

Letters

Optimal Hydrophobicity of Silica in Mixed Oil–Silica Antifoams

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Mixtures of a properly chosen oil (poly(dimethylsiloxane) (PDMS) or hydrocarbon) and hydrophobic particles (e.g., hydrophobized silica) have a strong deteriorating effect on foam stability, even when introduced in a very low concentration. These mixtures are widely used for foam control and are commonly termed antifoam compounds. In the present study, we check experimentally how the antifoam efficiency depends on the hydrophobicity of the solid particles. For this purpose, we prepare antifoam compounds by mixing silicone oil (PDMS) and hydrophilic silica at room temperature. The mild stirring of this mixture leads to a gradual PDMS adsorption on the silica surface, making it more hydrophobic. This process is very slow at room temperature and takes weeks before reaching the final, most hydrophobic state of the particles. Thus, we are able to check how the antifoam activity changes along the process of silica hydrophobization. Solutions of three surfactants (one ionic and two nonionic) are used as foaming media. In all of the studied systems, a well-pronounced maximum in the antifoam efficiency is observed at a certain optimal silica hydrophobicity, which depends on the used surfactant. The foam tests are complemented with several model experiments, and a plausible explanation of the observed phenomenon is suggested.

1. Introduction

Mixtures of oil (e.g., poly(dimethylsiloxane) (PDMS) or hydrocarbon) and hydrophobic solid particles (e.g., hydrophobized silica) are widely used for foam control in various technologies and consumer products.^{1–3} These mixtures are termed antifoam compounds, and it has been established that they are often much more efficient than their components, if taken separately.⁴

The synergistic antifoam action of oil and solid particles is explained by the different roles that they play in the mechanism of foam destruction. The oil globules are considered^{2–9} as being essential for the formation of unstable oil bridges between the two surfaces of the foam films, in the course of film thinning. These bridges either stretch and rupture in their center (bridging–stretching mechanism^{7,8}) or are dewetted by the surfaces of the foam

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film (bridging–dewetting mechanism^{2–6}). In both cases, the oil bridge induces a rupture of the foam film within several seconds after film formation. Many studies^{2–8,10–17} demonstrated, however, that the emergence (entry) of the oil globules at the foam film surface is not a spontaneous process; repulsive forces between the oil drop and the film surface must be overcome. As suggested by Garrett⁴ and later proven by several independent experiments,^{6,11,16} the main role of the solid particles in the antifoam compounds is to aid the entry of the oil globules. In the absence of solid particles, the oil drops are usually unable to enter the foam film surface and are expelled out of the foam film in the course of its thinning (into the neighboring Plateau borders).^{12,14–16} Consequently, the oil drops deprived of solid particles are either inactive as antifoams¹² or destroy the foam at a much longer time scale (typically, dozens of minutes).^{14–17}

The explanation of the role of solid particles given by Garrett⁴ implies that their efficiency should strongly depend on the particle hydrophobicity (see section 3.3 below for more details). We are aware of a single paper¹⁸ in which this relation is systematically studied. The hydrophobicity of silica particles was varied by treatment with different amounts of silicone oil. The hydrophobized silica was mixed with hydrocarbon oil, and the antifoam efficiency of the obtained compound was evaluated by foam tests. In parallel, the silica hydrophobicity was characterized by measuring the contact angle of aqueous drops placed on pressed silica pellets. The experimental results in ref 18 suggest that the antifoam efficiency increases significantly with the silica hydrophobicity. To the best of our knowledge, no further checks of this relation have been made, and it has been accepted as a general rule that more hydrophobic solid particles yield more active antifoams.

In the present study, we employ another, very simple procedure for a gradual variation of the silica hydrophobicity in mixed oil–silica compounds: Silica particles are mixed with silicone oil at room temperature, and this mixture is stored for a long period of time (see section 2.2.1 for details). Under these conditions, a gradual PDMS adsorption on the silica surface is known to occur.^{19–23} This process is very slow, and it takes weeks before the final, most hydrophobic state of the particles is reached.^{19,23} Thus, we are able to check how the antifoam activity of

the compound changes along the hydrophobization process. The results convincingly show that there is a well-pronounced, optimal silica hydrophobicity at which the antifoam is most efficient. An explanation, based on the mentioned role of the solid particles (to assist the oil drop entry), is suggested.

2. Experimental Details

2.1. Materials. Three surfactants are used as received: anionic sodium dioctyl-sulfosuccinate (C₂₀H₃₇O₇SNa, Sigma catalog no. D-0885; denoted hereafter AOT); nonionic octylphenol decethylene glycol ether (Triton X-100, product of Merck); and nonionic alkyl-C_{12/14}(glucopiranoside)_{1.2} of average molecular mass 495 Da, denoted APG (Henkel, Germany; commercial name Glucopon 600). The experiments are performed with aqueous solutions of concentrations 10 mM for AOT ($\approx 3.6 \times \text{cmc}$, critical micelle concentration), 1 mM for Triton X-100 ($\approx 6 \times \text{cmc}$), and 0.6 mM for APG ($\approx 4 \times \text{cmc}$). Deionized water from a Milli-Q purification system (Millipore, USA) was used for preparing the surfactant solutions.

The compounds are prepared with silicone oil 47V1000SH (Rhodia Silicones Europe, Saint-Fons, France) with a dynamic viscosity of 1000 mPa s. Two types of silica (Degussa, Germany) are used for preparation of two different antifoam compounds: hydrophilic silica A200 and hydrophobized silica R974. The silica A200 is of pyrogenic origin and has a specific surface area of approximately 200 m²/g.²⁴ R974 is obtained from A200 by grafting CH₃-groups onto the particle surface.²⁴

The silica concentration in the compounds is 4.2 wt %. For brevity, we will denote the compound prepared with particles of A200 as compound A, whereas the compound prepared with particles of R974 will be denoted as compound R. Compound A in the present study has a different composition (contains different solid particles) from compound A in refs 7, 17, 25, and 26.

The glassware was carefully cleaned by immersion in ethanol solution of KOH (at least for 12 h), followed by copious rinsing with deionized water.

2.2. Methods. 2.2.1. Preparation of the Antifoam Compounds. The antifoam compounds are prepared by mixing silicone oil and silica (A200 or R974) in a glass vessel under continuous stirring at ≈ 50 rpm (with mechanical stirrer ER10, MLW, Germany) and at room temperature. The silica particles are added in small portions (< 0.05 g). Each portion is added after the previous one has been entirely homogenized within the oil. The total amount of silica is introduced over about 20 min. Afterward, the sample stirring continues for another 4 h. Thus-prepared compounds are tested in the three surfactant solutions. In the following 40 days, the compounds are stirred every day for 4 h and their activity is tested immediately after stopping the stirring.

Microscope observations show that the compounds prepared in this homemade setup contain some relatively big (30–50 μm) silica agglomerates, along with many smaller agglomerates of size around and below 1 μm .

2.2.2. Automated Shake Test (AST). The foam stability tests are performed on a shake machine Agitest (Bioblock). A 100 mL quantity of the foaming solution is placed in a standard 250 mL glass bottle, and 10 μL of the compound (corresponding to 0.01 vol %) is introduced into this sample. A micropipet M800 (Nichiryo Co., Tokyo, Japan), which is specially designed to supply small volumes of viscous substances, is used to load the compound. The bottle is then mechanically agitated at a frequency of 360 min⁻¹ and an amplitude of 2 cm. After each cycle of agitation for 10 s, the solution remains quiescent for another 60 s. During this period, the defoaming time is observed; it is defined as the time for appearance of a clean water–air interface without bubbles. Afterward, a new shaking cycle is performed, and this procedure is repeated until the defoaming time exceeds 60 s in three consecutive cycles; this is considered as the moment of compound

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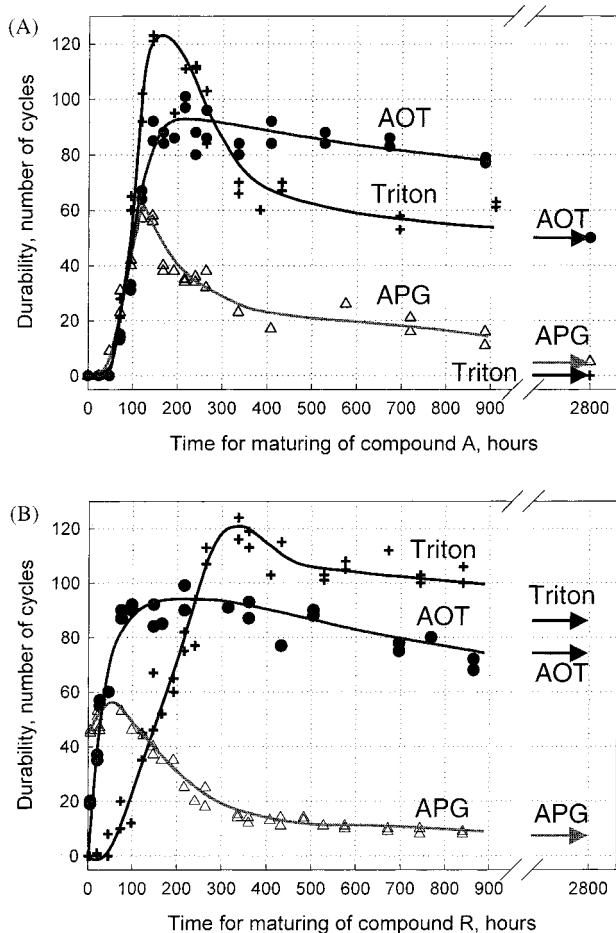


Figure 1. Durability of the antifoam compounds in AOT, Triton, and APG solutions (determined by the AST), as a function of the time of contact silica/PDMS: (A) compound A; (B) compound R.

exhaustion.²⁵ A larger number of cycles before the compound exhaustion corresponds to better antifoam durability (efficiency) and vice versa.

2.2.3. Film Trapping Technique (FTT). The entry barriers were measured by the FTT.^{16,27} In this technique, antifoam globules are captured in an aqueous wetting film on a glass substrate. The drops are observed from below, through the glass substrate, by means of an inverted optical microscope (Jenavert, Carl Zeiss, Germany). When the thickness of the wetting film becomes smaller than the globule diameter, the upper film surface presses the globules against the solid substrate. A meniscus is formed around each globule with a capillary pressure $\Delta P = (P_A - P_W)$, where P_A is the pressure of the gaseous phase above the film and P_W is the pressure in the aqueous film. P_A is increased by a pressure control system, and the critical capillary pressure, ΔP_{CR} , at which the globules enter the air–water interface, is measured (for details see refs 16 and 27). The moment of drop entry, which is accompanied with a significant local change in the meniscus shape, is clearly seen in the microscope. Higher values of ΔP_{CR} correspond to more difficult entry and vice versa. For brevity, we term ΔP_{CR} the “entry barrier”.

Micrometer droplets of the studied antifoams were obtained by pre-emulsification in the tested surfactant solutions; three standard shaking cycles in the AST were used for this purpose.

3. Experimental Results and Discussion

3.1. Foam Tests. The results from the foam tests with compounds A and R are shown in Figure 1. One sees that in all of the studied systems there is a maximum in the

antifoam durability as a function of time of silica–PDMS contact (i.e., of silica hydrophobicity). The maximums are particularly well seen with compound A: in this system, we start with very hydrophilic particles, when the compound is completely inactive in all three surfactant solutions, and end up with well-hydrophobized particles. Note that compound A again becomes inactive in Triton and APG solutions at the end of the hydrophobization process (see the arrows indicating the results for 2800 h of compound maturing). Its durability in AOT solutions decreases about 2 times after the maximum.

The maximums in the antifoam efficiency are less pronounced in the case of compound R (cf. parts A and B of Figure 1). The latter observation can be explained by taking into account the results from ref 19, where the kinetics of PDMS adsorption on the surface of silica particles in PDMS–silica mixtures (similar in composition to our antifoam compounds) is studied. It is found¹⁹ that the kinetics of PDMS adsorption is slower, and the amount of the final bound polymer is much lower in the case of silica whose surface has been pretreated by grafting CH_3 -groups (see Figures 5 and 7 in ref 19). The reason is that the CH_3 -groups block the reactive silanol groups on the surface of the silica particles, which makes the PDMS adsorption less favorable. Furthermore, our own contact angle measurements²³ with hydrophobized glass particles showed that the pretreatment of the glass surface with hexamethyl disilazane (which results in surface grafting of CH_3 -groups) leads to lower particle hydrophobicity after a subsequent treatment with PDMS. All of these results indicate that the particles in compound R change their hydrophobicity in a narrower range (the initial particles are partially hydrophobized and the final hydrophobicity is lower), as compared to compound A. This consideration explains why the maximums are less pronounced in compound R.

As seen from Figure 1, the position and height of the maximums depend on the type of surfactant used. Qualitatively, the maximum appears at a lower silica hydrophobicity in the systems in which the asymmetric oil–water–air films (formed when the antifoam globules approach the surfaces of the foam film) are thicker. As shown in previous studies,^{7,26} the films stabilized by APG are around 100–120 nm thick, whereas those stabilized by AOT are much thinner (around 15 nm). Respectively, the maximum in antifoam activity appears earlier (i.e., when the silica particles are less hydrophobic) for APG solutions in comparison with AOT. The liquid films stabilized by Triton X-100 have a thickness of around 20–25 nm, which is close to that of AOT, and consequently the maximum in the antifoam activity appears at a similar silica hydrophobicity for these two surfactants. A possible explanation of the correlation between the liquid film thickness and the optimal silica hydrophobicity is given in section 3.3.

On the other side, no correlation is established between the height of the maximum and the film thickness: the compound is the most active (at its maximum) in Triton solutions and the least active in APG solutions. This lack of correlation between the antifoam activity and film thickness is not surprising, because the stability of liquid films depends on a number of other properties as well (surfactant adsorption on the film surfaces, Gibbs elasticity, surface viscosity, etc.).^{28–31} In the present systems, the foam stability is affected also by the wettability of the

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Table 1. Critical Pressure to Entry, P_{C}^{CR} , Measured by the FTT for Globules of Compounds A and R Soon after the Compound Preparation (72 or 98 h), at the Maximum of the Compound Efficiency, and after 2800 h^a

surfactant solution	durability, no. of cycles	P_{C}^{CR} , Pa
10 mM AOT	72 h	14
	max	20 ± 2
	2800 h	2 ± 2
0.6 mM APG	72 h	90 ± 5
	max	4 ± 1
	2800 h	50
1 mM Triton X-100	72 h	20 ± 5
	max	15 ± 2
	2800 h	0–5
	98 h	48 ± 5
	max	19 ± 2
	2800 h	1 ± 1
		> 50

^a The durability was determined by the standard AST.

silica particles by the surfactant solution (see section 3.3), a factor which is not related to the liquid film thickness.

3.2. Role of the Entry Barrier. To get some insight into the possible reasons for the observed maximums in the antifoam activity, we measured the entry barriers for the antifoam globules of compound A in the three surfactant solutions, at different moments: (1) at the beginning, when the compound has low activity; (2) around the maximum in the compound durability; (3) at the end of the hydrophobization process, when the compound activity is reduced. The results from these measurements are shown in Table 1. One sees a clear correlation between the values of the entry barrier and the compound durability: the barrier is very low (1–3 Pa) when the durability is maximal and significantly higher before and after the maximum.

Furthermore, the measured values of the entry barrier for the two nonionic surfactants, APG and Triton, are relatively high at the end of the hydrophobization process, $\Delta P_{CR} = 48 \pm 5$ Pa and > 50 Pa, respectively. These values are well above the limiting value, which separates the fast (foam film breaking) from slow (Plateau border breaking) antifoams, $\Delta P_{CR} \approx 15$ Pa.^{16,17} These data explain why compound A, containing well-hydrophobized silica particles, is inactive in these surfactant solutions (at the time scale of interest): the antifoam globules are unable to enter the surfaces of the foam films and to break these films, due to the high entry barriers. In other words, the overhydrophobization of the solid particles reduces their activity as promoters of the antifoam globule entry.

3.3. Possible Explanation of the Reduced Activity of Antifoams Containing Overhydrophobized Silica. The idea that the solid particles, if sufficiently hydrophobic, facilitate the entry of the antifoam globules was expressed in quantitative terms by Garrett.⁴ He considered the equilibrium configuration of a solid sphere, which bridges the surfaces of the asymmetric oil–water–air film, formed when an antifoam globule approaches the surface of a foam film; see Figure 2. If the three-phase contact angles solid–water–oil, θ_O , and solid–water–air, θ_A , satisfy the condition

$$\theta_O + \theta_A \geq 180^\circ \quad \text{condition for dewetting} \quad (1)$$

there is no equilibrium position of the particle in the film, and the two contact lines would slide along the particle surface until they coincide; thus, the globule entry will be

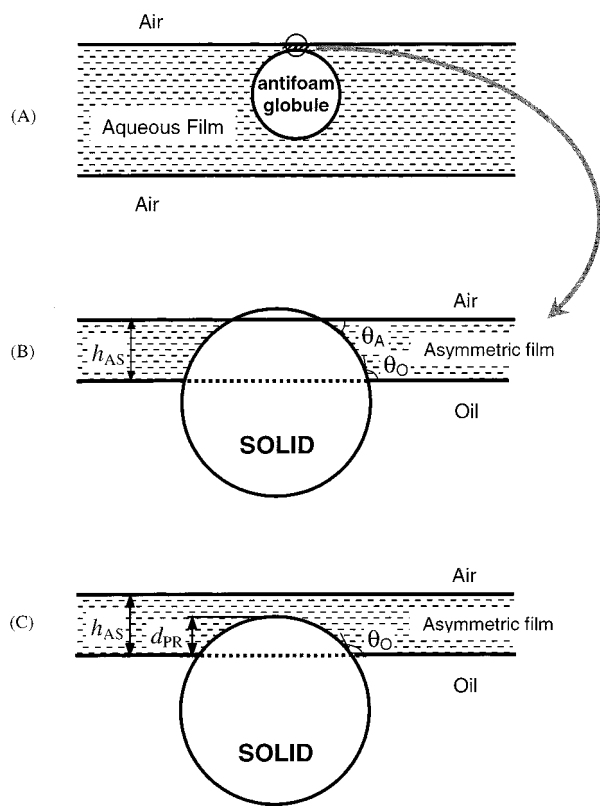


Figure 2. (A) When the antifoam globule approaches the foam film surface, an asymmetric oil–water–air film of thickness h_{AS} forms. (B) If the protrusion depth, d_{PR} , of the solid particle is larger than h_{AS} and the condition for dewetting is satisfied, the solid particle pierces the air/water interface and induces a film rupture. (C) If the protrusion depth is small, the solid particle is unable to pierce the asymmetric film, even if the condition for dewetting is satisfied.

assisted by the solid particle. On the contrary, if the solid particles are not sufficiently hydrophobic (condition 1 is not satisfied), they could even stabilize the asymmetric film and the globule entry will not occur.

An additional factor for the effectuation of the globule entry with the aid of the solid particles, which has not been considered in detail so far, is the protrusion depth of the solid particle in the aqueous phase, d_{PR} . Indeed, the particle dewetting is possible only if the particle has already bridged the surfaces of the asymmetric film, that is, when d_{PR} is larger than the thickness of the asymmetric film, h_{AS} ; see Figure 2B. If $d_{PR} < h_{AS}$, the particle is not in contact with the air–water interface (Figure 2C) and the dewetting cannot be realized. In other words, one can define an additional condition for piercing of the asymmetric film by the solid particles, which requires

$$d_{PR} \geq h_{AS} \quad \text{condition for piercing} \quad (2)$$

For solid spheres, this condition can be expressed in terms of the particle radius, R_p , and contact angle, θ_O , from simple geometrical considerations:

$$d_{PR} = R_p(1 + \cos\theta_O) \geq h_{AS} \quad \text{condition for piercing} \quad (2')$$

The comparison of conditions 1 and 2 shows that they contradict each other. The condition for dewetting is better satisfied with more hydrophobic particles (larger θ_O), while the condition for piercing is better satisfied for more hydrophilic particles (smaller θ_O). In the extreme case of perfectly hydrophobic particles, $\theta_O \rightarrow 180^\circ$, the protrusion

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depth approaches zero, that is, the particles are completely immersed in the oil phase and do not aid the entry of the antifoam globules (though the condition for dewetting is satisfied). From this consideration, it directly follows that, at least for spherical particles, there is an optimal contact angle (optimal particle hydrophobicity) at which the globule entry is easiest and the antifoam would be most active. One can deduce from eq 2' that the optimal contact angle is around

$$\cos \theta_0 \approx h_{AS}/R_p - 1 \quad \text{optimal angle} \quad (3)$$

and therefore depends on the particle radius as well. One can expect that *qualitatively* similar should be the case with nonspherical solid particles, like those used in our study and in the actual antifoams. Note, however, that the size of the solid particles affects many other properties of the antifoam like its stability against particle sedimentation, typical size of the antifoam globules, and so forth, so that the particle size cannot be varied in a very wide range in practical systems.

The above explanation is in agreement with the experimental fact (section 3.1) that the optimal hydrophobicity of a given antifoam is lower for surfactant systems in which the film thickness is larger. Indeed, condition 2 requires more hydrophilic particles for piercing of thicker asymmetric films. When the particles are overhydrophobized, their protrusion depth becomes smaller than the film thickness, the entry barrier increases, and subsequently the antifoam loses its activity (Table 1).

The above consideration assumes that the thickness of the asymmetric film, h_{AS} , is close to the equilibrium one. This assumption is well justified for the typical antifoam globules, because the time for reaching the equilibrium film thickness is very short for films of diameter in the micrometer range. An approximate estimate of the time, τ_{DR} , for reaching the equilibrium film thickness (defined as the period elapsed between the formation of the asymmetric film and its thinning down to h_{AS}) can be made from the formula (see, e.g., section VI.B in ref 29)

$$\tau_{DR} \approx \int_{h_{AS}}^{h_{IN}} \frac{dh}{V(h)} \quad (4)$$

where h_{IN} is the initial thickness of the asymmetric film and $V(h)$ is the rate of thinning of this film. $V(h)$ can be estimated from the Reynolds equation,

$$V(h) \approx \frac{2}{3} \frac{P_C h^3}{\eta R_{AS}^2} \quad (5)$$

$P_C \sim 10^3$ Pa in eq 5 is the capillary pressure which drives the thinning of the asymmetric film ($P_C \sim 2\sigma_{OW}/R_D$; $\sigma_{OW} \approx 10$ mN/m is the tension of the oil–water interface; $R_D \approx 10$ μ m is the radius of the antifoam globule), $\eta \approx 1$ mPa s is the dynamic viscosity of the aqueous phase, and $R_{AS} \approx 1$ μ m is the radius of the asymmetric film. The

substitution of eq 5 into eq 4 leads to the following expression for the drainage time of the asymmetric film:²⁹

$$\tau_{DR} \approx \frac{3}{4} \frac{\eta R_{AS}^2}{P_C} \left(\frac{1}{h_{AS}^2} - \frac{1}{h_{IN}^2} \right) \quad (6)$$

Taking the above estimates for the parameters entering eq 6, $h_{AS} \approx 10$ nm and $h_{IN} \gg h_{AS}$, one finds that the drainage time $\tau_{DR} \sim 10$ ms.

One can conclude that the drainage of the micrometer-sized asymmetric films formed between the antifoam globules and the surfaces of the foam film (Figure 2) occurs almost instantaneously in the time scale of interest, which is on the order of seconds.

Further systematic experiments are under way to retrieve more detailed information about the relation between the hydrophobicity of the silica particles, the physicochemical properties of the studied compounds, and their antifoam efficiency.

4. Conclusions

In this paper, we study how the activity of mixed PDMS–silica antifoams depends on the hydrophobicity of the incorporated solid particles. The results with two different antifoams and three different surfactant solutions convincingly show that there is a well-defined, optimal silica hydrophobicity at which the antifoam is most active (Figure 1). The optimal hydrophobicity depends on the used foaming solution. The antifoam efficiency correlates well with the barrier to entry of the antifoam globules, as measured by the film trapping technique (Table 1).

The maximum in the antifoam activity is explained as a result of two contradictory requirements to the particle hydrophobicity, which directly stem from the main role of the solid particles in mixed antifoams, namely, to assist the antifoam globule entry by piercing the asymmetric oil–water–air films.⁴ The first requirement, formulated by Garrett,⁴ is that the particles should be sufficiently hydrophobic to be dewetted by the oil–water and air–water interfaces. The other requirement is that the particles should protrude sufficiently deep into the aqueous phase (in order to bridge the surfaces of the asymmetric oil–water–air film), and it is better satisfied by more hydrophilic particles. Therefore, an optimal hydrophobicity is expected, at which both requirements are balanced and the antifoam is most active. For spherical particles, this idea can be expressed in terms of an optimal three-phase contact angle; see eq 3. If either of these requirements is strongly violated, the antifoam should be inactive.

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