PROCESS BULLETIN

Silicone Emulsions

Description

Silicones are semiorganic polymers consisting of silicon atoms alternating with oxygen atoms with methyl groups attached to the silicon atoms. The basic polymer structure is polydimethylsiloxane. By substituting other organic groups for the methyl groups or by cross-linking the polymer chains, unique properties can be obtained from these polymers. Silicone polymers or silicone oils have many desirable properties:

- They are unaffected by high or low temperatures; viscosity and/or shear properties show little change with temperature;
- The polymers have thermal oxidative stability;
- They possess unusually low surface tension;
- Most materials have low adherence to surfaces coated with the polymer;
- They produce water repellency in coatings;
- They have high dielectric strength and can be used for electrical applications;
- Many silicone oils are physiologically inert[1].

Because of these important physical properties, silicone oils are used in a number of emulsions such as silicone antifoams, mold release agents, cosmetic products and textile emulsions. Manufacturers' trade bulletins list many applications of these emulsions, in some cases, as many as fifty different applications. Some of these include: food (fermentation, beverages, meat and poultry processing, syrups), chemical (distillation, resin manufacturing, detergents, cutting oils, fertilizers, mold release), petrochemicals, wastewater treatment, paper/printing, adhesives/coatings and textiles[2-6].

Antifoam - These emulsions are used to control or eliminate foaming in many products and processes. Silicone oils are used in antifoams because they are effective in many systems under a broad range of operating conditions[7]. The criteria for an effective oil in an antifoam are that the oil should have a low solubility in the system and that it should possess a positive spreading coefficient. The sequence of events which leads to foam reduction includes: "dispersion of antifoam in the foaming solution, transport of antifoam droplet from bulk to the bubble interface, entry of the droplet into the gas/liquid interface, spreading, and bubble rupture."[7].

Many types of antifoam contain hydrophobic filler particles such as fumed silica. It is believed that these silica particles in the silicone oil droplet are carried to the bubble surface by the oil. At the bubble surface the silica becomes coated by surfactant molecules and is drawn into the aqueous phase. This process depletes the surface agents at the bubble wall, causing the bubble to collapse.

Antifoams are quite effective even in low concentrations and are used in amounts of 10 to 200 ppm.

Textile Emulsions - Silicone oil-in-water emulsions are used for textile applications. These emulsions impart many desirable properties to textile products. Some of these are: durable water repellency, spot and stain resistance, sewability, increased tear resistance, improved wrinkle recovery and improved shrinkage resistance.

Mold Release Agents - This type of silicone emulsion would be sprayed into a mold to release the formed object from the mold. These release agents are used for tire molding, rubber and plastic molding, and for the manufacture of medical appliances.

The objective is to produce an emulsion of silicone oil-in-water with physical characteristics appropriate to its application. For example, a textile emulsion usually contains 25% to 75% oil and should be stable in storage for six months, stable to freezing and thawing, able to provide adequate silicone pick-up on cloth, compatible with different finishing agents and have no adverse dermatological effects. The average droplet diameter of this type of emulsion is usually less than one micrometer. On the other hand, an antifoam emulsion may not require as small an average diameter as the textile emulsion, and the antifoam emulsion most likely will not require freeze/thaw stability.

In general, these emulsions should have good shelf life, little or no separation and must be compatible with the intended process or product. The emulsions may be formulated with anionic, nonionic or cationic emulsifiers; but nonionics are most commonly used. In some cases, the pH is adjusted to 5-7 to minimize any gassing of hydrogen. Viscosity can vary from 100 cSt to 100,000 cSt (25°C).

Processing

Silicone emulsions can be prepared using the homogenizer or colloid mill. The choice of equipment depends on the viscosity of the silicone oil, the amount of oil in the formulation and the droplet size desired in the finished emulsion.

Through an understanding of the product characteristics that influence the efficiency of each piece of equipment, some predetermination can be made regarding which machine can do the job. For example, the homogenizer is most efficient when product viscosity is low, especially the disperse phase8. If the silicone oil viscosity exceeds 1000cP (Newtonian), then the homogenizer will not produce a good emulsion. Even at high pressures, 5000 to 8000 psi, the homogenizer will be very inefficient at reducing droplet size. Ideally, the viscosity should be less than 500cP for the most efficient use of the homogenizer. Heating a silicone emulsion may not be of benefit, since many silicone oils do not exhibit a significant drop in viscosity with temperature. Figure 1 shows an example of the change in viscosity for a particular silicone oil. In this case heating would help reduce the oil viscosity to make homogenization more efficient. The colloid mill should be used to prepare emulsions with high viscosity oils.

If the percentage of oil exceeds 50%, then the colloid mill would be preferred over the homogenizer, because the homogenizer may overwork and break an emulsion at these oil levels.

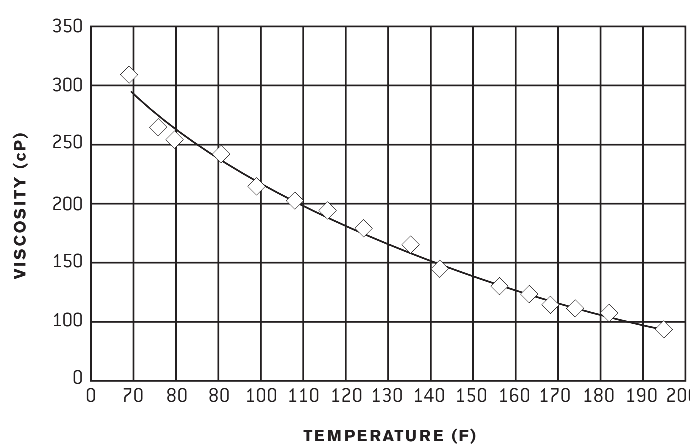
If the viscosity of the oil is low and the percentage of oil is less than 50%, then the homogenizer would generate the smallest droplet size, because of its high-energy input. However, in some special cases a very small average droplet-size emulsion can be generated using a colloid mill by inverting the emulsion. This technique involves preparing a water-in-oil emulsion that is almost at the inversion point, usually indicated by a very high viscosity. If this emulsion is passed through the colloid mill at a gap setting of about 0.005 inches, the emulsion will invert resulting in an oil-in-water emulsion with a very small average diameter, in many cases, less than one micrometer.

If fumed silica is to be dispersed into silicone oil, the homogenizer can be used to accomplish this operation. The oil and silica would then be emulsified into the water phase by premixing and then passing it through the appropriate piece of equipment.

Methods of Analysis

Silicone emulsions can be evaluated using shelf life tests, microscope evaluation, freeze/thaw stability or separation and creaming. If the droplet size is below about three micrometers, then the emulsion can be checked using dynamic light scattering, such as with the NICOMP Particle Size Analyzer, or by optical turbidity, such as with the Gaulin EQA instrument. There is also a technique to measure the effectiveness of an antifoam emulsion. The apparatus to do this bubbles nitrogen gas through a sample of surfactant and water and measures the increase in foam volume with time. Measurements are made without antifoam and then with different amounts of antifoam. The curves generated from this data will indicate the effectiveness of the silicone emulsion at reducing or preventing foam.

VISCOSITY VS. TEMPERATURE FOR A SILICONE OIL



References

1. D. M. Considine D. M. (ed), *Chemical and Process Technology Encyclopedia* (New York: McGraw-Hill 1974).

2. *GE Silicone Fluids Bulletin*, General Electric Company, Waterford, New York (1985).

3. *Harcros Antifoams Bulletin*, Harcros Chemicals Inc., Kansas City, Kansas (1989).

4. *Dow Corning Silicone Foam Control Agents Bulletin*, Dow Corning Corp., Midland, Michigan (1987).

5. *PPG/Mazer Specialty Chemicals Bulletin*, Mazer Chemicals, Gurnee, Illinois (1988).

6. *Union Carbide Silicone Fluids Bulletin*, Union Carbide, Danbury, Connecticut (1982).

7. R. D. Kulkarni, E. D. Goddard and M. R. Rosen, *J. Soc. Cosmet.* Chem. 30 (1979): 10-5-125.

8. W. D. Pandolfe, *J. Disp. Sci. and Tech*, 2, 4 (1981) 459-474.

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