Antifoam Technologies for Lubricating Oils

E. Galgoci[1], J. Mykietyn[1]

[1]Munzing North America LP, Bloomfield, New Jersey, United States of America

Abstract

Antifoams are a critical part of lubricating oil formulations. Generally, the antifoam should exhibit surface foam control, persistency, and compatibility with the lubricant. The optimal choice of the antifoam is often best determined empirically, but experience and first principles can be used as guidelines to narrow the search. This paper will describe: foam generation and stabilization; the thermodynamics of the action of antifoams; and their general formulation. The relative performance of various antifoam chemistries is discussed along with some of the latest developments, which include a hybrid that delivers a combination of excellent foam control and air release.

Keywords:
Antifoam; foam; hybrid; air release

1 INTRODUCTION

Foam is a concentrated dispersion of a gas in a liquid. This gaseous dispersion resides at the surface of the liquid but, in the extreme case, the liquid system can be converted entirely to foam. The foam layer exhibits a distinct phase boundary with the liquid, which itself can contain a large fraction of entrained air. The entrained air buoyantly moves to the surface to create, replenish or increase the foam. Minimizing foam during use of a lubricating oil is required to maintain maximal lubrication. Additionally, it is also important to minimize the air content (foam and entrained air) to reduce fluid oxidation, which will degrade the fluid and eventually lead to potentially costly and premature fluid replacement. Other negative effects of foam and entrained air in non-aqueous systems include cavitation, pressure fluctuations and, in the extreme, loss of lubricant through vents.

To mitigate these issues, an antifoam is a necessary and critical component of the fluid formulation. Antifoam refers to a substance which suppresses foam as it forms; it is added directly to a formulation before use and is designed to disrupt the interfacial forces that stabilize the foam bubbles. In contrast, a defoamer is a material added during use of the fluid to break any undesired foam build up and to provide a period of foam suppression before another addition may be necessary. In practice, the terms antifoam and defoamer are often used synonymously, since their compositions are essentially the same or very similar and they perform the same ultimate function. For non-aqueous systems, the term antifoam is generally more precise since, for practical reasons, defoamer additions are almost never done. Although the criteria for choosing an antifoam will vary depending on the specific fluid and requirements, the antifoam must generally exhibit strong initial defoaming, persistent (longevity) defoaming, and compatibility (no separation) with the fluid.

1.1 Foam Stabilization Mechanisms

The mechanisms for foam stabilization in non-aqueous systems such as lubricating oils are not as clear as that for aqueous systems, which have been extensively studied. Foam stabilization in oils appears to be more related to bulk and surface viscosities, as an increase in either or both leads to retardation of foam lamella (the liquid structure surrounding a foam bubble) drainage, which is necessary for foam to break. Callaghan [1] described several studies [2,3] that showed these viscosities to be important for foam in several oil-based systems, but several other studies [4,5] that were cited reportedly did not show a correlation. Friberg [6] presented a review on the topic of the stability of non-aqueous foams and concluded that surface forces were not important and the stability was dependent on the drainage rate. Further, he concluded that liquid crystal and/or solid phases in the liquid provide the foam stabilization. Blazquez [7] came to similar conclusions as Friberg. It is well known that the presence of additives (excluding the antifoam) in an oil will generally lead to increased foaminess, so at least some of these additives must influence the surface or intra-lamellar viscosities or affect the lamella surface. In a study by Ross and Suzin [8], it was shown that certain additives and especially their combinations led to increased foam stability. Binks et al [9] studied additives in a polyalphaolefin (PAO) base oil and concluded that foam correlated with proximity to a phase separation boundary, where the soluble additive concentrations were relatively high (above ~ 1 weight %) and the tendency to adsorb at the gas bubble surfaces was thereby optimized.

1.2 Thermodynamics of Defoaming

For an antifoam to work, it cannot be completely soluble in the liquid to be defoamed, since it would not exhibit the necessary surface activity. Therefore, it must exist as a droplet to enter the foam lamella and then spread at the interface. Another requirement is that the antifoam droplet must eventually bridge the gap between the two interfaces of the lamella. The properties of entering, spreading, and bridging are dependent on the surface tensions of the liquid film (γ_L) and the antifoam droplet (γ_D) and the interfacial tension (γ_{LD}) between the two. Entering (E), spreading (S), and bridging (B) coefficients are defined such that, when maximized (i.e., greater than zero), optimal defoaming is achieved. The respective equations are shown below [10-13].

$$E = \gamma_L + \gamma_{LD} - \gamma_D > 0 \qquad (1)$$

$$S = \gamma_L - \gamma_{LD} - \gamma_D > 0 \qquad (2)$$

$$B = (\gamma_L)^2 + (\gamma_{LD})^2 - (\gamma_D)^2 > 0 \qquad (3)$$

As can be deduced from these equations, a necessary requirement for defoaming is that the active component has a surface tension (γ_D) which is lower than the surface tension (γ_L) of the liquid medium. In the case of non-aqueous lubricating oils, silicones (e.g., PDMS = polydimethylsiloxane) are the only common liquids with sufficiently low surface tensions (~20-22 mN/m) and low solubilities in lubricating oils (surface tensions for mineral oils of ~30-35 mN/m) [14].

1.3 Kinetics and Droplet Size

Although thermodynamic requirements are important for considering why certain materials are useful as antifoams, kinetic and other factors may be equally if not more important. For an antifoam to function, it must have a low solubility in the liquid to be defoamed, such that it exists as dispersed droplets in the medium. The reason for this requirement is that, if the antifoam is soluble, there is no thermodynamic driving force for it to act at the interface. Therefore, it is apparent that the number of droplets and their size distribution are important. The number of droplets affects the kinetics, while the size distribution affects the effectiveness of spreading and bridging. Of course, for a given amount of antifoam, the number of droplets is directly related to the size distribution. Shearer and Akers [15] determined that the diameter of droplets of a silicone antifoam should be less than 100 µm to be effective and that, if the silicone was completely soluble in the oil, it would be a "pro-foamant." A simple thought experiment regarding two extreme examples can elucidate the point of droplet size distribution. In one case, where the antifoam exists as a single droplet in the system, it will defoam effectively in its vicinity, but there will be far too few droplets to rapidly break the foam bubbles in the rest of the system. On the other hand, if the droplets are exceeding small, they will have a low mass and be less effective at spreading and bridging. For a given system, there will be an optimal droplet size distribution for defoaming but, in practice, it is rarely determined.

1.4 Air Entrainment and Release

Although surface foam is an important consideration, air entrained in the liquid can also have a negative impact on lubrication. The rate at which entrained travels to the surface is controlled by the viscosity of the fluid and the size of the air bubbles. In a pure liquid, Hadamard and Rybczynski [16,17] derived the following equation to describe the rise velocity of an air bubble in a liquid for the case where the internal gas in the rising air bubble can circulate ("soft bubble").

$$V_s = g\rho r^2/3\eta \qquad (4)$$

where g is the gravitational constant, ρ is the density of the liquid (assuming the density of air to be negligible), r is the bubble radius, and η is the viscosity of the liquid. In contrast, Stokes' law predicts the following for the case of a rigid sphere.

$$V_r = 2g\rho r^2/9\eta \qquad (5)$$

As can be seen, the ratio of V_s/V_r is 1.5. Levich [18] explained the ratio of 1.5 as arising because the velocity of the liquid is not zero at the air bubble boundary for a soft bubble but, for the case of a rigid sphere, it is zero. While air bubbles are not ordinarily considered rigid spheres, their rise velocities in formulated lubricating oils is often found to match more closely to that predicted by Stokes' law. This behavior appears to arise from the presence of surface active agents, which impart an elasticity (Gibb's) that immobilizes the surfaces of the air bubbles. For example, it was observed that as little as 10 ppm of silicone oil in a mineral oil could reduce the velocity of an air bubble (radius of 0.11 cm) from that predicted by Hadamard and Rybczynski to nearly that of Stokes' law [19]. As silicone oils are common antifoaming agents, there is a desire for alternatives that have a small or negligible effect on the rate of air release.

1.5 Antifoam Formulation

For lubricating oils, antifoams are typically formulated only with liquid actives and carrier solvents. The most common actives used are silicones (main chemistry employed) and polyacrylates. Silicones are the most effective at defoaming, but they can negatively affect air entrainment. Polyacrylates are not as effective antifoams, but they tend to have minimal impact on air entrainment. Appropriate carriers will reduce viscosity to aid incorporation, improve compatibility, and sometimes enhance defoaming. In some cases, combinations (usually added separately) of silicones and polyacrylates provide an effective balance of defoaming and air entrainment to lubricating oil systems. Hybrid antifoams, where the silicone and polyacrylate are combined intimately in a single formulation, can often provide synergistic benefits. This paper will focus on the relative performance of a hybrid antifoam compared to that of conventional silicone and polyacrylate types.

2 EXPERIMENTAL

Antifoams of various chemistries were tested in commercially obtained lubricating oils. The lubricating oils were fully formulated with additive packages without antifoam. For commercial reasons, the specific identities of the lubricating oils cannot be disclosed, but the oils will be described generically. In several cases, control antifoams (i.e., the currently-used product) were provided with the lubricating oil samples. The general antifoam chemistries tested are silicone (polydimethylsiloxane), polyacrylate (acrylate esters copolymer), and hybrid silicone-polyacrylate (HSPA). The hybrid chemistry is an intimate combination of silicone and polyacrylate (PA).

The antifoams were added to the oils using a paddle-type stirrer at a speed to create a slight vortex. Foam testing was performed using the ASTM D892 method [20], while air entrainment/release was tested according to ASTM D3427 [21]. The compatibility of the antifoam in the lubricating oil was judged subjectively by evaluating the surface (e.g., antifoam droplets or slick), body (e.g., haze), and bottom (e.g., sediment) of the sample. For each of the 3 sections of the sample, a rating of 1 (best, no observed incompatibility) to 5 (worst, high degree of incompatibility) was given. The individual ratings were aggregated to provide a total rating on a scale of 3 (best) to 15 (worst).

3 RESULTS AND DISCUSSION

In the following subsections, the results of testing in various lubricating oils will be provided.

3.1 Automatic Transmission Fluid (ATF)

The currently-used antifoam (silicone type) for this ATF was used at an actives level of 100 ppm. Table 1 shows that the antifoams exhibited excellent compatibility (best rating of 3) in the ATF

Antifoam	Actives, ppm	Compatibility
Blank (no defoamer)	0	3.0
Control (Silicone-1)	100	3.0
HSPA	7	3.0
HSPA	3.5	3.0

Table 1: Compatibility after aging for 1 week at room temperature.

The control antifoam (Silicone-1) was purported to have poor performance in Sequence I of ASTM D892, and the data in Table 2 show that to be the case. Generally, a foam tendency (FT) of <50 mL is desired. The best performance was obtained with the hybrid silicone-polyacrylate (HSPA) antifoam. Even at an actives level of <10% of the control antifoam, the HSPA (7 ppm actives) showed no foam in Sequence I and better foam control and excellent foam break in Sequences II and III.

Antifoam	Sequence I		Sequence II		Sequence III	
	FT	T_0	FT	T_0	FT	T_0
Blank	65	55	30	20	70	55
Control	240	250	25	15	20	35
HSPA (7)	0	0	10	16	0	0
HSPA (3.5)	20	15	20	10	25	30

Table 2: ASTM D892 defoaming performance. Use levels are the same as in Table 1. FT = foam tendency in mL. T_0 = time in seconds to zero foam.

3.2 Compressor Oil

For this oil, the antifoam samples were tested at a use level of 500 ppm, and the samples were aged for 7 days at room temperature (RT) prior to testing. The antifoams introduced a slight incompatibility (Table 3), which was manifest as haze. For air entrainment (Table 4), the HSPA did affect the air release, but the air release time (i.e., time to recover to 99.8% of the original density) was much closer (about 1.7 times greater) to that of the blank oil than the silicone antifoam, which was over 3.5 times that of the blank. The polyacrylate (PA-1) antifoam was not tested in ASTM D3427 due to its relatively poor performance in ASTM D892 (Figure 1). The defoaming results show that the HSPA performed the best in all 3 ASTM D892 Sequences; no foam was observed in Sequences I and III. The foam collapse time in Sequence II for the HSPA was 10 seconds, which was better than the other antifoams in any Sequence.

Antifoam	Compatibility
Blank	3.0
Silicone-2	3.5
HSPA	3.5
PA-1	3.5

Table 3: Compatibility after 7 days at RT.

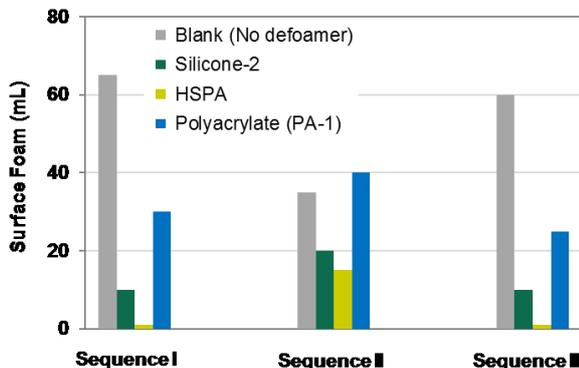| Antifoam	Air Release Time, min
Blank	2.4
Silicone-2	8.5
HSPA	4.0

Table 4: ASTM D3427 air release results.

Figure 1: ASTM D892 defoaming comparison.

3.3 Gear Oil

In this oil, the antifoam samples were tested at a use level of 2000 ppm, and the treated oil samples were tested after 1 day at RT. A polyacrylate control antifoam (PA-2) was current being used in this oil. Table 5 shows the compatibility data. Except for PA-1, the antifoams introduced some haze into the oil, which was itself slightly hazy. The PA-2 control created the most haze. For ASTM D892, the antifoams tested had much less than 50 mL of foam in Sequences I and III. However, in Sequence II, the blank was very foamy (560 mL), and only the HSPA (25 mL foam) was able to achieve the requirement of less than 50 mL of foam (Figure 2).

Antifoam	Compatibility
Blank	3.5
PA-1	3.5
Silicone-3	4.0
HSPA	4.0
PA-2 (control)	4.5

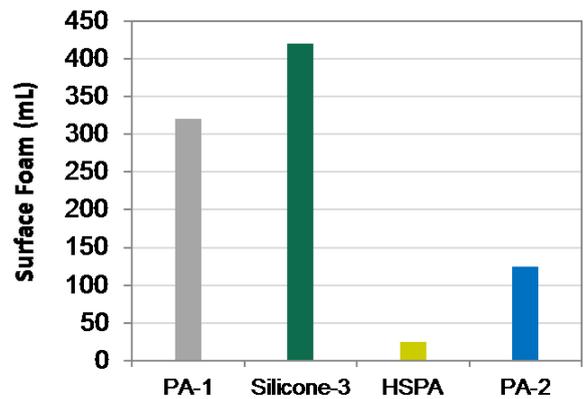Table 5: Compatibility after 1 day at RT.

Figure 2: ASTM D892 Sequence II defoaming results.

3.4 Hydraulic Oil

The requirement for this oil was that the antifoam should have excellent compatibility, foam less than 50 mL, and air-release time less than 60 seconds above the blank. All antifoams were tested at a use level of 100 ppm, and the samples were aged for 7 days at RT. All samples had a compatibility rating of 3 (no observed incompatibility). ASTM D892 Sequence II showed the most foam, while little to no foam was generally seen for Sequences I and III. Figure 3 shows the data for Sequence II plotted along with the data for ASTM D3427 (data shown as the time difference between the antifoam samples and the blank). Silicone antifoams generally showed poor air release. Only the PA-3 and HSPA met the air release target, but the HSPA provided better defoaming. In general, the silicones showed poor air release.
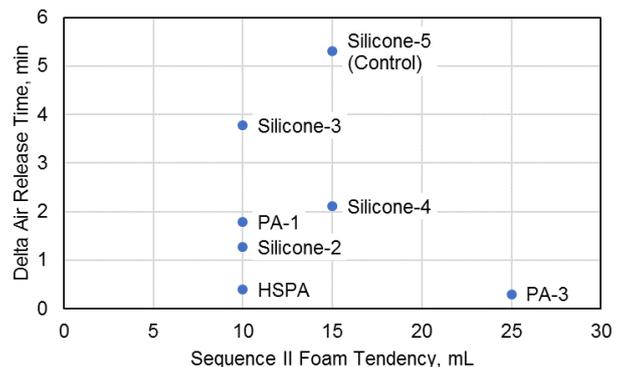

Figure 3: ASTM D3427 and D892 results.

4   SUMMARY AND CONCLUSIONS

Foam stabilization in lubricating oils is primarily controlled by the bulk and surface viscosities, which can be affected by various additives in the oil. Silicones are generally the most effective and most commonly used antifoams, but they negatively affect air release properties. Polyacrylates do not affect air release, but they are generally relatively poor antifoams. A hybrid antifoam (HSPA), in which a silicone and a polyacrylate were combined intimately, was shown to offer an excellent balance of defoaming and air release performance in a variety of lubricating oils. Compared to standard silicones, the HSPA had comparable or better ASTM D892 defoaming with better ASTM D3427 air release properties. Versus standard polyacrylates, the HSPA provided similar or better air release and better defoaming. In addition, the HSPA showed good compatibility in the oils.

6   REFERENCES

[1]   Callaghan, I. C., 1993, Antifoams for Nonaqueous Systems in the Oil Industry, in Defoaming: Theory and Industrial Application, Surfactant Science Series Volume 21, Garrett, P. R. (Ed.), Marcel Dekker, New York, NY.

[2]   Brady, A. P. and Ross, S., 1944, The Measurement of Foam Stability, J. Am. Chem. Soc., 66, 1348-1356.

[3]   McBain, J. W. and Robinson, J. V., 1949, Surface Properties of Oils, Natl. Advisory Comm. Aeronaut., Tech. Note No. 1844.

[4]   Mannheimer, R. J. and Schecter, R. S., 1970, Shear-Dependent Surface Rheological Measurements of Foam Stabilizers in Nonaqueous Liquids, J. Colloid Interface Sci., 32, 212-224.

[5]   Scheludko, A. and Manev, E., 1968, Critical Thickness of Rupture of Chlorbenzene and Aniline Films, Trans. Faraday Soc., 64, 1123-1134.

[6]   Friberg, S. E., 2010, Foams from non-aqueous systems, Current Opinion in Colloid and Interface Science, 15, 359-364.

[7]   Blazquez, C., Emond, E., Schneider, S., Dalmazzone, C., and Bergeron, V., 2014, Non-Aqueous and Crude Oil Foams, Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 69, No. 3, 467-479.

[8]   Ross, S. and Suzin, Y., 1982, Lubricant Foaming and Aeration Study, Air Force Wright Aeronautical Laboratories, AFWAL-TR-82-2090.

[9]   Binks, B. P., Davies, C. A., Fletcher, P. D. I., Sharp, E. L., 2010, Non-aqueous foams in lubricating oil systems, Colloids and Surfaces A: Physicochem. Eng. Aspects, 360, 198–204.

[10]   Kulkarni, R. D., Goddard, E. D., and Kanner, B., 1977, Mechanism of Antifoam Action, J. Colloid Interface Sci., 59 (3), 468-476.

[11]   Hill, R. M. and Fey, K. C., 1999, Silicone Polymers for Foam Control and Demulsification, Silicone Surfactants, Surfactant Science Series Volume 86, Hill, R. M. (Ed.), Marcel Dekker, New York, NY, 166.

[12]   Princen, H. M., 1969, The Equilibrium Shape of Interfaces, Drops, and Bubbles. Rigid and Deformable Particles at Interfaces, in Surface and Colloid Science, Matijevic, E. (Ed.), Wiley-Interscience, New York, NY, Vol. 2, 56.

[13]   Garrett, P. R., 1980, Preliminary Considerations Concerning the Stability of a Liquid Heterogeneity in a Plane-Parallel Liquid Film, Journal of Colloid and Interfacial Science, 76 (2), 587-590.

[14]   CRC Handbook of Lubrication: Theory and Practice of Tribology, Volume II: Theory and Design, Booser, E. R. (Ed.), 1983, CRC Press LLC, Boca Raton, FL, 246.

[15]   Shearer, L. T. and Akers, W. W., 1958, Foaming in Lube Oils, J. Phys. Chem., 62, 1269-1270.

[16]   Hadamard, J. S., 1911, Mouvement permanent lent d'une sphere liquide et visqueuse dans un liquide visqueux, CR Acad. Sci., 152, 1735–1738.

[17]   Rybczynski, W., 1911, Uber die fortschreitende Bewegung einer flüssigen Kugel in einem zähen Medium, Bull. Int. Acad. Sci. Cracovie, A, 40–46.

[18]   Levich, V. G., 1962, Motion of Drops and Bubbles in Fluid Medium, Chapter VIII, in Physiochemical Hydrodynamics, 2nd Edition, p. 435, Prentice-Hall, Inc., Englewood Cliffs, NJ.

[19]   Interfacial Phenomena in Apolar Media, Surfactant Science Series Volume 21, Eicke, H. F and Parfitt, G. D. (Ed.), 1987, Marcel Dekker, New York, NY.

[20]   ASTM D892-06, 2006, Standard Test Method for Foaming Characteristics of Lubricating Oils, ASTM International, West Conshohocken, PA.

[21]   ASTM D3427-03, 2003, Standard Test Method for Air Release Properties of Hydrocarbon Based Oils, ASTM International, West Conshohocken, PA.