Silicone Polymers as Foam Control Agents

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Over the last decade, the European detergent industry has made tremendous strides to meet the ever-changing demands of both consumers and regulatory bodies for improved detergent formulations. This has resulted in changes to almost every component of the traditional formulation, from the active system and the builder system to special nondetergent benefits. However, the magnitude of most of these improvements is dependent on effective foam control throughout the wash cycle, because European washing machines are lather intolerant. Optimum detergency can be achieved only when foam is controlled and the fabric is immersed in the wash liquor.

In order to implement these formulation changes, the industry has sought improved foam control systems that are more effective than the traditional soap system. One such system is based on polydimethyl siloxane polymers. With proper formulation, these polymers provide performance over a wide temperature range and in a broad range of novel detergent formulations. Equally important is that they function at very low addition levels, thereby creating the formulation latitude for the inclusion of other wash active materials.

The performance of these foam control agents in the detergent formulation is dependent on the method of incorporation. It is only with the advent of suitable processing techniques that such materials have become cost-effective ingredients in new European detergent formulations. Finally, they represent a safe alternative as exhaustive testing over the past 30 years has established these materials as essentially innocuous and free of any significant toxicity.

Foam is generated by entraining air in a surfactant-containing solution. The stability and persistence of the foam will depend on the nature and concentration of the surfactants present, and the degree of turbulence within the system. During the washing process in a front-loading washing machine, air is introduced in four ways:

- Turbulence as the wash load is lifted out of the wash liquor by the baffles on the horizontally rotating drum
- Turbulence as the wash load falls back into the wash liquor as the drum continues to rotate
- Turbulence as the wash liquor flows through the perforations in the rotating drum
- Turbulence caused by water boiling off the electrical heating elements during high temperature wash cycles.

If foam is inadequately controlled, the wash load will become suspended in the foam generated and there will be insufficient contact between the wash liquor and the fabric being washed. This results in poor wash performance for the consumer. In the worst case, foam will actually overflow from the machine. It is therefore essential that laundry detergents, developed for use in front-loading washing machines, have a low foam profile throughout the washing cycle. This is achieved by the incorporation of carefully selected foam control additives.

EUROPEAN WASHING PRACTICES

Fabrics are washed predominantly in front-loading washing machines in Europe. These machines allow the user to select a suitable wash program based on the level of soil present and the nature of the fabric being washed. The programs invariably correspond to the wash programs recommended on fabric care labels. Once the program is selected, the temperature of the wash cycle and its duration are set automatically.

The temperature of the main wash cycle can vary from 30 C for delicate fabrics to 95 C for normal to heavily soiled white cotton or linen fabrics, and the duration can vary from 25 min for a "warm wash" set at 40 C to 60 min for a "boil wash" set at 95 C. Clearly, when assessing the suitability of a foam control agent in a given detergent formulation, the wide variation in temperature and duration of the wash cycle must be taken into account.

Another feature of the front-loading washing machine is that clothes are washed in a very high wash load to liquor ratio. For example, to wash 3.5 kg of dense cotton fabric, as little as 17 l of water will be present in the washing machine during the main wash cycle. Since the normal recommended dose is 150 g of detergent powder, the surfactant concentration in the wash liquor will be high. Controlling foam in solutions containing high levels of surfactants represents a significant challenge.

Finally, even within relatively small geographical areas, it is possible to get tremendous variations in water hardness. As a result the foam control agent present in the formulation must be effective when either hard or soft water is used to fill the machine. The most severe condition encountered is a lightly soiled load washed in soft water.

EUROPEAN WASHING TRENDS

The consumer is aware, through fabric care labels, that different fibers and finishes require different washing conditions. However, because of the increasing complexity of the wash bundle, it is not always practical to divide the bundle so that each item is washed under optimum conditions. In practice, the consumer selects a bundle of articles that can be washed under similar conditions and washes the bundle at a temperature that will not damage the most delicate of the articles present (1). As a result, there has been a significant shift away from high temperatures (95 C) to medium and low temperatures (60, 40 or 30 C). This has been further accelerated by an increasing awareness that long, high temperature wash cycles are costly in terms of time and energy. On most washing machines, temperature and duration of the wash cycle are related. Therefore, by programming the machine to a lower temperature the consumer automatically reduces the duration of the wash cycle. The challenge that the detergent manufacturers must meet is to provide products which have improved performance at lower temperatures and shorter wash cycles, with an increasingly complex mixture of fibers and finishes.

Consumers are also aware, through the successful launch of multifunctional or combination products, that benefits such as softening can be incorporated into a product that is designed primarily to clean. They are also willing to evaluate alternative product forms, as in the case of heavy duty liquids. The challenge to the detergent manufacturers is to develop new products to meet rapidly changing consumer habits.

Last, but not least, are the changes that have been forced onto detergent manufacturers by legislative bodies, the most important being the reduction or elimination of phosphates from detergent products in certain European countries.

In order to meet the changing requirements of consumers and regulatory bodies, the detergent industry has had to make substantial changes to their formulation. For example:

- Changing the surfactant system to provide detergency at lower temperatures, shorter wash times with less effective builder systems
- Introducing bleach activators to improve the removal of chromophoric soils at lower temperatures
- Introducing enzymes to aid removal of proteins at lower temperatures and shorter wash times
- Developing alternative builder systems to phosphates
- Introducing new polymers to reduce soil redeposition in mixed load washing
- Introducing additives to provide fabric softening during the wash cycle
- Introducing new product forms such as liquid detergents and high bulk density powder detergents.

As front-loading washing machines are lather intolerant, some of these changes have necessitated the search for novel foam control agents. These new materials must be more efficient in a broader surfactant base, and work effectively at higher surfactant concentrations and at lower addition levels than conventional foam control systems. Furthermore, they must be able to cope with the wide variation in the temperature and duration of the wash cycles and with the water hardness that is encountered across Europe.

FOAM CONTROL ADDITIVES

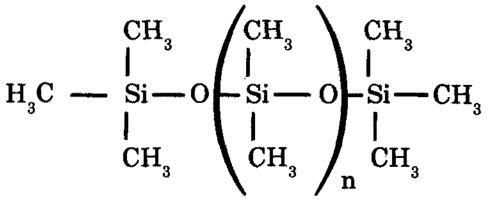
The classical method of controlling the foam of a synthetic detergent solution is by the addition of soap (2). The soap complexes with the calcium ions present in the solution to form an insoluble, solid, calcium soap film. The islands of calcium soap disrupt the foam-stabilizing ability of the adsorbed detergent surfactant, and the foam collapses.

However, this technique of foam control applies only to surfactants and surfactant blends that do not penetrate the insoluble film and hence significantly limits the choice of surfactants that can be used. For example, a stearic acid soap will control the foam of a solution of sodium dodecylbenzene sulphonate, but not a solution of sodium myristyl sulphate or cetyl sulphate. The fact that foam control is achieved through the formation of large areas of calcium soap film implies that high levels of addition are required. Typically 3-5% of soap would be added to control a detergent powder containing 9% actives, where the actives are sodium dodecylbenzene sulphonate and a non-ionic surfactant in a ratio between 2:1 and 3:1.

Clearly, with the changes in the active system required to provide improved product performance at lower temperatures and shorter wash cycles, new foam control agents are required. Ideally, these new agents should also be more efficient, thus making room in the detergent composition for the addition of increased levels of other wash active substances. Typical of non-soap antifoam compounds are alkyl phosphate esters (3-5), mineral oil or wax based antifoam compounds (6-9) and silicone based antifoam compounds (10-28). The remainder of the paper will concentrate on the use of the last of these.

SILICONE POLYMER BASED ANTIFOAM COMPOUNDS

Traditional silicone antifoam compounds are proprietary combinations of polydimethylsiloxane polymers, commonly known as silicone fluids:



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

and finely divided silica particles. The fluids have a very low surface tension, 22 dynes/cm at 25 C, and spontaneously spread over the surface of most surfactant-containing solutions. However, on their own they show little or no foam inhibiting ability. It is only when they are combined with finely divided silica particles that an effective foam inhibitor is produced.

A foam is stabilized by the adsorption of surfactant molecules at the air-water interface. It is envisaged that the silicone fluid spreads across the interface and, as it does so, exposes the hydrophobic silica particles in the silicone antifoam compound to the interface (29-31). Once the silica particles become exposed, surfactant molecules move across the interface to reduce the interfacial surface tension between the exposed silica particles and the aqueous medium, thereby decreasing the surfactant concentration at the interface in the vicinity of the exposed particles. As they move across the interface, the surfactant molecules will drag with them the water associated with their hydrophilic heads, causing localized thinning of the foam film in the vicinity of the exposed silica particles. The combination of film thinning and reduction in surfactant concentration is sufficient to cause the film to rupture.

The mechanism that is proposed is that the hydrophobic silica particles are the foam breakers and the silicone fluid is their means of transport to the water-air interface. Therefore, the art of formulating an effective silicone antifoam compound is to combine the silicone fluid and silica in such a way that the most efficient antifoam compound is produced. The uniqueness of the silicone fluid lies in its physical properties:

- Clear, colorless fluid.
- Low surface tension, 22 dynes/cm.
- Able to spread spontaneously on most aqueous solutions.
- Insoluble in aqueous medium.
- Incompatible with surfactants.
- Difficult to emulsify.
- Chemically inert.

These properties make the material ideal as an effective carrier medium, and by incorporating finely divided silica particles it is possible to formulate products that can perform effectively in most foaming systems. Furthermore, silicone antifoam compounds provide significant benefits over the traditional soap-based foam control system. For example, performance is independent of water hardness; they are effective in more foaming systems; do not cause yellowing of fabric; effective at lower addition levels, and effective across a wider range of usage conditions.

These properties and benefits make this class of foam control agent ideal for the new generation of detergent products that are emerging to meet the changing laundry habits of the modern consumer.

INCORPORATION IN DETERGENT POWDERS

The performance benefits of silicone antifoam compounds can be readily observed simply by mixing these compounds into a detergent powder and examining the foam profile in a front-loading washing machine. Typical addition levels, required to give a low level of foam throughout the main wash cycle, range from 0.05 to 0.4% depending on the performance of the antifoam compound, the surfactant concentration and the type of surfactants present. However, if this same powder is stored over a period of weeks, a gradual deterioration in the foam profile is observed (11). This loss of performance can be accelerated by using higher temperature storage conditions. Finding ways to minimize this storage drift has been a major hurdle to their use in detergent powders.

The mechanism of this performance drift is best described by referring to Figure 1. When the antifoam compound is dispersed onto a detergent powder matrix, it is possible to visualize the compound being present as discrete droplets adsorbed onto a small part of the available surface area. If the powder is immediately introduced into the washing cycle, the substrate dissolves and releases a small number of relatively large, discrete droplets of compound. These will effectively control the foam throughout the wash cycle by the mechanism described previously. However, if the powder is stored prior to testing, this allows time for the compound to spread within the powder matrix and adsorb over a much larger surface area. In this case, dissolution of the substrate will give rise to the release of a greater number of smaller, discrete droplets of compound. Unfortunately, even though the volume of antifoam compound released is the same, the period over which foam is controlled is shorter.

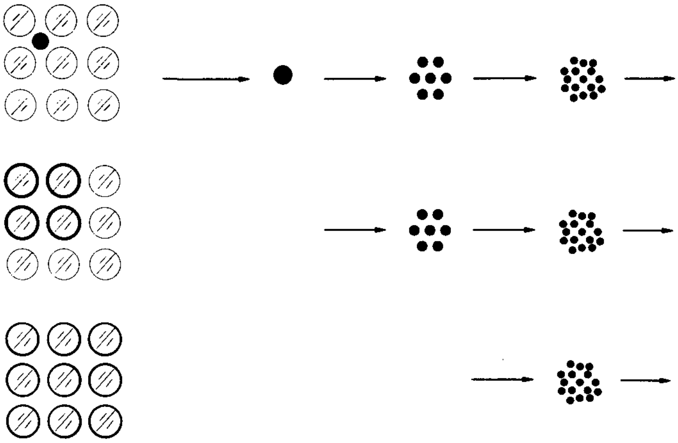


FIG. 1. A schematic representation of the silicone antifoam compound spreading within the powder matrix during storage, and the changes in the particle size distribution when the powder is dissolved in the wash liquor.

The relationship between antifoam compound droplet size and its ability to control foam can best be illustrated by referring back to the mechanism of foam control described earlier. These materials perform by delivering silica particles to the air-water interface at a controlled rate (28). Once the silica particles are exposed at the interface, surfactant molecules will rapidly adsorb on the exposed surface, causing the surface to become hydrophilic. When the surface is sufficiently hydrophilic, the particles will transfer to the aqueous phase and play no further part in the foam control process. If the size of the antifoam compound droplets is relatively large, then the silica will be released gradually over a long period of time, resulting in adequate foam control throughout the whole wash cycle. However, if the size of the droplets is small the silica will be released much more rapidly and depletion will occur over a shorter period of time, resulting in a loss of foam control toward the end of the wash cycle.

The solution is to prevent the silicone antifoam compound from migrating within the powder matrix such that the droplet size of the antifoam compound released into the wash liquor is the same regardless of the storage conditions. Since the early 1970's, a significant number of patents have emerged describing how this can be achieved (10-12, 14-20, 22-28). These essentially describe four different techniques.

In the first method, the silicone antifoam compound is encapsulated in a water-soluble or water-dispersible wax (11,12,24). The process involves dispersing the antifoam compound in a molten wax and then spraying the molten mixture onto a fluidized bed of a particulate, water-soluble or water-dispersible, solid carrier to form coated granules. As soon as the droplets of the mixture come into contact with the powder carrier, the wax solidifies and immobilizes the antifoam compound within the wax matrix. The resultant product is a crisp, free-flowing powder that can be dry-mixed into the granular detergent composition to give a low-foaming, laundry detergent powder whose foam control performance is unaffected by extended storage. Alternatively, it is possible to spray the molten mixture directly onto the granular detergent base powder and thereby eliminate a processing step (18,25) or use a combination of the two techniques (22).

The second technique is similar except that the silicone antifoam compound is adsorbed onto a carrier prior to coating with a suitable melting point wax (17,20). The resultant granules are then dry-mixed with the granular detergent composition and have been shown to provide effective foam control after extended storage at elevated temperatures and high relative humidity. Alternatively, it is possible to spray a molten mixture of the antifoam compound and the wax onto the adsorbent (23).

Yet another technique is to microencapsulate the silicone antifoam compound with film-forming polymers (19). The process involves preparing an aqueous dispersion of the antifoam compound and the water-soluble or water-swellable, film-forming polymers, and then spray-drying the dispersion in combination with the aqueous detergent slurry to give a spray-dried granular powder. It is believed that the polymers microencapsulate the antifoam compound within the powder granules during the spray-drying process, thus providing the necessary protection to give storage stable, foam control.

Finally, there is a method which describes adsorbing the silicone antifoam compound on specially prepared, porous, surfactant-free carriers (15,16,28). The first step involves preparing a suitable carrier by spray-drying an aqueous slurry of inorganic salts. The antifoam compound is then adsorbed on this carrier to give a free-flowing, granular powder that can be readily mixed into the remainder of the detergent powder. Alternatively, it is possible to obtain the granules directly by spray-drying an aqueous slurry that consists of the antifoam compound, nonionic surfactant, water-dispersible polymer and inorganic salts (14,27).

These techniques not only provide a solution to the problems associated with the migration of the silicone antifoam compound within the detergent powder, but also a means of incorporating very low levels of a viscous liquid to give a free-flowing, low-foaming laundry detergent product.

INCORPORATION IN DETERGENT LIQUIDS

The emergence of liquid detergent products presents a different challenge to the formulator. Here the problem is to maintain a uniform dispersion of the silicone antifoam compound throughout the liquid matrix such that the consumer dispenses the prescribed amount of foam control agent each time. Recent patents detail how this can be achieved (13,21). The former (13) claims the addition of an emulsion of a silicone antifoam compound at levels of 0.2 to 0.4%. In this case, the antifoam compound is already dispersed in an aqueous medium prior to addition to the liquid detergent composition. The latter (21) claims the incorporation of the silicone antifoam compound at addition levels of 0.2 to 0.3% directly into a micellar, structured, liquid detergent composition. Here it is postulated that the individual droplets of the antifoam compound are held separately in suspension by the structure of the micellar liquid and hence unable to coalesce. In both patents, the antifoam compound is present as a dispersion of discrete droplets. This implies that this type of foam control agent can only be used currently in the formulation of non-clear, low-foaming, liquid detergent compositions.

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