RESEARCH PAPER

Effects of Hydrophobic Silica on the Performance of Silicone-Based Antifoams

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Abstract

The efficiency of an antifoam consists of polydimethylsiloxane oil, hydrophobe silica particles, and either Sodium Dodecyl Sulfate (SDS) as an anionic surfactant, or Octyl phenyl deca ethylene oxide (Triton X-100) as nonionic surfactant for use in aqueous system is investigated. The performance of different combinations of oil, silica particles, and surfactant in control of foam height was determined using Bickerman Shaking test. The effect of surfactant in reducing the surface tension was determined using Wilhelmy test. The sizes of dispersed oil droplets and silica particles were determined using both optical and electronic microscopy. It was found that increasing the silica content of the antifoam mixture and using sharp-edged particles increase the performance of antifoam and decrease the foam disappearance time. This Observation was the same for both cases of using anionic and nonionic surfactants. It was also found that, as the inert gas purging rate increases, the time of deactivation decreases to less than a minute; a favorable performance for good quality antifoam.

Introduction

Excessive foaming may cause serious problems in many industrial processes and this is the reason some additives as antifoams or defoamer are widely used to reduce the volume of undesired foam in different processes such as pulp and paper production, food industries, textile, fermentation, wastewater treatment, and more importantly oil industries. A typical antifoam or defoamer compound consists of oil and hydrophobic solid particles, or a mixture of both [1-3]. The nonpolar oils such as mineral and silicone oils, and polar oils such as fatty alcohols and acids, alkyl amines, alkyl amides, tributyl phosphate, tioethers, and many others, have been successfully used [4,5]. The solid particles may be inorganic materials such as silica, aluminum oxide, titanium dioxide, or organic materials such as wax or magnesium stearate, or polymeric materials such as polyamide or polypropylene [6]. It was found that mixtures of oil and hydrophobic solid particles have much higher antifoam efficiency compare with each individual components; oil or solid particles; separately used [8]. The hydrophobic solid silica particles and oil as antifoams show different performances in the deforming processes. At first, the oil droplets spread on the surface of the foam film and construct oil lens which is the most important factor in decreasing the surface tension. Then the oil droplets form a bridge on the foam film and finally the film became thin and torn by the stretching the bridge mechanism [9]. The mixed antifoams (oil-silica), due to the presence of hydrophobic silica, rupture the film by

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the dewetting mechanism [10-13]. Some observations show that the entrance of oil droplets to the surface of the film is not spontaneous but is an overcoming repulsive process between the film surface and the oil droplet. In the absence of hydrophobic solid silica, the oil droplets are too weak to enter to the surface of the film. Thinning the film as a result of oil droplets entrance in the absence of the solid silica, deactivates the antifoam performance in a long time period which known as slow antifoam [14-16]. It should be noted that the size, shape, and the contact angle of the solid particles are the most important factors in the activity of the antifoam [17, 18]. Experimental and theoretical studies show that the critical contact angle measurements in the dewetting mechanism is ninety degree according to the shape of solid particles as circle, disc, oval and round. The foam film raptures when the contact angle between the particle and air-water interface becomes larger than ninety degree. In contrast, when the particles are less hydrophobic (contact angle less than 90 degrees), the foam film is stabilized by the blocked adjacent plateau channel [19].

In this work, the role of hydrophobic silica particles in a mixed silica-polydimethylsiloxane oil system and the efficiency of different concentrations of silica are studied. The shape and size of silica particles as important factors in the performances of the antifoam are investigated by using shaking test and surface tension measurement. The effects of two types of silica in the nano and micron size on the rate of destruction of foam film are also studied in the presence of anionic and nonionic surfactants.

Experimental

Material

Two surfactants, anionic type Sodium Dodecyl Sulphate (SDS), and nonionic type Octylphenol Decaethylene Glycol ether (Triton X-100) analytical grate used as received. Polydimethylsiloxsane (PDMS) of viscosity 500cp provided by the Farm Pars, a local company. Hydrophobic silica R974 with average 50m size and fume silica used as micro-and nanosize silica fillers respectively.

Characterization

Scanning Electron Microscopy (SEM), model Vega II from Tescan, used to study morphology and determine the silica particle size. Light microscopy model Olympucx21 and Canon Power shot, SX40HS, used to determine the droplet and oil sizes and measure surface tension.

Method and Apparatus

Foam-rise Method also, Called Bikerman Test or Bubbling Method

The method and apparatus are used to study the antifoam effectiveness by bubbling through antifoam solution. The test is called foam-rise or Bikerman method. The schematic is shown in Fig. 1. The system consists of a glass tube with a high L/D ratio of about 10 equipped with a glass sintered separator. A continuous stream of dry nitrogen gas flow through the separator and produces a uniform flow of gas bubble with the very monodisperse distribution of bubble size. In each experiment 100mL of a 2-5% aqueous solution of each surfactant was placed in the glass tube, and a flow of 1 ml/sec nitrogen gas is a conductor through separator for 10 sec. After stopping the gas stream, the foam height was measured as V_F (t) concerning time which is a measure of antifoam activity.
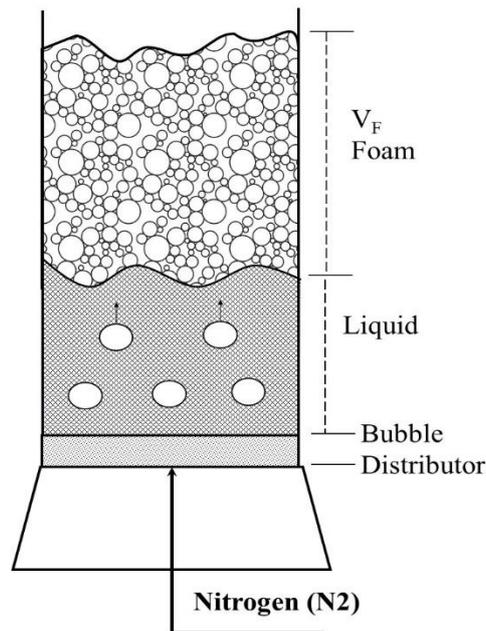
Fig. 1. Foam rise (bubbling) by the Bickerman method

Results and discussion

Effect of Ionic and Nonionic Surfactant on the Stability of Foam

The decrease in the foam stability of the ionic and nonionic surfactant compared using a solution containing 0.02 gr surfactant without antifoam. Fig. 2 shows the decrease in the height of foam for two surfactant solutions to time using the standard and similar shaking method for both solutions, while the initial height of the formed foam layer is 6.8 cm and 3.7 cm for ionic (SDS) and nonionic(Triton X-100) respectively.
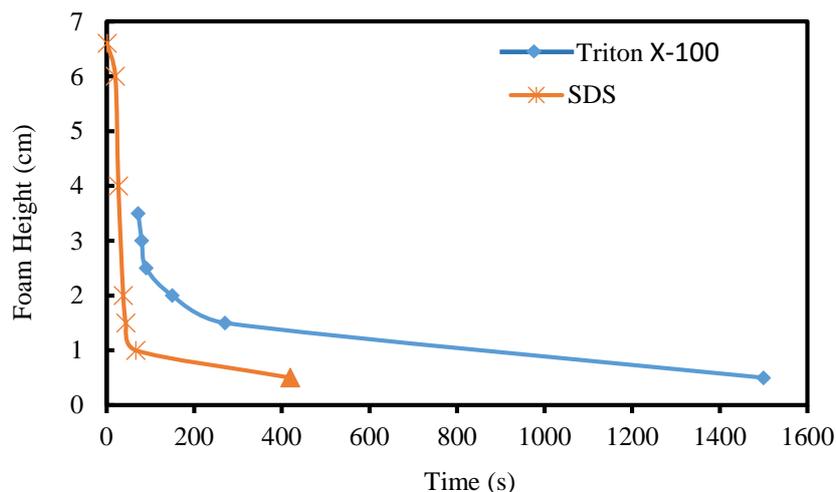

Fig. 2. Foam height with time for both surfactants. Triton X-100 (3.7 cm) SDS, (6.8 cm)

The optical observations show that the foam films stabilized by nonionic or anionic surface-active agents rupture through the stretching-bridge mechanism. Thus, there was no difference in the mechanisms of these surfactants and FTT has confirmed its results that the entry barrier

for nonionic surfactant is much higher that of ionic, namely 125 Pa compere with 3Pa respectively [20]. It should be noted that the FTT characterizes the entry barrier at fully saturated surfactant adsorption layers due to the relatively long duration of the experiment [21]. The FTT results also show that the antifoam globules are unable to enter the surfaces of Triton X-100 stabilized foam films. The globule entry and the foam film rupture are possible if the film surfaces are depleted from surfactant during foaming. In contrast, due to the low entry barrier of ionic surfactant even when the surfactant adsorption layers are fully saturated, the globule entry and subsequent film rupture are probable. Thus the foam destruction time for the nonionic surfactant (Triton X-100) is higher than the time for foam destruction of the ionic surfactant (Fig. 2).

Synergistic Effect of Oil and Silica

The synergistic effect of silicon oil and silica particle in the presence of anionic surfactant is investigated. Fig. 3 shows antifoam performance as height decrease concerning the time when foam generated from an as aqueous solution of anionic surfactant for the different component as, silicon oil a combination of silicone oil and hydrophobic silica particles R794, and fumed silica.
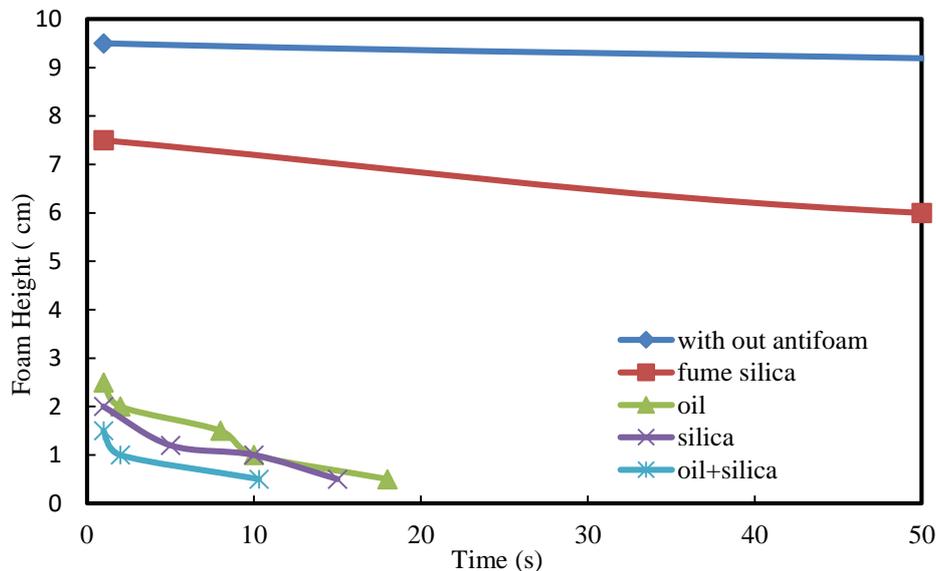

Fig. 3. Foam volume (V_F) versus time (t) for antifoams by Bikerman test from a solution of the anionic surfactant Triton X-100 in the absence of antifoam and the presence of 0.1 gr of four different antifoams (a) fume silica (b) oil silicon (c) silica R794 (d) compound of silicone oil +hydrophobized silica particles

The activity of antifoams characterizes their ability to prevent foam generation during agitation and rapid destruction of preformed generated foams. Thus the higher antifoam activity means less generated foam and faster foam destruction. Antifoam exhaustion or deactivation is a process in which the antifoam loses its activity in the course of foam destruction. The durability of antifoam characterizes its ability to destroy a larger total amount of foam before exhaustion [22]. The synergistic effects of the antifoam mixture are represented in Fig. 3. As shown the synergistic effect of silicon oil and silica combination is much higher than the individual components as fumed silica, silica particles, and silicon oil. This means that a combination of silica particles and silicone oil causes a faster reduction in foam height and foam down time. In the absence of silicone oil, the silica particles absorb the ionic surfactant from the solution, lose their hydrophobicity behavior and become more hydrophilic, which leads to decrees in the antifoam activity. According to Fig. 3, the antifoam activity of silica alone is

more than that of silicone oil without using silica particles. The foam destruction mechanisms by oil droplets and solid particles are comparable due to dispersion of oil droplets and deformation of oil Bridge. In most cases, the oil droplets destroy the initial accumulation of foams in plateaus and nodes. This is due to the high entry barrier of surfactant solution. When the entry barriers are low, the oil droplet acts as fast antifoam and may break film by the stretching-bridge mechanism. One way to reduce the entry barrier and convert the oil drops to a fast antifoam is the adding of the hydrophobic solid particles. The adsorption of added hydrophobic silica particles on the silicon oil droplet surfaces increases the adsorption of surfactant, decreases the surface elasticity and the entry barrier. This increases the rate of diffusion to the foam film, decreases the surface tension, (Table 1), and consequently increases the activity of antifoam compared with when silicone oil or silica is solely used.

Table 1. Reduction in the surface tension in the antifoam with and without distribution of the antifoam oil, silica and   mixed oil (R974) / silica

Surface tension (mN/m)		
Oil-silica	Silicon oil	silica
14	20	22.6

The position of hydrophobic silica particles in the oil droplets plays an important role in the antifoam performance. Fig. 4 shows a confocal microscopic image of hydrophobic silica in deformation formed lens in the surfactant solution, where the dark regions show the silica particles. As it is clearly shown, most silica particles accumulate on the oil surface near a three-phase contact line. For foam breaking, the hydrophobic particles must migrate to the oil surface.
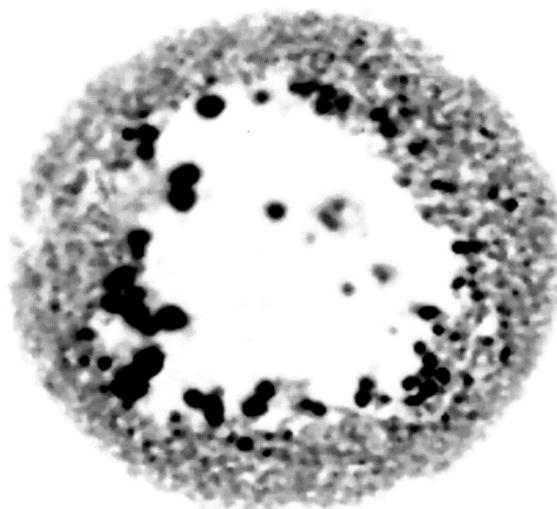

Fig. 4. View of antifoam lens sitting on surfactant solution (not visible). The dark objects are fluorescently labeled hydrophobic silica sitting on the aqueous-oil interface

Oil-silica Composition Effect

In a series of experiments, the effect of silica (R974) concentration and polydimethylsiloxane oil as major factors in a mixed oil-silica system were investigated. As it is shown in Fig. 5, the optimum concentration of silica to destabilize foam in the short time for SDS containing solution and Triton X-100 containing solution are 0.3 and 0.03 gr respectively (Figs. 5a and 5b) while the optimum oil concentration for both surfactants is 0.1 gr (Fig. 5c).
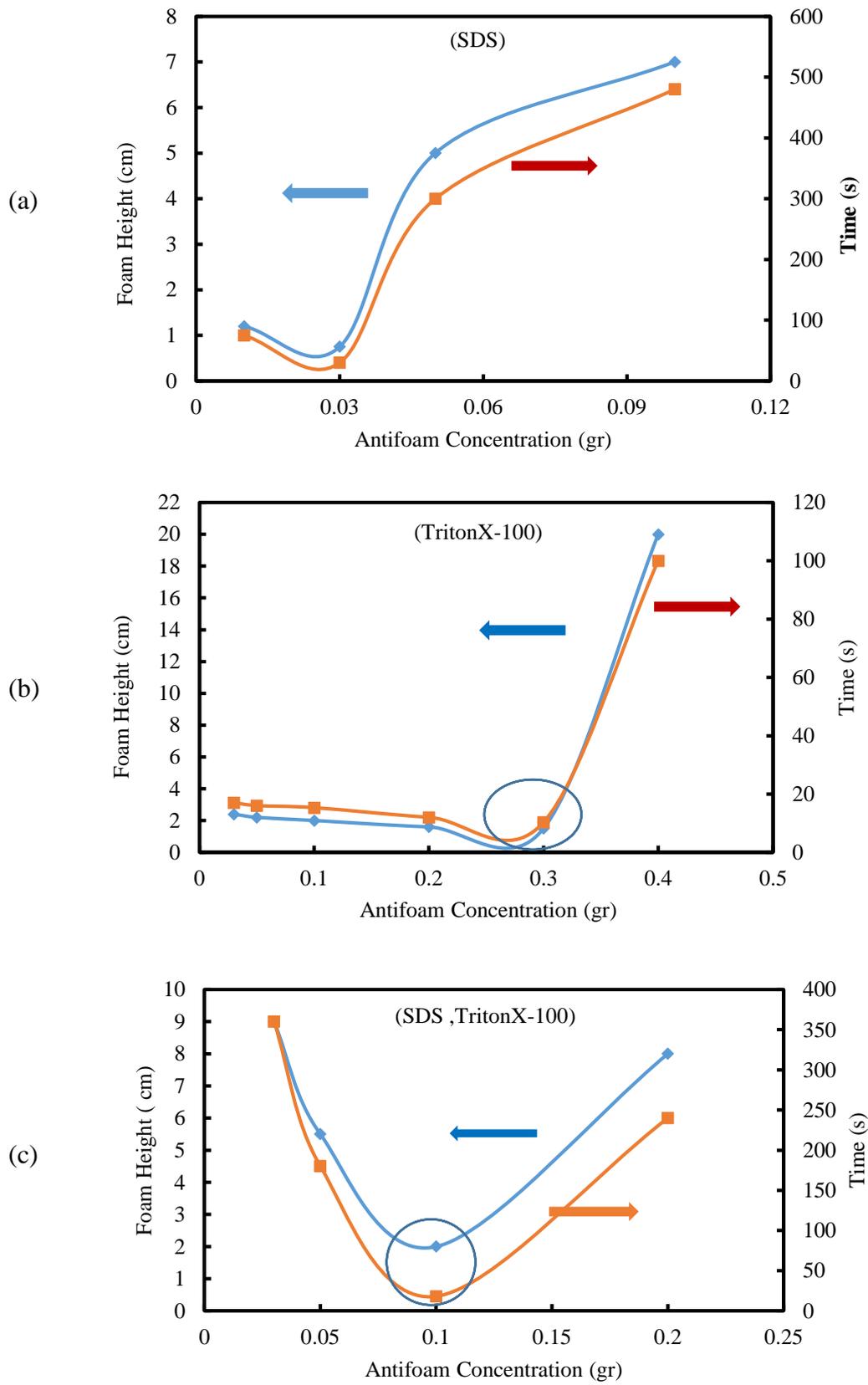
Fig. 5. The effect of different concentrations 0.01, 0.03, 0.05, 0.1 and 0.3g (a,b) 0.03,0.05,0.1,0.2,0.3 and 0.4 g oil viscosity, 500 cP (c) in both types surfactant solutions containing (0.02 g), anionic (SDS) and nonionic (Triton X-100)

The major role of polydimethylsiloxane is the ability to deform the oil globule, which is a critical requirement to rupture foam film by stretching-bridge mechanism. At concentrations higher or lower than the optimal values, the reduction or the increase due to the excessive distribution on the surface of the polymer foam film, the entry barrier increased and the entrance of oil to the foam film became difficult which reduces the effectiveness of antifoam. The increase or decrease deviation from optimum silica concentration leads to formation of a rigid three dimensional network and decrease the penetration depth respectively [23]. To measure the droplet size of polydimethylsiloxane oil and two types of silica particles, we used the optical microscope, Fig. 6, and the SEM, Fig. 7, respectively. As Fig. 6 is shown, the size of the oil droplet is about 10 microns which a suitable size for antifoam performance. The size of the oil droplet is an important factor in foam destruction. As the size of oil droplets decreases, the antifoam activity rapidly decreases. To have the oil droplet to the optimum size the concentration should be high and the polymer should be active. The remaining foam height after anti-foaming performance indicates that the size of the globule is higher than the size of the middle part of the plateau (less than 5 microns). The globules are trapped faster and destroyed. The film on less the entry barrier would be high or the concentration of droplet be too low. Considering the antifoam activity, the optimum globule size is adjusted by the thickness of the foam film. On the other hand, due to the deactivation of antifoam, the larger particles with more survival chances are more important [24-26]. According to Fig. 6 and our observations, the optimum globule size for high activity of most durable antifoams is about 5-30 micron.

Fig. 6. Optical microscopy image of antifoam oil (500cP) with 10Mm size

As previously mentioned, the size, shape, and hydrophobicity of the silica particles have significant effects on the performance of defoamers. The contact angle for completely dewetting solid particles (such as spherical, disk, circle, and ellipse) is 90 degrees. If a solid particle makes a contact angle with an oil-water interface of more than 90 degrees, the foam film is disrupted. The silica particles with 6-7 microns are large enough to touch the contact angle between film surfaces and the forming angle is greater than 90 degrees. As it is shown in Fig. 7a, the sharp edges of silica particles by induction of pin effect on the foam film and increasing the penetration depth increases the antifoam performance. But if the hydrophobicity of the silica particles is low or particles without suitable size and shape forms, make the contact angle less than 90 degrees, Fig. 7b. This type of silica has smooth edges and by blocking in the plateau, decreases the dewetting rate. The particles at first reduce the foaming, but after a long time cause thinning of the film and water drying due to the force of gravity and the pressure difference between both sides of the film curve, capillary forces. This trend continues until the film reaches a critical thickness. At the critical thickness, the foam film is flat and capillary

pressure is zero. At this point, the direction of curvature is reversed where produces balanced capillary forces to oppose the thinning of the film and stabilizes the foam film [27-32].
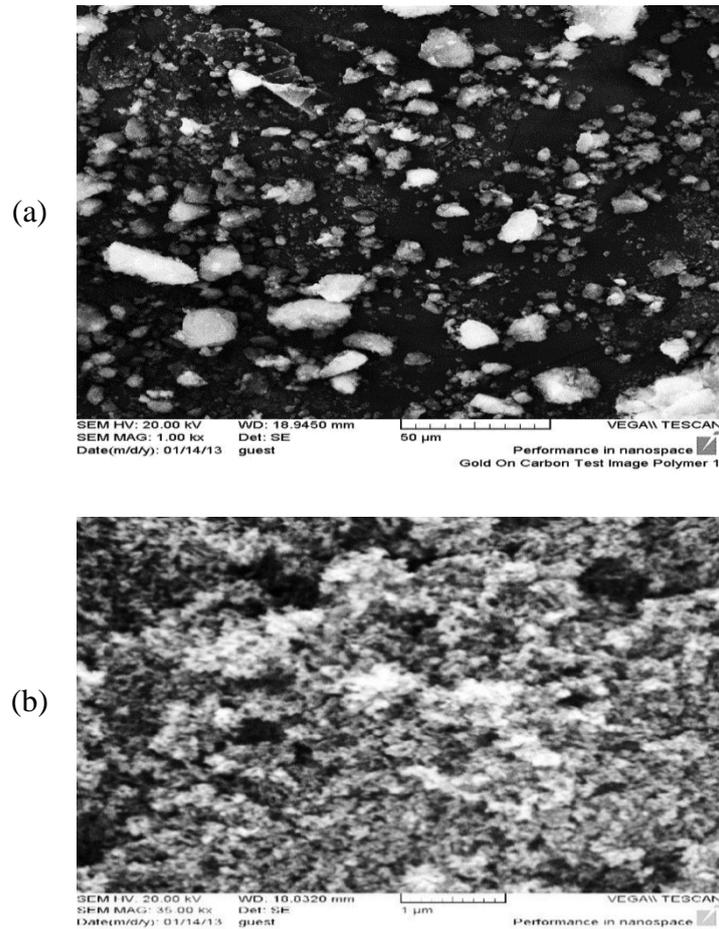

Fig. 7. SEM images of the two types of antifoams hydrophobic silica (a) silica R794 (b) fume silica

Exhaustion of Oil – Silica Antifoam

The exhaustion of antifoam or the deactivation time in the operation is a major property. Fig. 8 shows the exhaustion curve of antifoam power with respect to the increasing number of cycles of bubbling in antifoam solution of 0.1 gr polydimethylsiloxane 0.3 gr silica particles (R974) 0.02gr SDS.

As it is shown, the initial activity or the average defoaming time during the first few cycle is a very short time, i.e., 3 seconds. The foam destruction time increases very slowly up to 10 cycles. The rate of destruction increases with more slope from 50 to 80 cycles and finally, it increases exponentially after 80 cycles. It should be noted that the foam destruction for more than the 60s does not necessarily mean a complete inhibition of the antifoam activity [33] the foam formed in the glass jar disappears even after 100 shaking cycles. However, a much longer time is needed for the accomplishment of this process.
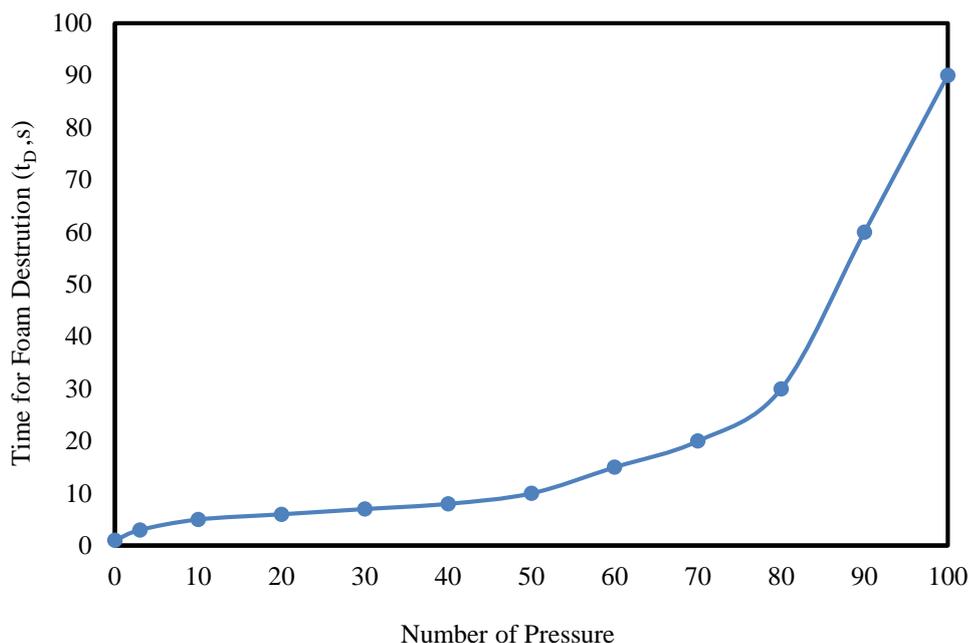
Fig. 8. Typical curve of exhaustion of antifoam in aqueous solution of 0.02 gr SDS

Conclusion

The effects of silicon oil, ionic and nonionic surfactants and two types of silica particles on the antifoam performance have been studied. The effectiveness and properties of the antifoam solutions have been determined using Bikerman test and microscopic observations.

The optimum amounts of hydrophobic silica (model R974) and fume silica in the polydimethyl siloxane oil with 500cP viscosity and particle size of (6-7 mm) are 0.03 and 0.3gr respectively.

The large-sized silica particles may easily touch the surface foam film and sharp edges make a contact angle of more than 90°. With the formation of the effect of the pin on the foam film and with increasing penetration depth, the surface tension of foam films decreases and the foam film breaks faster than oil and silica alone-based antifoams. The optimum size and concentration of polymer are 20 microns and 0.1gr respectively. The synergistic effect of oil and silica on the performance of the antifoam as decreasing the foam height and durability is impressive. With increasing the silica amount, the contact angle of more than 90 degrees formed, the foam height is reduced and more time is required for foam exhaustion and durability of antifoam.

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