during food handling, from production to end use. But uncontrolled foaming media are a source of severe loss of production capacity, including inefficient mixing or pumping, downtime from clogged lines, overflows, spillage hazards and product waste. Therefore, foam control technologies (either mechanical or based on chemical additives) have been developed to overcome these problems and reduce costs to a minimum [6-7-8].

Chemical additives designed to reduce such foaming problems are called antifoam agents, foam control agents or defoamers. But the choice of ingredients for applications in the food industries is limited because of regulations and the need to ensure that such ingredients do not cause harmful effects.

Silicone oils are effective ingredients in antifoaming agents. In food and beverage applications, only PDMS materials are used because of their low surface tension, water insolubility, thermal stability and chemical inertness. PDMS of sufficient molecular weight does not penetrate though biological membranes, and orally is not metabolised, but excreted unchanged. These PDMS materials are mixed with hydrophobic particles and formulated as powders, compounds or emulsions.

The pathway followed by food materials starts from their production (e.g., plant growth), their processing and their uses. Foam can be produced in each of these steps.

Silicone Antifoams in Food Production. Crop treatment often requires the spraying of various chemicals on plant leaves. Surface active materials, including silicones such as silicone polyethers, are often needed to help the wetting of the very hydrophobic plant leaves. This is often associated with foaming problems and antifoams are required; for example, during tank-filling operations.

Silicone Antifoams in Food Processing. In the production of sugar from sugar beets, foaming is a serious problem, starting from the beet-washing stage to diffusion and evaporation stages. The foam is attributed to the numerous nonsugar materials present, such as cellulose, lignin, protein, vegetable bases (betaine and choline), and especially saponin [9]. Foam controllers employed in the beet-washing process are likely to appear in wastewaters. Therefore, their environmental profile is important to consider. Because sugar is intended for human consumption and trace amounts of antifoaming agents may be present in the finished product, various legal and health issues must also be considered. Furthermore, steam-volatile components must be avoided during the evaporation and boiling steps.

Fermentation processes such as the production of drugs, yeasts or simply ethanol require antifoams to control the level of foam during the microorganisms' growth and the end-product formation. Biomaterials in the growing media often have a high foaming tendency, whether they are present in the blend of several carefully selected materials like protein extract, sugar, or as byproducts of other food production processes like sugar cane, sugar beet molasses or corn liquor production. On top of this, proteins are often produced by microorganisms and released during the fermentation process, making the foam harder to control. Apart from their essential antifoam properties, the ideal foam control agent for fermentation processes should not be metabolized by the microorganisms, be nontoxic to these microorganisms and to humans, should not cause problems in the extraction and purification of the final product, should not have detrimental effects on oxygen transfer and be heat sterilizable.

Processing potatoes or vegetables requires a wash bath. Intensive foaming of potato juice, starch slurry and processing water is caused by proteins, other nitrogenous compounds and starch found in potatoes or vegetables. Starch foam is very stable and difficult to counter, and antifoam is the most practical and universal application solution.

Beverages are also prone to foam problems during filling and bottling of alcohol beverages, coffee drinks, flavored water and fruit drinks, or when reconstituting powdered drinks like instant coffee or tea with water.

Typical foam control agents recommended for use in food processing or packaging must:

- have Kosher certification
- comply with FDA Regulation 21 CFR 173.340 (secondary direct additives).

Silicone Lubricating Oil in Food Processing

Silicones suitable as food grade lubricating oils are generally straight-chain PDMS. They may be formulated with treated fume silica to obtain a grease and the right rheology profile, including a yield point. Silicone lubricating oil with incidental food contact must meet FDA regulation 21 CFR 178.3570. Immiscibility with many organic fluids, low temperature dependence of their physical characteristics, physiological inertness and high temperature stability are some of the key properties making silicone lubricating oils better than organic alternatives for these applications.

Silicone lubricating oils are used in bearings, gears with rolling friction, on plastic surfaces and on rubber parts encountered on equipment used for food processing.

References

[1] Garret, P. R. The Mode of Action of Antifoams. In *Defoaming: Theory and Industrial Applications*; P. R. Garrett, Ed.; Surfactant Science Series; Marcel Dekker: New York, 1993, Vol. 45, Chapter 1.

[2] Denkov, N. D. *Langmuir* 2004, *20(22)*, 9463-9505.

[3] Wasan, D. T.; Christiano, S. P. Foams and Antifoams: a Thin Film Approach. In *Handbook of Surface and Colloid Chemistry*; Birdi. K. S., Ed.; CRC Press: New York, 1997; Chapter 6.

[4] Kulkarni, R. D.; Goddard, E. D.; Chandar,P. Science and Technology of Silicone Antifoam. In *Foams: Theory, Measurements and Applications*; Prud'homme, R. K., Khan, A., Editors; Marcel Dekker: New York, 1996; Chapter 14.

[5] Denkov, N. D.; Tcholakova, S.; Marinova, K.; Hadjiiski, A. *Langmuir* 2002, *18*, 5810-5817.

[6] Byron, K. J. *Crit. Rep. Appl. Chem.* 1990, *30*, 133-161.

[7] HoÅNfer, R. et al. Foams and Foams control. In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag, 2002; DOI: 10.1002/14356007.all_465.

[8] Lichtman, I.; Gammon, T. Defoamers. In *Kirk Othmer Encyclopedia*, Wiley-VCH Verlag, 2002; DOI: 10.1002/0471238961.0405061515230514.a01.pub2.

[9] Morgan, B. P.; Moynihan, M. S. Steroids. In *Kirk Othmer Encyclopedia*, Wiley-VCH Verlag, 2002; DOI: 10.1002/0471238961.1920051813151807.a01.

This article has been published in the chapter "Silicones in Industrial Applications" in *Inorganic Polymers*, an advanced research book by Nova Science Publishers (www.novapublishers.com); edited by Roger De Jaeger (Lab. de Spechtrochimie Infrarouge et Raman, Univ. des Sciences and Tecn. de Lille, France) and Mario Gleria (Inst. di Scienze e Tecn. Molecolari, Univ. di Padoa, Italy). Reproduced here with the permission of the publisher.