

Model Studies of the Effect of Silica Hydrophobicity on the Efficiency of Mixed Oil–Silica Antifoams

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Mixtures of poly(dimethylsiloxane) oil and hydrophobized silica are used for foam control and are termed antifoam compounds or mixed oil–silica antifoams. In a previous study, we found experimentally a well-pronounced maximum in the antifoam efficiency at a certain optimal silica hydrophobicity. The reasons for this peculiar dependence are studied in the present paper by performing two series of experiments. First, compounds of silica and oil are prepared under different conditions (with and without heating and/or stirring) and the antifoam efficiency of these compounds is compared by foam tests. Second, several characteristics of the studied compounds, such as viscosity, entry barrier, and thickness of the layer of spreading oil, are measured, and their contribution to the compound performance is analyzed. The results show that the optimal hydrophobicity of the silica particles is related to a minimum in the entry barrier (measured by the film trapping technique), which determines how easily the compound globules emerge on the surface of the foam films. Another factor (particularly important for compounds containing insufficiently hydrophobized particles) is the compound yield stress, which governs the deformability of the antifoam globules. If the compound has large yield stress, its dispersiveness in the foaming solution and the oil spreading are inhibited, and the antifoam is inactive. The obtained results clarify the physicochemical properties which determine the antifoam activity of mixed oil–solid compounds.

1. Introduction

Mixtures of oil (e.g., poly(dimethylsiloxane), PDMS) and hydrophobic solid particles (e.g., hydrophobized silica) are used for foam control in various technologies and consumer products.^{1–5} These mixtures, termed antifoam compounds, are usually much more efficient than their components, if taken separately.⁵

The synergistic antifoam action of oil and solid particles is explained by the different roles 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. It was recently shown^{8,9} for mixed PDMS–silica antifoams that the oil bridges, once formed in the foam films, rapidly stretch in the radial direction and eventually rupture in the bridge center (bridging–stretching mechanism). In this way, the

oil bridges induce a rupture of the foam film within several seconds after film formation. Many studies^{2,3,5–17} 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 Garrett⁵ and proven experimentally,^{7,11,16} 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, minutes or dozens of minutes).^{14–17}

In a recent study,¹⁸ we employed a simple procedure for a gradual increase of silica hydrophobicity in mixed oil–silica compounds: Silica particles were mixed with silicone oil (PDMS) at room temperature, and this mixture was stored for a long period of time (up to 4 months). Under

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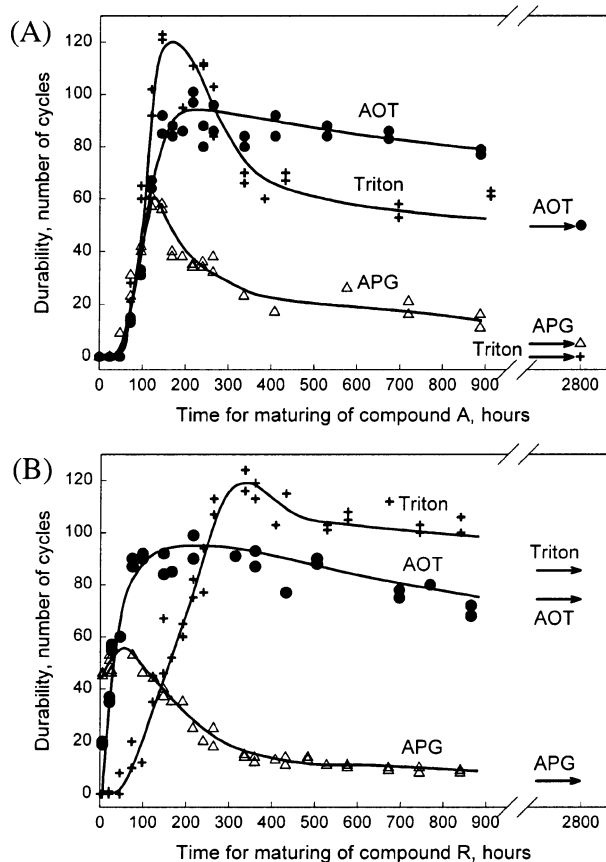


Figure 1. Durability (number of foam formation/destruction cycles before antifoam exhaustion in the AST) of antifoams in AOT, Triton, and APG solutions, as a function of the time of silica/PDMS contact (ref 18): (A) compound A (corresponding to compound A4CS in this work); (B) compound R (corresponding to compound R4CS in this work).

these conditions, a gradual PDMS adsorption on the silica surface occurs in a slow process until the final, most hydrophobic state of the particles is reached.^{18–23} Thus we were able to check how the antifoam efficiency of the compound changed during the hydrophobization process. The results obtained with various systems (two different types of silica particles and three different surfactant solutions) showed a well-pronounced, optimal silica hydrophobicity corresponding to the highest antifoam efficiency; see Figure 1. In a new series of experiments, we showed that the antifoam efficiency exhibited a maximum, when plotted as a function of PDMS adsorption on the silica particles in the compound; see Figure 2. The maximum corresponded to about 3–4 mg/m² of adsorbed PDMS, and the further increase of the amount of adsorbed polymer resulted in a sharp decline of the antifoam efficiency (Figure 2B).

The observed maximum in the antifoam efficiency was explained¹⁸ as a result of two requirements for the particle hydrophobicity, which stem from the main role of the silica particles, namely, to assist the globule entry by piercing

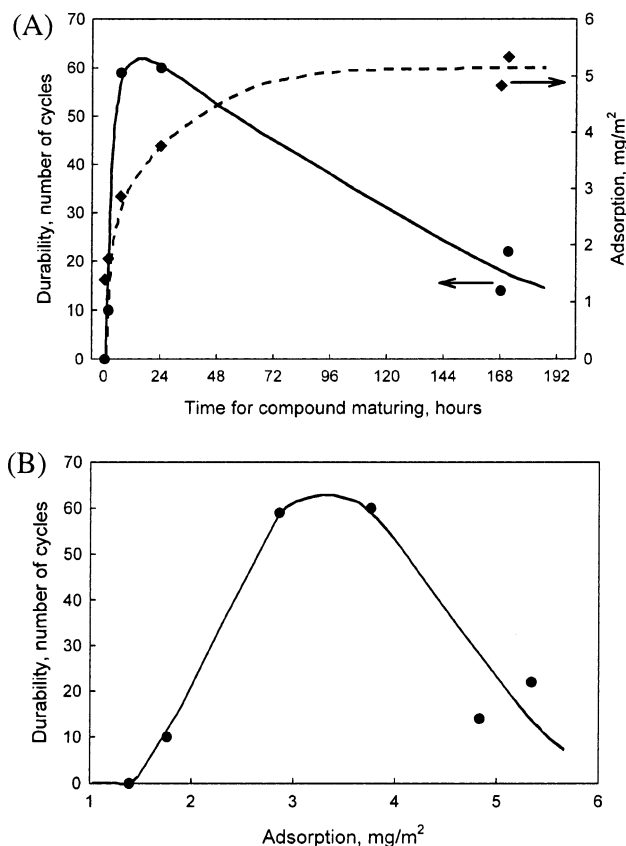


Figure 2. (A) Durability of an antifoam compound (circles, solid curve) and amount of adsorbed PDMS on the silica particles in the same compound (diamonds, dashed curve), as functions of the time of PDMS–silica contact (maturing time). (B) Durability of the same compound plotted as a function of the adsorbed PDMS. The compound was prepared by mixing hydrophilic silica particles and silicone oil at room temperature. The foam tests were performed with solutions of a nonionic surfactant (technical grade) at a concentration of $3 \times \text{cmc}$. The PDMS adsorption was determined from the height of the peaks at 1260 and 2963 cm⁻¹ in the IR spectra of the treated silica particles, after their washing by heptane.

the asymmetric oil–water–air films (see Figure 3). The first requirement, formulated by Garrett,⁵ is that the particles should be sufficiently hydrophobic to be dewetted by the oil–water and air–water interfaces. The other requirement¹⁸ 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, the entry barrier is low, and the antifoam is most active. For spherical particles, the optimal hydrophobicity can be expressed in terms of a most favorable three-phase contact angle.¹⁸

In the present study, we apply several experimental methods to analyze in more detail the role of particle hydrophobicity in the antifoam efficiency. The new results support the concepts illustrated in Figure 3, and a perfect correlation is found between the antifoam efficiency and the entry barrier measured by the film trapping technique.^{16,24} In parallel, we study how the conditions during compound preparation (heating, stirring) affect its activity. It has been known for a long time²⁵ that the dispersing

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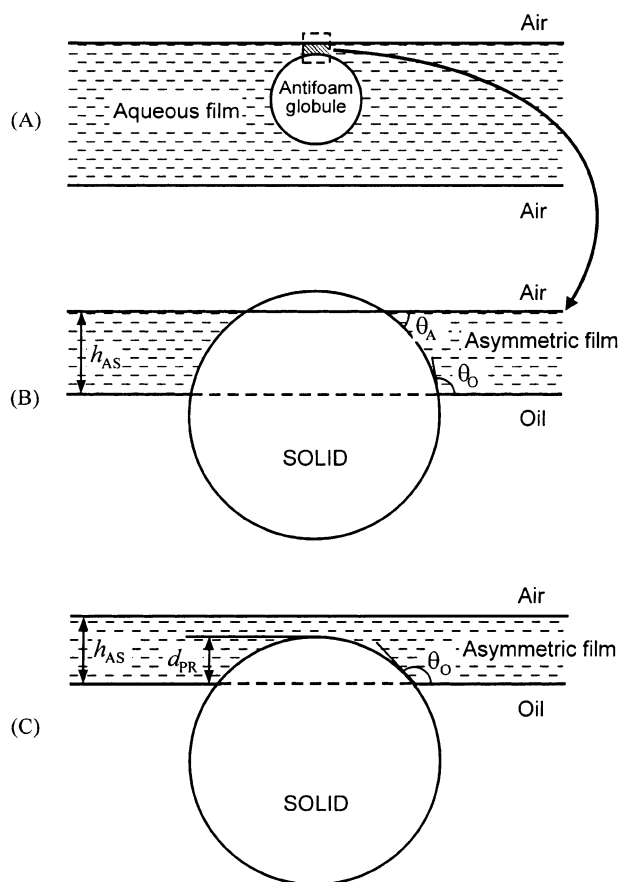


Figure 3. (A) When an antifoam globule approaches the foam film surface, an asymmetric oil–water–air film of thickness h_{AS} forms. (B) If the protrusion depth, d_{PR} , of the solid particle is larger than h_{AS} and the condition for dewetting, $\theta_O + \theta_A > 180^\circ$, is satisfied, the 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.

of hydrophilic silica (like particles A200, Figure 1A) in PDMS is difficult: jellylike compounds are initially formed, which are very intractable for handling. These jellylike compounds have no antifoam activity and have been sometimes termed α -dispersions.²⁵ The heating and/or stirring of α -dispersions leads to their transformation into typical fluid antifoams called β -dispersions.²⁵ This process is still not well understood, and the new information might be useful for a better control of the process of “in situ hydrophobization” of silica by PDMS, which is often used in practice.²⁶

2. Experimental Details

2.1. Materials. Three surfactants are used as received: anionic sodium bis(2-ethylhexyl) sulfosuccinate ($C_{20}H_{37}O_7SNa$, Sigma catalog no. D-0885; named hereafter AOT); nonionic octylphenol decaethylene glycol ether (Triton X-100, a product of Merck); and nonionic alkyl- $C_{12/14}$ (glucopyranoside)_{1.2} of average molecular mass 495 Da, named APG (Henkel, Germany; commercial name Glucopon 600). The experiments are performed with aqueous solutions with concentrations of 10 mM for AOT ($\approx 3.6 \times$ critical micelle concentration (cmc)), 1 mM for Triton X-100 ($\approx 6 \times$ cmc), and 0.6 mM APG ($\approx 4 \times$ cmc). Deionized water from a Milli-Q purification system (Millipore, Bedford, MA) 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 antifoam compounds: hydrophilic silica A200 and prehydrophobized silica R974. The silica A200 is of pyrogenic origin (primary silica spheres with diameter 12 nm are formed by flame hydrolysis of silicon tetrachloride, and the spheres partially fuse with one another forming submicrometer-sized, branched aggregates) and has a specific surface area of approximately $200 \text{ m}^2/\text{g}$.²⁷ R974 is obtained from A200 by grafting dimethylsilyl groups onto the particle surface.²⁷

The silica concentration in the compounds for most experiments is 4.2 wt %. In one series of experiments, compounds of different silica concentration were used, which were prepared as explained in section 2.2.1.

The used glassware was carefully cleaned by immersion in an 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 (PDMS) and silica particles A200 or R974 in a glass vessel equipped with a mechanical stirrer (ER10, MLW, Germany). The silica particles are added in small portions ($< 0.05 \text{ g}$) under continuous stirring at a speed of $\approx 50 \text{ rpm}$. The total amount of silica is introduced for about 20 min, and the sample stirring continues for another 4 h.

Microscope observations show that the compounds prepared in this way contain some relatively big ($30\text{--}50 \mu\text{m}$) silica agglomerates, along with many smaller agglomerates of size around and below $1 \mu\text{m}$. To decrease the size of the biggest agglomerates, some of the compounds, as explained below, are additionally stirred by an Ultra-Turrax T25 homogenizer (Janke & Kunkel GMBH & Co., IKA Labortechnik, U.K.) at 8000 rpm for 40 min.

The original compound, prepared with 4.2 wt % silica, was split into several fractions, which were further treated in different ways. Thus a series of several compounds of the same oil–silica composition but prepared under different conditions were obtained. The compounds, prepared with silica A200, are as follows:

- (1) A4CN (cold, nonstirred): this is the original compound (prepared at room temperature by continuous stirring at $\sim 50 \text{ rpm}$ for 4 h), which was stored at room temperature without further stirring or heating.
- (2) A4CS (cold, stirred): this sample was additionally stirred every day for 4 h at $\sim 50 \text{ rpm}$ at room temperature.
- (3) A4HN (heated, nonstirred): this fraction was additionally heated at 150°C for 4 h and afterward stored at room temperature without stirring.
- (4) A4HS (heated, Ultra-Turrax stirred): this portion was additionally heated at 150°C for 4 h, and after cooling to room temperature, it was stirred by the Ultra-Turrax homogenizer at 8000 rpm for 40 min.

In a similar manner, we prepared a series of compounds containing prehydrophobized R974 particles. The respective compounds are hereafter denoted as R4CN, R4CS, R4HN, and R4HS.

The notation of the compounds contains a starting letter A or R, which indicates the silica type, and the number indicates the silica level (e.g., 4 stands for 4.2 wt %). CN means cold nonstirred; CS, cold stirred; HN, heated nonstirred; and HS, heated and stirred by Ultra-Turrax.

Note that compounds A4CS and R4CS fully resemble compounds A and R, respectively, from Figure 1 and ref 18.

In another series of experiments, we studied the effect of silica concentration on the antifoam activity and viscosity of CS compounds prepared with A200 particles. For that purpose, a 9 wt % quantity of A200 particles was dispersed in PDMS at room temperature. Small portions of this “mother” compound were diluted every day to give compounds of concentrations 7, 4.2, and 2.5 wt %. The viscosity and the antifoam efficiency of these compounds were measured as a function of the time of maturing. The notation for these compounds is A9CS, A7CS, and so forth.

2.2.2. Automated Shake Test (AST). The foam stability tests are performed on a shake-machine Agitest (Bioblock). The

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foaming solution (100 mL) 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 by using a micropipet M800 (Nichiryo Co., Tokyo, Japan), which is specially designed to supply small volumes of viscous substances. 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 exhaustion.²⁸ A larger number of cycles before the compound exhaustion corresponds to better antifoam durability and vice versa.

In the current paper, we use the terms antifoam “durability” and “efficiency” as synonyms. We concentrate our study on the antifoam durability and do not discuss the so-called “initial antifoam activity” (which is defined as the average of the defoaming time during the first three cycles in the AST) for two reasons: First, the antifoam durability presents a considerable interest from a practical viewpoint, because the antifoams should be able to destroy the foam in as large a number of foam formation/destruction cycles as possible. Second, in all of the studied systems the antifoams were either inactive (defoaming time above 60 s) or their initial activity was very high (around 3–5 s), except for a very narrow period during compound maturing, when a given antifoam transformed from the inactive to the active state. Therefore, all active antifoams had very similar initial antifoam activity in our experiments.

2.2.3. Film Trapping Technique (FTT). The entry barriers were measured by the FTT.^{16,24} 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 $P_C^{\text{CR}} = (P_A - P_W)$, 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, P_C^{CR} , at which the globules enter the air–water interface, is measured (for details see refs 16 and 24). The moment of drop entry, which is accompanied by a significant local change in the meniscus shape, is clearly seen in the microscope. Higher values of P_C^{CR} correspond to more difficult entry of the antifoam globules and vice versa. For brevity, we term P_C^{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.

2.2.4. Viscosity Measurement. The viscosity of the compounds is measured on a Brookfield Rheoset laboratory viscometer, model LV (Brookfield Engineering Laboratories, Inc.), controlled by a computer. Spindle CP-52 (cone–plate geometry, cone angle = 3° and radius = 1.2 cm, viscosity range = 50 ÷ 1 × 10⁵ cP) is used. The spindle velocity is usually set at 1 or 2 rpm, but in some of the experiments other velocities, between 0.2 and 4 rpm, are used to have a torque which falls in the range of the instrument. The experimental checks showed that the measured viscosity did not depend on the spindle velocity, except for the gel-like samples which possess non-Newtonian rheological behavior. All measurements are performed at room temperature, 20 ± 1 °C.

2.2.5. Ellipsometry. Ellipsometry is applied to assess the thickness of the spread oil layer when a compound is placed in contact with the surface of the solution. The used instrument is described in ref 30 (see also ref 28). All experiments are performed at an angle of incidence of 50°, which is close to the Brewster angle for water, 53.1°. One microliter of the compound is placed in contact with the solution surface for several seconds by using

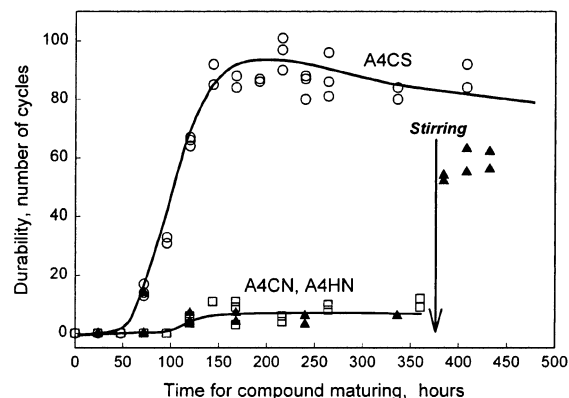


Figure 4. Durability of different compounds of type A, as measured by the AST in 10 mM AOT solutions. Empty circles, A4CS (cold, stirred); empty squares, A4CN (cold, nonstirred); full triangles, A4HN (heated, nonstirred). The compound A4HN was stirred after 380 h of maturing (see the vertical arrow), and its durability immediately improved.

a Nichiryo M800 micropipet. The changes in the ellipsometrical angles, Ψ and Δ ,^{30,31} are afterward measured for a period of 10 min and analyzed to calculate the thickness of the spread layer. To interpret the ellipsometrical data, we assume that the spread oil forms a homogeneous layer of refractive index equal to that of the bulk silicone oil, $n_{\text{OIL}} = 1.404$, sandwiched between air and solution bulk phases with their respective refractive indices. This model gives an effective thickness of the spread oil, d_{EFF} , which is averaged over the observation area, ≈ 2 mm in diameter, on the solution surface.

All experiments are carried out at the ambient temperature (20 ± 1 °C).

3. Experimental Results

3.1. Foam Tests. 3.1.1. Compounds Prepared with Silica A200. The first series of our experiments was aimed to explore in more detail how heating and stirring during compound preparation affect the antifoam performance.

The nonheated, stirred compound A4CS is used as a reference. As seen from Figure 1A, no antifoam activity was observed during the first 2 days with this compound in any of the studied surfactant solutions. The introduced compound remained as a single, nondeformable lump of irregular shape on the solution surface and did not disperse during shake tests. The bad dispersibility of the compound was caused by its gel-like consistency, which evidenced that the compound had large yield stress (see section 3.2). At the third day (72 h), a weak antifoam activity was observed to appear simultaneously in the solutions of all three surfactants, followed by a very rapid increase of the antifoam durability during the next few days. At that stage (and afterward, until the end of the observation period), the compound behaved as a typical fluid: it spontaneously formed circular liquid lenses, when deposited on the solution surface, and easily dispersed in the form of spherical oily drops upon shaking. A maximum in the compound durability is observed between the fifth and ninth days (depending on the used surfactant), which is followed by a decline during the next weeks of observation.

In Figure 4, we compare the results from the foam tests for the stirred compound A4CS with those for the nonstirred compounds A4CN and A4HN. For clarity, only the results with AOT solutions are shown; the results with APG and Triton were similar. The nonstirred compounds demonstrated a very poor antifoam efficiency

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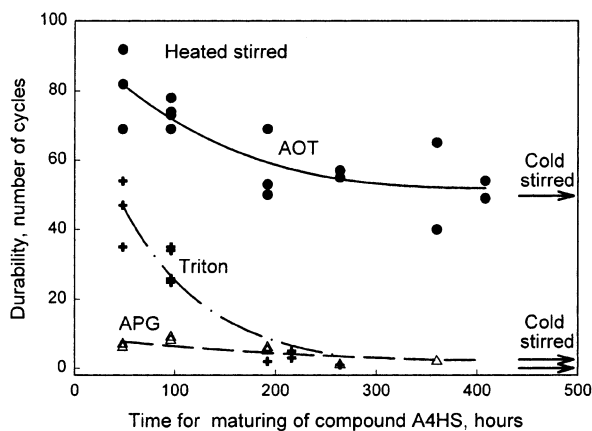


Figure 5. Durability of compound A4HS (heated, stirred by Ultra-Turrax) in solutions of 10 mM AOT, 0.6 mM APG, and 1 mM Triton X-100. For comparison, the durability of the cold stirred compound A4CS after 2800 h of maturing is shown by horizontal arrows.

during the entire period of observation (2 weeks). The visual examination of the samples in the shake test showed that the main problem with these compounds was their poor dispersibility; the compound introduced into the foaming solution remained as a nondeformable lump of irregular shape. After 16 days (≈ 380 h) of maturing, we applied mild mechanical stirring for 2 h on the heated compound A4HN, which had a strong effect on its consistency; the compound lost its gel-like appearance and transformed into a fluid with a viscosity of 3700 cP. Remarkably, a significant antifoam activity was immediately registered with the stirred compound (about 60 cycles, see Figure 4). These experiments clearly show that the heating alone is insufficient to transform an α -dispersion into a β -dispersion; mechanical stirring is necessary to break apart the gel structure and to activate the antifoam.

In contrast, the heated and stirred compound A4HS showed initially high durability in AOT and Triton solutions, which however decreased with time, approaching the durability of the cold stirred compound A4CS; see Figure 5. The durability of compound A4HS in APG solutions was very low during the entire period of observation, though this compound was fluid and easily dispersed in the foaming solutions upon shaking. These results are easily explained if one accepts that the combined treatment by heating for 4 h at 150 °C and intensive Ultra-Turrax stirring had resulted in so great a degree of silica hydrophobization that the optimal hydrophobicity had been surpassed during the compound preparation. In other words, the continuous decline of the durability of compound A4HS (Figure 5) corresponds to the observed decrease of the durability of compound A4CS after 400 h of maturing (Figure 1A), as a result of the silica overhydrophobization.

In another series of experiments, we checked how the maturing profile of compound A depends on silica concentration. In Figure 6, we compare the antifoam efficiency, as a function of the maturing time, for compounds A2CS, A4CS, A7CS, and A9CS. As seen from the figure, the evolution of compounds containing 2.5–7 wt % silica is very similar: the compounds become active after a certain period of maturing (and stirring), and clear maximums of the antifoam durability are observed, followed by a slow decline. Only the compound containing 9 wt % of silica (A9CS) behaved in a different manner; its antifoam activity remained very low during the entire period of observation. Visual observations showed that

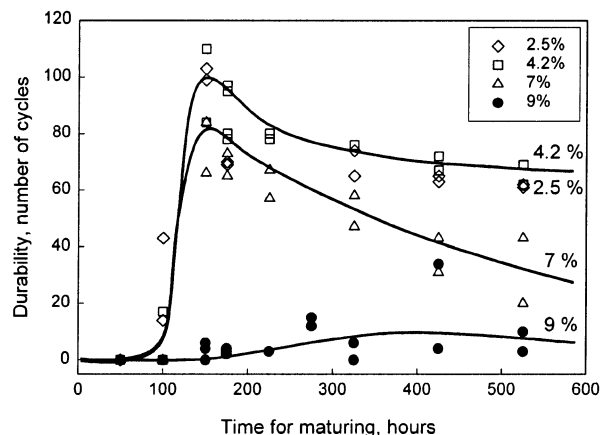


Figure 6. Durability of compounds of type AXCS ($X = 2, 4, 7,$ or 9) in 10 mM AOT solutions, as a function of time of silica/PDMS contact. The curves are guides to the eye.

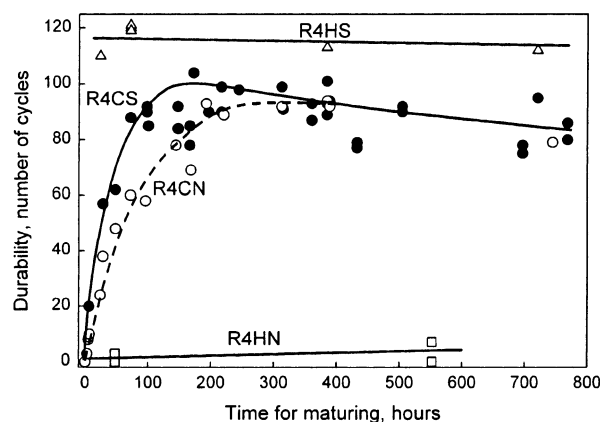


Figure 7. Durability of different compounds of type R, as measured by the AST in 10 mM AOT solutions: solid circles, R4CS; empty circles, R4CN; empty squares, R4HN; empty triangles, R4HS.

there were several problems with this compound, which contained A200 particles of high concentration: the compound had a higher mass density than the surfactant solution and sank to the bottom of the jar used in the shake test, instead of attaching to (and spreading on) the solution surface; the compound did not disperse well due to problems with its higher viscosity and higher density; the compound easily stuck to the wall and to the cap of the jar in the shake test. No other studied compound exhibited similar behavior.

3.1.2. Compounds Prepared with Silica R974. The stirred compound R4CS, prepared at room temperature, is used as a reference for comparison in this series. As seen from Figure 1B, this compound was active in AOT and especially in APG solutions immediately after its preparation, whereas an additional 3 days of maturing was needed for its activation in Triton solutions. The heights of the observed maximums in the compound durability were similar to those for the compounds prepared with A200 silica (cf. parts A and B of Figure 1).

The durability of compounds R4CS, R4CN, R4HN, and R4HS in AOT, as a function of the maturing time, is shown in Figure 7. The cold nonstirred compound R4CN showed a very similar evolution to that of the stirred compound R4CS, with the main difference being that the processes are about 2 times slower. Note that this result is in contrast to those obtained with compounds of type A, where a qualitative difference was observed between the stirred and nonstirred compounds (cf. Figures 4 and 7). The main

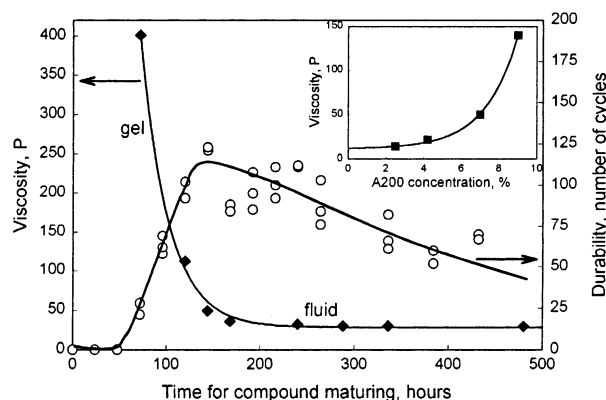


Figure 8. Viscosity (solid diamonds) and durability in 1 mM Triton solution (empty circles) of compound A4CS as a function of the time of silica/PDMS contact. The inset shows the dependence of the compound viscosity (after 300 h of maturing) as a function of the silica concentration in compounds of type A-CS.

reason for this difference is that the nonstirred compound prepared at room temperature with R974 particles was fluid, in contrast to the gel obtained with silica A200 (see section 4.2 for further discussion).

Compound R4HN (heated without stirring) showed very poor antifoam activity, which was related to the formation of a gel during heating. In contrast, the fluid compound R4HS (heated and homogenized by Ultra-Turrax) showed an excellent durability of about 110 cycles, which remained almost unchanged during the entire period of examination.

The maximal durability achieved by R4CS and R4CN (cold, stirred and nonstirred compounds) was virtually the same, 90–95 cycles, but smaller than that of the heated and vigorously stirred compounds R4HS (100–120 cycles). Thus, the heating and stirring of the compound led to best results for the antifoams of type R.

3.2. Compound Viscosity and Microscope Observations. The visual observations of the compounds, described in section 3.1, indicate that the compounds' consistency (especially the transition gel–fluid) is related to their antifoam activity. In the present section, we study in a more quantitative manner this relation. In addition, the compounds' rheological characteristics, such as viscosity and yield stress, reflect (and can be used for assessment of) the possible structuring of silica in the compounds.^{20,32} That is why we compared the viscosity of the various compounds and studied how it changed during maturing. We had no appropriate instrument to measure directly the compounds' yield stress. Instead, we present below an estimate of the critical yield stress, which separates the inactive gel compounds (α -dispersions) from the active fluid antifoams (β -dispersions). The gel compounds were easily recognized for their specific appearance. Also, whenever we were able to measure the viscosity of the gel compounds, we observed a gradual viscosity decrease upon shear in the viscometer. This temporal dependence of the compound viscosity is an indication for the destruction of the silica network in the gel, as a result of the mechanical stirring (see section 4.2 for additional explanations). In contrast, the fluid compounds behaved as typical Newtonian fluids: their viscosity did not depend on the shear rate and remained unchanged upon shear.

3.2.1. Compounds Prepared with Silica A200. In Figure 8, we plot the viscosity of compound A4CS and the respective antifoam durability in Triton solutions as

functions of the maturing time. During the first 3 days of maturing, the compound was a gel, and the torque on the viscometer spindle was too high to be measured by our instrument. A rapid decrease of compound viscosity, from about 40 000 cP down to 3000 cP, was measured between the fourth and seventh days of maturing, and the viscosity remained virtually constant afterward. The observed viscosity decrease reflected the transformation of the compound from a gel (α -dispersion) into a fluid (β -dispersion) and coincided with the onset of the antifoam activity. Note, however, that there is no correlation between the observed significant decrease of the antifoam efficiency after the maxima in Figure 1A and the compound viscosity (the latter remained almost unchanged during this period).

The shear stress which was needed for starting a rotation of the viscometer spindle in compound A4CS in the period of its transition from gel to fluid (and from inactive to active antifoam, respectively; see Figure 8) was around 20 Pa. This value can be interpreted as a critical yield stress, $\tau_{CR} \approx 20$ Pa, above which the compound behaves as an inactive gel.

Compounds A4CN and A4HN were gels during the entire period of observation of 2 weeks, and we were unable to measure their viscosity, which was above 50 000 cP. These results are in agreement with the poor antifoam activity of these two compounds, Figure 4. In contrast, compound A4HS was fluid immediately after its preparation; its viscosity was 2400 cP and remained constant during the subsequent period of observation. Note that the observed significant reduction of the antifoam efficiency of A4HS in AOT and Triton solutions at long maturing times (Figure 5) cannot be explained by variations of the compound rheological properties.

The temporal changes in the viscosity of compounds A2CS, A4CS, and A7CS were very similar (for clarity, only the result for A4CS is shown in Figure 8). The only difference between these compounds was that their viscosity increased with the silica concentration; this trend is illustrated in the inset of Figure 8.

3.2.2. Compounds Prepared with Silica R974. The rheological properties of compounds prepared with R974 particles at room temperature were somewhat different from those of their analogues prepared with A200 particles. No gel was formed when R974 was mixed with silicone oil at room temperature; compounds R4CN and R4CS were fluid immediately after their preparation with a viscosity of about 2600 cP. Furthermore, the viscosity of the nonstirred compound R4CN increased with the maturing time and reached the value of 5600 cP at the ninth day of shelf storage. In contrast, the viscosity of the everyday-stirred compound R4CS slightly decreased with time to about 2200 cP after 40 days of storage. Note that no correlation between these variations in the viscosity of compounds R4CN and R4CS and their antifoam efficiency is observed, cf. Figure 7.

The heated and nonstirred compound R4HN had a gel-like appearance, and its viscosity was above the range of the used viscometer. As expected, compound R4HS (heated and stirred by Ultra-Turrax) was fluid. Its viscosity slightly increased with time (from 1900 to 2300 cP after 30 days), which is due to the fact that this compound was not stirred during shelf-storage.

One can conclude from the above results that except for the gel–fluid transition, the variations in the compound viscosity are relatively small and do not correlate with the antifoam efficiency. In addition, clear trends are observed for increase of the viscosity when the compounds

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are stored without mechanical agitation, whereas the viscosity decreases upon stirring.

3.2.3. Microscope Observations. Microscope observations showed that all compounds (except those stirred by Ultra-Turrax) contained many big agglomerates of size up to 50 μm . A slow decrease of the agglomerate size was observed in compounds A4CS and R4CS with time, as a result of the mild (but prolonged) every-day stirring. Much smaller (less than 10 μm in diameter) agglomerates were observed in compounds A4HS and R4HS which were stirred by Ultra-Turrax. In general, we did not find a correlation between the size and concentration of the large agglomerates and the rheological properties of the compounds. This observation implies that the gel formation is due primarily to the formation of a rigid three-dimensional (3D) network from micrometer and submicrometer silica particles (invisible in the optical microscope), dispersed in the silicone oil. Such structure formation and the respective rheological properties have been studied in the literature,^{20,32} in relation to the silica application as a filler in synthetic rubbers.

3.3. Oil Spreading. A series of ellipsometrical measurements was performed to see the changes in the spreading behavior of compound A4CS in the course of its maturing. The thickness of the spread oil layer on the surface of AOT, APG, and Triton solutions was measured as explained in section 2.2.5.

The results from all experiments showed that two regimes of spreading could be clearly distinguished: (1) spreading of oil from a gel and (2) spreading of a fluid compound:

When the compound had a gel-like appearance (up to 72 h of maturing), no oil layer was detected to spread when 1 μL of the compound was set in contact for several seconds with the solution surface. The sensitivity of the used ellipsometer is better than 0.2 nm, which means that if there was some spread oil layer, its thickness was below this value. If a larger amount of compound, 3–4 μL , was placed for a long period of time on the surface of AOT and Triton solutions, a thin layer of oil (0.5–2 nm) was observed slowly to spread on the surface. This layer was in equilibrium with the deposited compound lump, which had irregular shape. No oil spreading was detected at all from gel compounds on the surface of APG solutions.

On the contrary, after 100 h of maturing, when the compound was transformed into a fluid state, a rapid spreading was observed on the surface of all three surfactant solutions. Even when 1 μL of compound was placed in contact with the solution surface for several seconds, a significant amount of the compound was observed to spread: for AOT, a layer with an effective thickness $d_{\text{EFF}} > 20$ nm was detected; for Triton, a thin layer with $d_{\text{EFF}} \approx 2$ –3 nm in equilibrium with large lenses of compound was observed; for APG, a thick layer with $d_{\text{EFF}} \approx 100$ nm was formed. The same spreading behavior was observed when pure silicone oil was used instead of compound.

These observations clearly show that the silica network in the gel compounds retains the silicone oil from spreading. If the silica network remains stable when the compound is placed on the solution surface, the impregnating oil is retained, most probably kept by capillary forces. However, once the silica network is disrupted and the compound becomes fluid, its spreading behavior becomes very similar to that of pure silicone oil and the compound easily disperses in the form of small drops and lenses in the foaming solution.

3.4. Entry Barriers. Entering of the antifoam globules at the surfaces of the foam films is the first prerequisite

for a foam film rupture. A complete series of measurements of the critical pressure to globule entry, P_{C}^{CR} , was performed by the FTT with compound A4CS during its maturing. The obtained results for AOT, APG, and Triton solutions are shown in Figure 9. Note that the results presented in Figure 9 were obtained with a newly prepared compound A4CS (different from the one in Figure 1A). The durability of the new compound A4CS (Figure 9) was measured in parallel with P_{C}^{CR} and coincided with the data for the former compound (Figure 1A) within the experimental error.

A very clear correlation between the antifoam durability and the value of the entry barrier is observed in all three surfactant solutions: the compound becomes active when P_{C}^{CR} decreases below the critical value of ca. 20 Pa; the maximum of the durability coincides with the minimum of the entry barrier; and a gradual slow increase of P_{C}^{CR} is detected in parallel with the slow decline of the antifoam durability in the course of compound maturing.

After 2700 h of maturing (not shown in Figure 9), P_{C}^{CR} exceeds more than 2 times the critical value of 20 Pa in APG and Triton solutions (48 Pa and above 50 Pa, respectively), and as a result, the compound is already inactive in these solutions, cf. Figure 1A. In AOT solutions, P_{C}^{CR} for the matured compound is still rather low, 4 Pa, and the compound has a significant durability, 50 cycles. A similar correlation between the entry barrier and the compound durability was observed for compound R4CS, as well; see Table 1 in ref 18. These results confirm the crucial role of the entry barrier for the efficiency of silicone-based antifoams.

4. Discussion

4.1. Importance of the Studied Factors for the Antifoam Efficiency. The presented results show that two of the studied factors are of crucial importance for the antifoam efficiency: the entry barrier and the yield stress of the compounds.

Whenever the critical pressure to entry P_{C}^{CR} is above ca. 20 Pa, the antifoam is inactive in the time scale of interest (up to 60 s). When the entry barrier is below this value, a clear correlation between the antifoam durability and P_{C}^{CR} is observed (Figure 9). This relation is particularly important for long times of maturing, where a significant reduction of the antifoam efficiency is observed (up to a complete suppression in APG and Triton solutions) due to the increase of P_{C}^{CR} as a result of particle overhydrophobization. As explained in ref 18, the overhydrophobization of the solid particles leads to their "encapsulation" in the oil globules, so that the synergistic effect between oil and silica is lost. The entry barrier is important also for short times of maturing, when the particles are insufficiently hydrophobized, so that their dewetting is not favored. For solid spheres, the requirements for dewetting and piercing predict that the optimal contact angle should be around

$$\cos \theta_0 \approx h_{\text{AS}}/R_{\text{p}} - 1 \quad (1)$$

where θ_0 is the three-phase contact angle particle–water–oil, h_{AS} is the thickness of the asymmetric oil–water–air film, and R_{p} is the particle radius (see Figure 3).

The other factor, the yield stress, is particularly important for compounds in which the particles are not sufficiently hydrophobized. If the yield stress is above a certain critical value, $\tau_{\text{CR}} \approx 20$ Pa (section 3.2.1), the compound introduced into the foaming solution behaves as a nondeformable lump which is unable to disperse and to break the foam. The antifoam efficiency of the gel

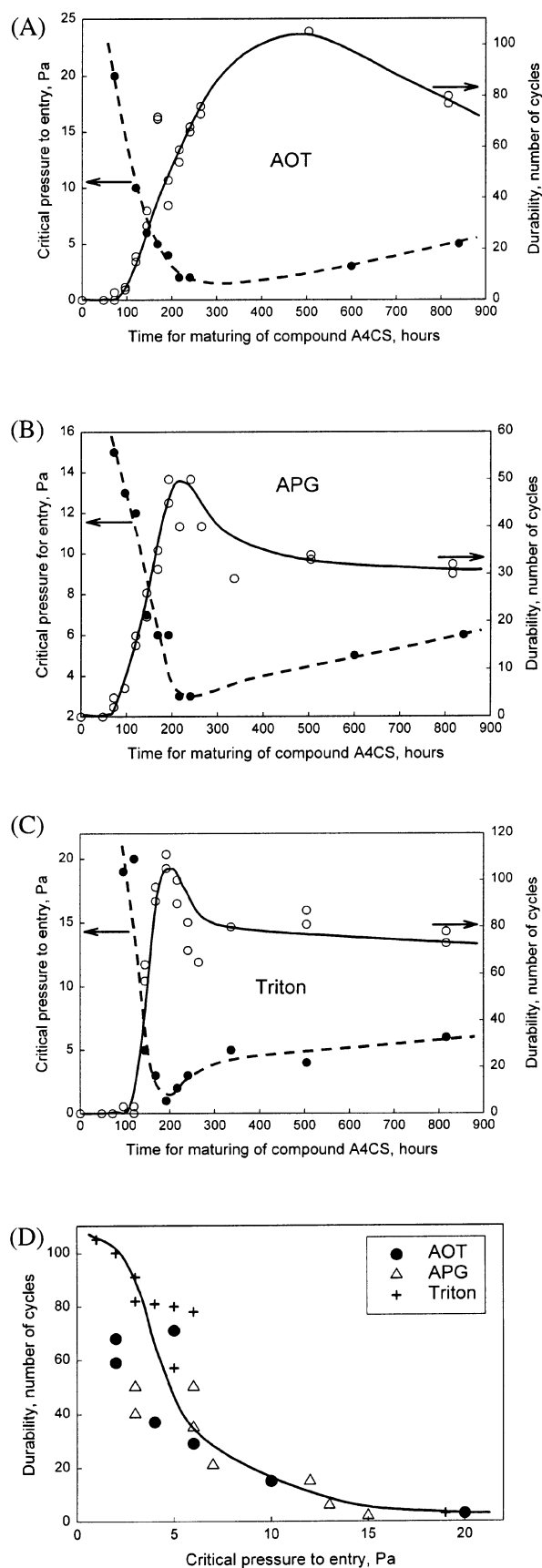


Figure 9. Critical pressure for globule entry, P_C^{CR} (full circles), and durability (empty circles) of compound A4CS, as functions of the time of compound maturing in (A) 10 mM AOT, (B) 0.6 mM APG, and (C) 1 mM Triton X-100 solutions. The dependence of the compound durability on P_C^{CR} is shown in (D) for the three studied surfactant solutions.

compounds is impeded for several reasons: First, the bridging–stretching mechanism, which was shown^{8,9,28} to be operative in these systems, requires a significant deformation and stretching of the antifoam globule for a foam film rupture to occur. Second, the gel compounds do not disperse in the foaming solution. Third, as evidenced by our ellipsometric measurements, the oil spreading from the gel compounds is strongly suppressed. Although the exact role of oil spreading in antifoaming is still a matter of discussion in the literature,^{5–9,11,17,33–35} various studies show that the spread oil could facilitate the foam film rupture by silica–silicone oil antifoams via several effects, for example, by reducing the barrier to entry of the antifoam globules^{8,17,35} and by supplying oil into the oil bridges, transforming them from stable to unstable ones.^{8,9}

The value of $\tau_{CR} \approx 20$ Pa is comparable to the capillary pressures, which act on the antifoam globules captured in foam films or deposited on the solution surface. For comparison, the capillary pressure of a foam bubble with a surface tension of about 25 mN/m and a radius of 2 mm (typical values for our systems) is 25 Pa. In other words, if the compound has large yield stress, the silica network in the compound remains more or less intact in the foam tests, because the capillary pressures are too weak to break it. Once the yield stress of the compound becomes lower than the critical value of about 20–25 Pa (due to increased silica hydrophobicity and/or to mechanical stirring), the compound is easily dispersed in the foaming solution and exhibits a pronounced antifoam efficiency.

4.2. Reasons for the Observed Differences between Compounds of Types A and R. There are several important differences between the compounds prepared with A200 and R974 particles: (1) The compounds prepared with A200 particles at room temperature are initially gels, whereas their analogues prepared with R974 particles are fluids. (2) Compound A4CS becomes active almost simultaneously in all of the studied surfactant solutions, whereas compound R4CS becomes active in the various solutions at different moments after its preparation; cf. parts A and B of Figure 1. (3) The efficiency of compound R4CS after a long time of maturing (2800 h) is noticeably higher in comparison with that of compound A4CS.

Observations 1 and 2 can be explained by analyzing the interactions between the silica particles in the silica–PDMS mixtures. At a molecular level, the gel formation is due to bridging of the silica particles by adsorbed PDMS molecules. The bridging can be effectuated by various types of bonds: for example, by chemical bonds between the terminal HO-groups of the PDMS molecules and the silanol groups on the silica surface and by physical adsorption of the backbone of the PDMS molecules (via hydrogen bonds with the surface silanol groups). An additional mechanism of particle adhesion could be the direct formation of chemical bonds between two silica particles in the points of their contact (by dehydration of neighboring silanol groups). Without stirring, all these bonds create a 3D network of linked solid particles. Upon stirring, the particle–particle contacts are disrupted and each particle becomes covered by its own adsorption layer of PDMS. As a result, the gel transforms into a fluid with negligible yield stress.

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The above picture explains why the process of gel formation is particularly pronounced for A200 particles: their surface is densely covered with reactive HO-groups. In the case of R974 particles, most of the silanol groups have been already blocked by dimethylsilyl groups, which were grafted onto the particle surface during the prehydrophobization of particles with dichlorodimethylsilane.²⁷ That is why no gels are formed when 4 wt % of R974 particles are mixed with oil at room temperature (observation 1). Observation 2 is explained by the fact that compound A4CS became active around the moment of its transformation from a gel into fluid (this moment obviously does not depend on the used surfactant). On the other hand, compound R974, being fluid from the very beginning, became active when the entry barrier fell below the critical value of ≈ 20 Pa (see Table 1 in ref 18).

Observation 3 can be explained by taking into account the results from ref 19 about the adsorption of PDMS on the surface of silica particles. It was found there¹⁹ that the amount of bound PDMS at the end of the adsorption process is much lower in the case of silica whose surface has been pretreated by grafting CH₃-groups (see Figures 5 and 7 in ref 19). Furthermore, our own contact angle measurements²³ with glass particles showed that the pretreatment of the glass surface with hexamethyldisilazane (which results in grafting of CH₃-groups) leads to lower particle hydrophobicity after a subsequent adsorption of PDMS, as compared to the hydrophobicity of particles that were hydrophilic before immersion in PDMS. All these results indicate that the particles in compound R4CS change their hydrophobicity in a narrower range (the initial particles are partially hydrophobized and the final hydrophobicity is lower) as compared to compound A4CS. This consideration explains why the final efficiency of compound A4CS is significantly lower (the silica is too hydrophobized) as compared to compound R4CS.

5. Conclusions

The antifoam performance of two series of compounds, comprising silicone oil and silica particles (hydrophilic silica A200 or prehydrophobized silica R974), is monitored in solutions of several surfactants and compared to the results from several model experiments. In parallel, a systematic study of how stirring and heating during preparation of the compounds affect their properties, and especially their antifoam efficiency, is performed. The main results can be summarized as follows:

The silica hydrophobization by silicone oil is a relatively slow process at room temperature, which requires days and weeks. Mechanical stirring and especially heating at 150 °C accelerate the hydrophobization process of the solid particles. However, the stirring has an additional im-

portant role: to prevent the formation of a developed 3D network of silica, which leads to gelling of the compound.

The heating without stirring leads to gelling of the compounds with both A200 and R974 particles. The gelled compounds have large yield stress and very poor antifoam activity. The respective antifoam globules behave as nondeformable entities in the surfactant solutions and are unable to destroy the foam. The gelled compounds do not disperse in the foaming solution, and the spreading of oil from them is strongly impeded. However, even a mild stirring is sufficient to transform these preheated gels into fluid compounds, which have high antifoam efficiency (unless the silica is overhydrophobized).

The mixing of PDMS oil and hydrophilic silica A200 at room temperature, under moderate stirring, produces a gel. After several days, during which the particles are hydrophobized in situ by adsorbed PDMS molecules, the gel transforms into a fluid compound with high antifoam activity. However, after a long period of shelf-storage at room temperature, the efficiency of these compounds is strongly reduced as a result of particle overhydrophobization.

The mixing of PDMS and prehydrophobized silica R974 at room temperature produces a fluid antifoam, which is active in some of the studied solutions (APG) and inactive in others (Triton, AOT); additional hydrophobization of the R974 particles by adsorption of PDMS is needed to activate the compound in the latter case. Again, the efficiency of the compound is reduced at long storage times but to a lesser extent in comparison with that of A200 particles.

A very good correlation between the antifoam durability and the height of the entry barriers, measured by FTT, was established for all systems, in which the compound was fluid (nongelled). Poor antifoam efficiency of compounds containing overhydrophobized silica was observed in APG and Triton solutions, due to the high entry barriers in these systems. Therefore, the entry barrier is one of the main factors determining the antifoam durability of the silicone-silica compounds.

The results from the present study confirm and complement the results from our previous study, ref 18.

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