MECHANISM OF DEACTIVATION (EXHAUSTION) OF MIXED OIL-SILICA ANTIFOAMS

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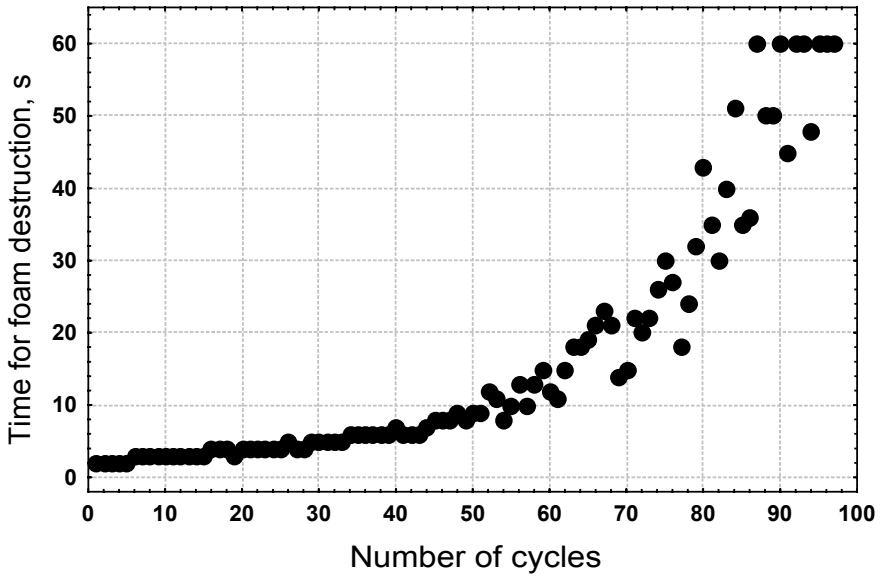
Deactivation (exhaustion) of antifoams - the gradual loss of their antifoam activity in the course of foam destruction.



10 μL Antifoam in 100 mL 10 mM AOT.

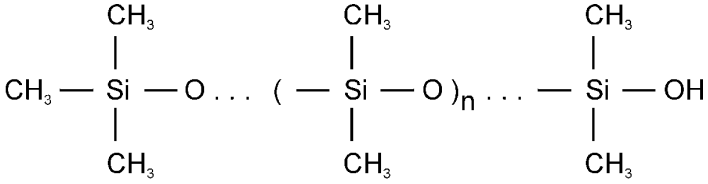
A cycle consists of 10 s shaking plus 60 s at rest.

Aims: To clarify the mechanism of exhaustion.

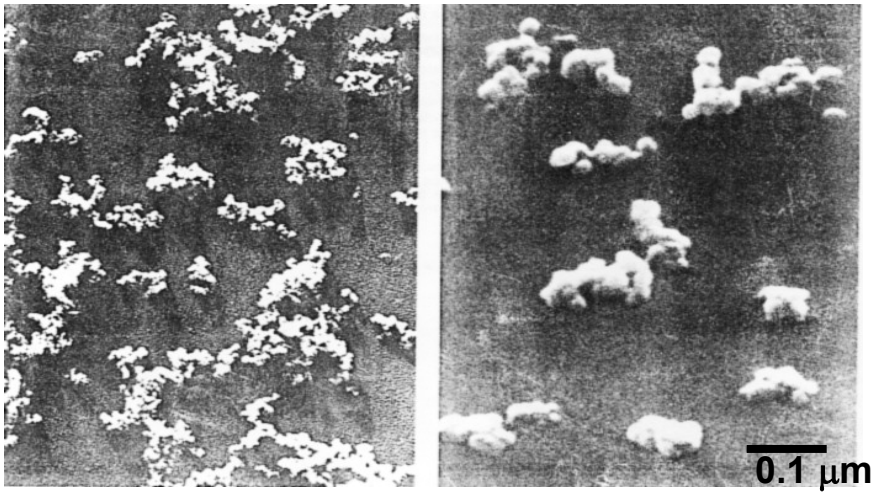
To quantify the antifoam durability (phenomenological model).

Mixed oil-silica antifoam consists of:

(1) Oil phase – silicone oil (PDMS):

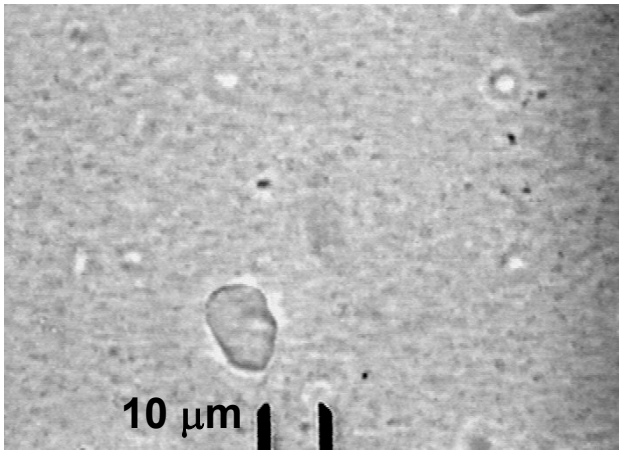


(2) Solid particles – SiO_2.

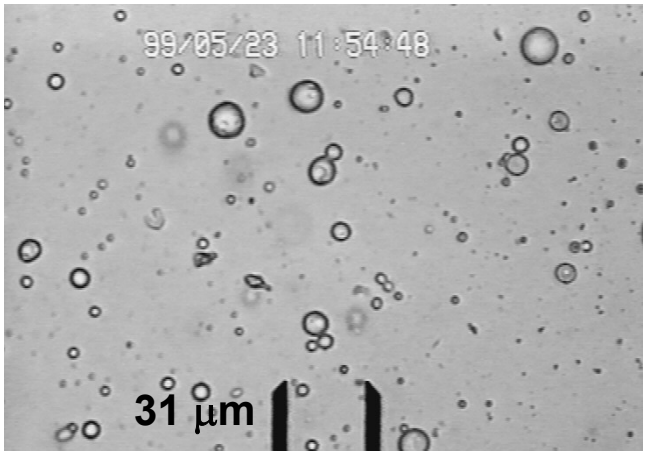


Silica aggregates before immersion in oil (electron microscopy, Degussa Technical Bulletin, 1988)

Antifoam **compound** - dispersion of SiO_2 partcles in PDMS**:**



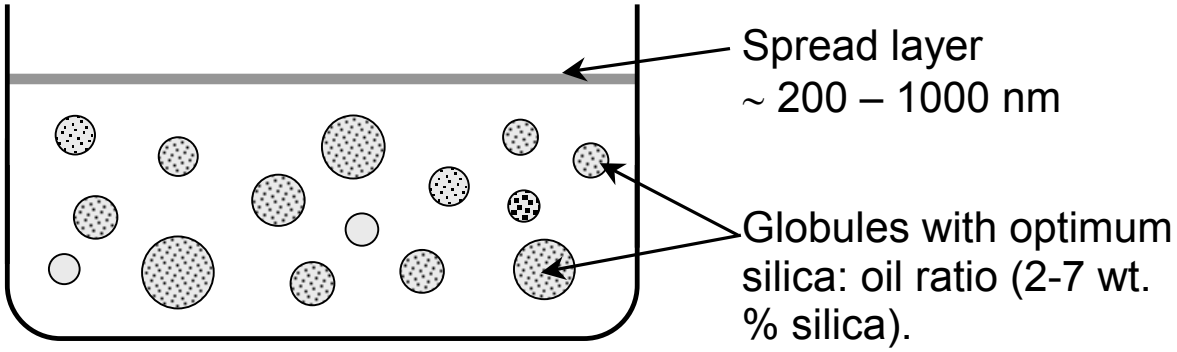
Antifoam **emulsion** - emulsified compound:



The mixed antifoam is much more effective than the oil or silica alone – synergistic effect.

Experimental procedure:

1. Antifoam (~ 100 ppm) is added to the surfactant solution:



2. Shaking, i.e. foaming followed by foam destruction.

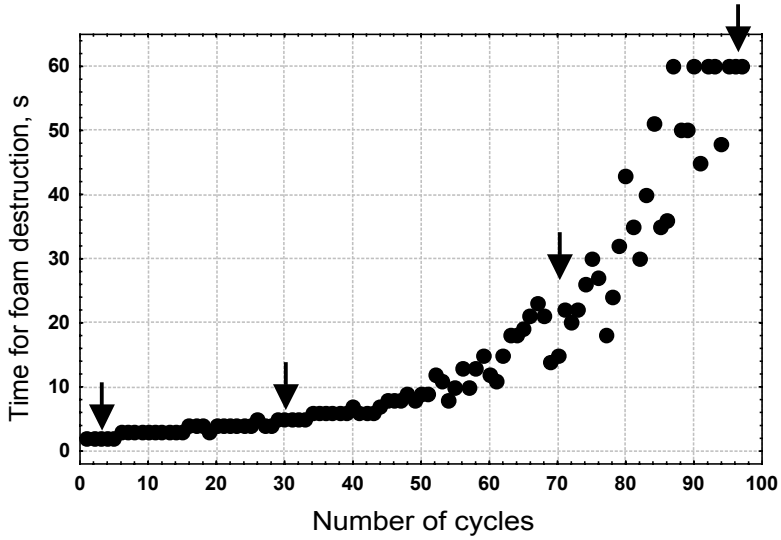
- **During the shaking the spread oil layer is either emulsified or spread over the surfaces of the formed air bubbles.**
- **After the foam destruction the oil in the bulk remain only as drops.**

We apply:

1. Ellipsometry – to follow the changes of the spread oil layer.

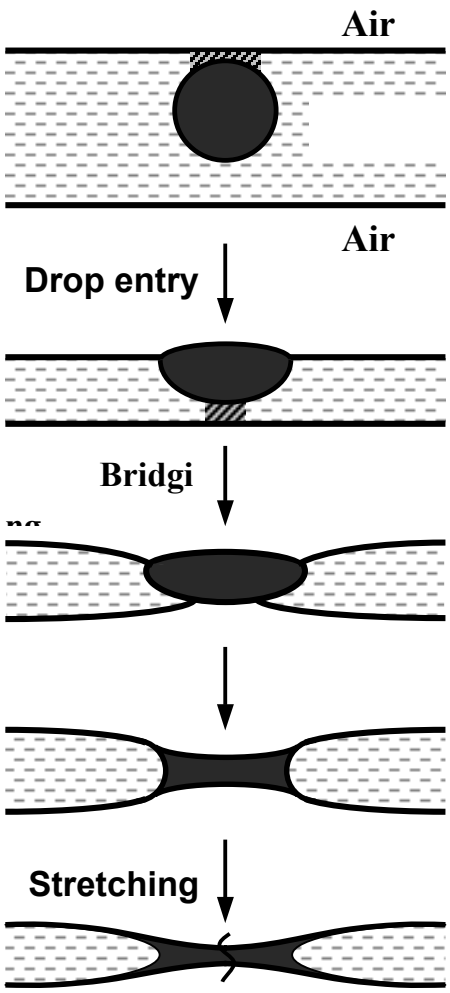
2. Film Trapping Technique (FTT) - to determine the entry barrier of the antifoam globules, to observe their size and deformability.

The samples are taken after the 3rd, 30th, 70th, 95th, and 300th shaking cycles:



Mechanism of action of silica-silicone antifoams: "Bridging-stretching" (Denkov et al., 1999)

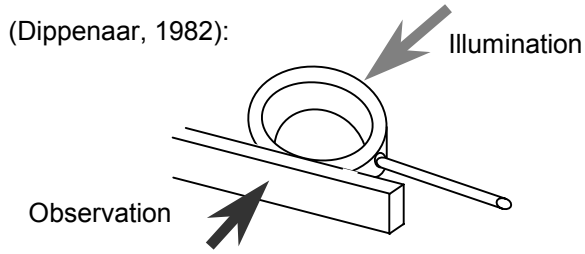
Schematic presentation:

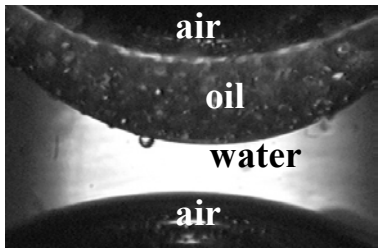


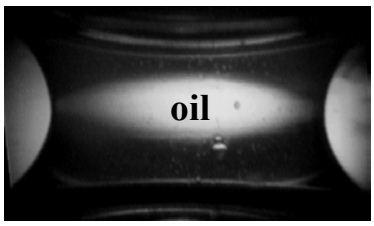
Film Rupture

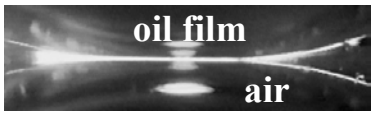
Films in the Dippenaar cell:

(Dippenaar, 1982):







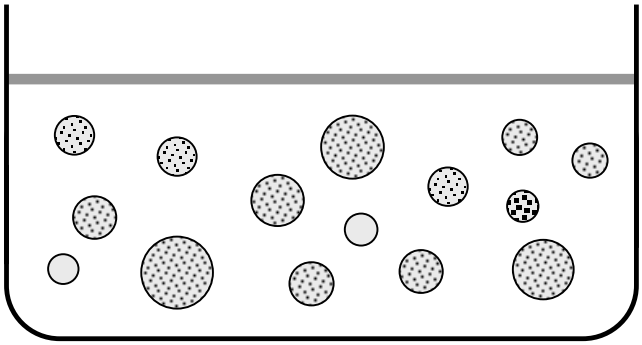


Main role of the solid particles - to destabilize the asymmetric film, thus facilitating the drop entry.

(Garrett 1993, Koczo et al. 1994, Bergeron et al. 1997, Hadjiiski et al. 2001)

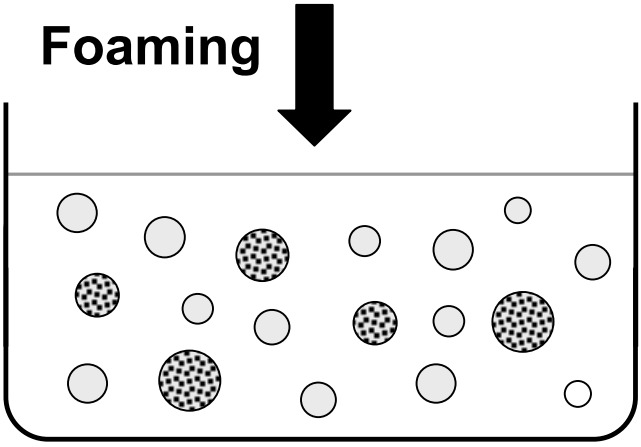
Scheme of the process of antifoam exhaustion

(Denkov et al. 2000)



Active Antifoam
Globules: Optimum Silica/Oil Ratio
Spread Oil Layer: Yes

Foaming



Exhausted Antifoam
Globules: Silica-rich and Silica-free (both inactive)
Spread Oil Layer: No

Questions:

1. Why are the silica-enriched and silica deprived globules inactive?

2. What is the relation of the exaustion to the disapearance of the spread oil layer?

3. Why are globules disproportioned in two types?

Answers by:

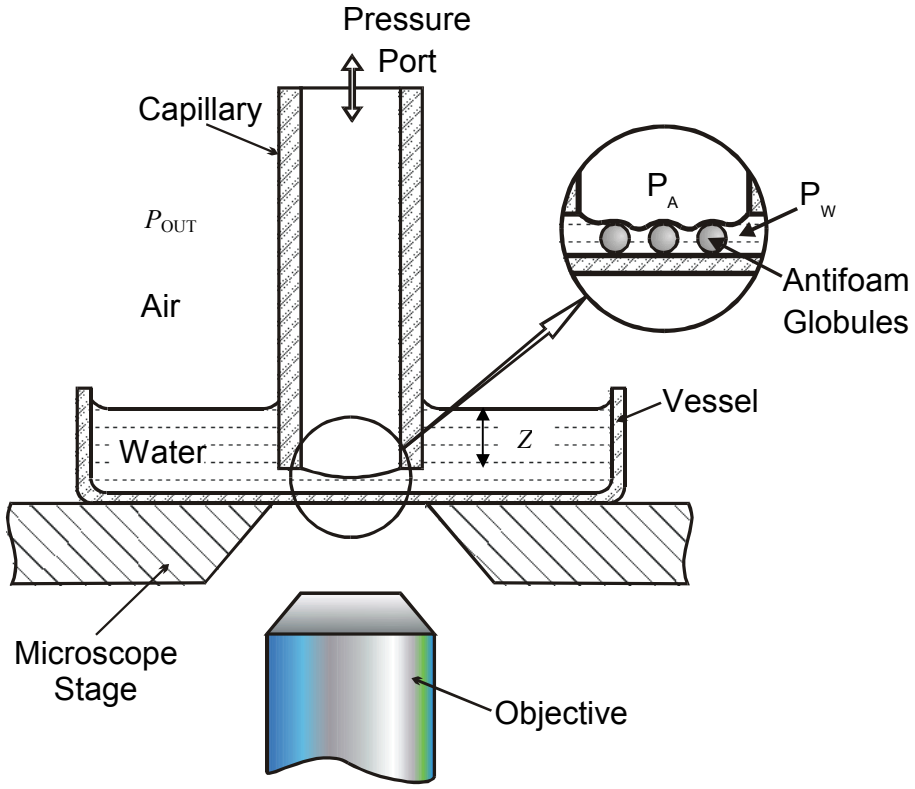
1. Film Trapping Technique.

2. Ellipsometry.

Film Trapping Technique

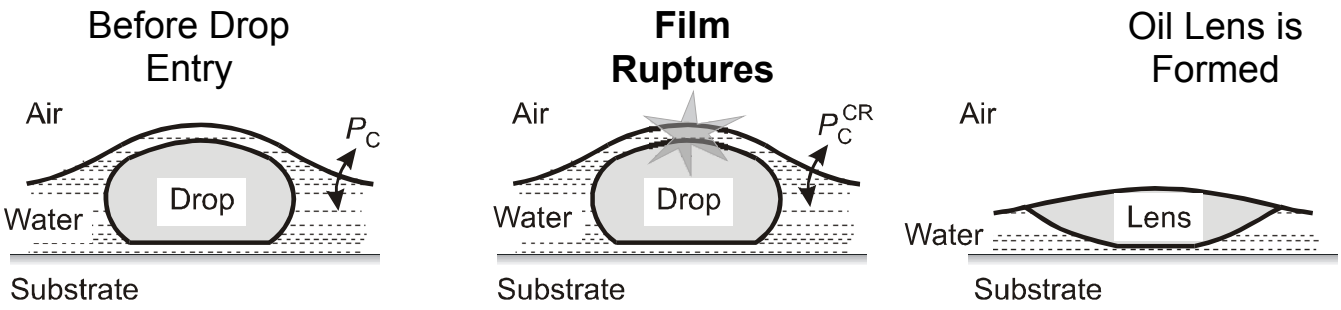
(Hadjiiskji et al. 1996, 2001, 2002)

Basic experimental method to evaluate the stability of the asymmetric thin films between the antifoam globules and the surfaces of the foam films.



Capillary pressure: $P_C^{CR} = P_{IN} - P_{OUT} - \rho g Z$

Process of Drop Entry



$P_C^{CR} = P_C$ **in the moment of rupture**

The size and deformability of antifoam globules is observed in transmitted light.

Experimental Results

Solutions (10 mM AOT) containing antifoam at different levels of exhaustion.

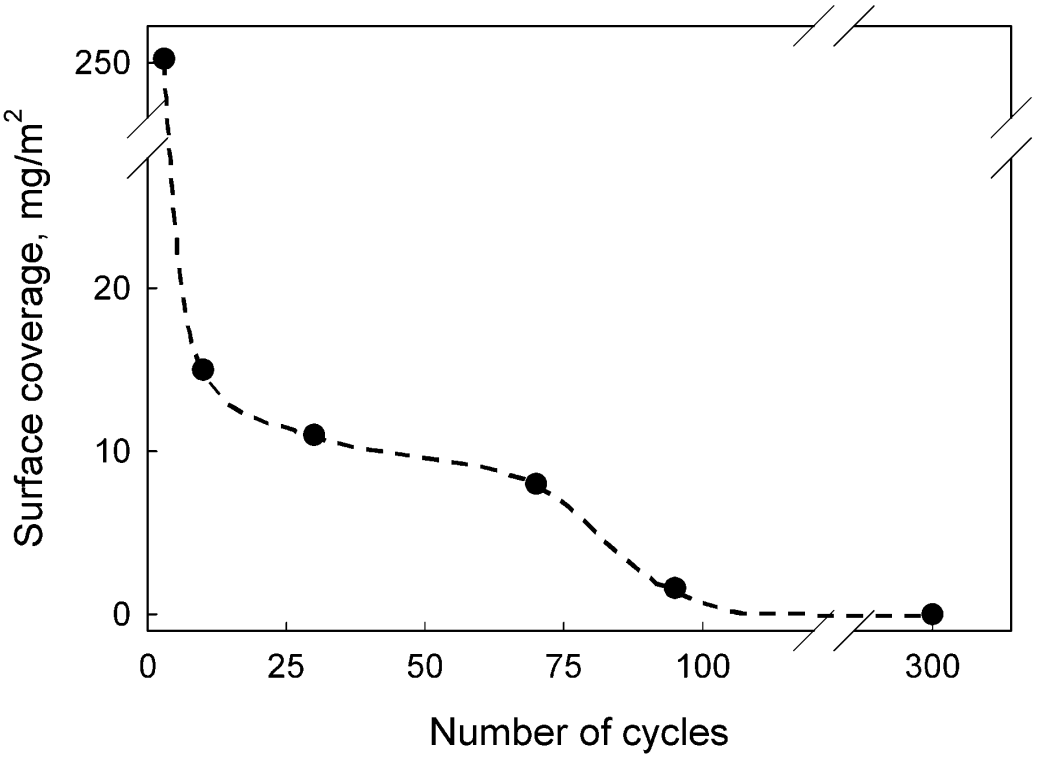
Number of cycles	**3**	**30**	**70**	**95**	**300**
Time for foam destruction, τ_D, s	2	4	22	> 60	> 600
P_C^{CR}, Pa	**3 ± 2**	**4 ± 2**	**9 ± 1**	**7 ± 2**	**18 ± 3**
Deformable globules, %	100	100	45	26	26
Diameter of the deformable globules, μm	6 ÷ 24	7 ÷ 25	6 ÷ 25	5 ÷ 12	3 ÷ 7
Spread oil, Γ, mg/m^2	250	11	8	2	< 0.5
Non-deformable lumps, %	**0**	**0**	**55**	**74**	**74**
Size of the non-deformable lunps, μm	-	-	6 ÷ 26	4 ÷ 50	5 ÷ 100

The fresh samples contained mainly deformable globules with low P_C^{CR}.

In the course of exhaustion:

- P_C^{CR} increased.
- The spread oil layer gradually disappeared.
- **The fraction of deformable globules decreased, at the expense of non-deformable lumps.**

Spread oil layer on the solution surface



- 99 % of the antifoam is emulsified after the 10th shaking cycle.
- The exhausted samples do not have spread layer of oil.

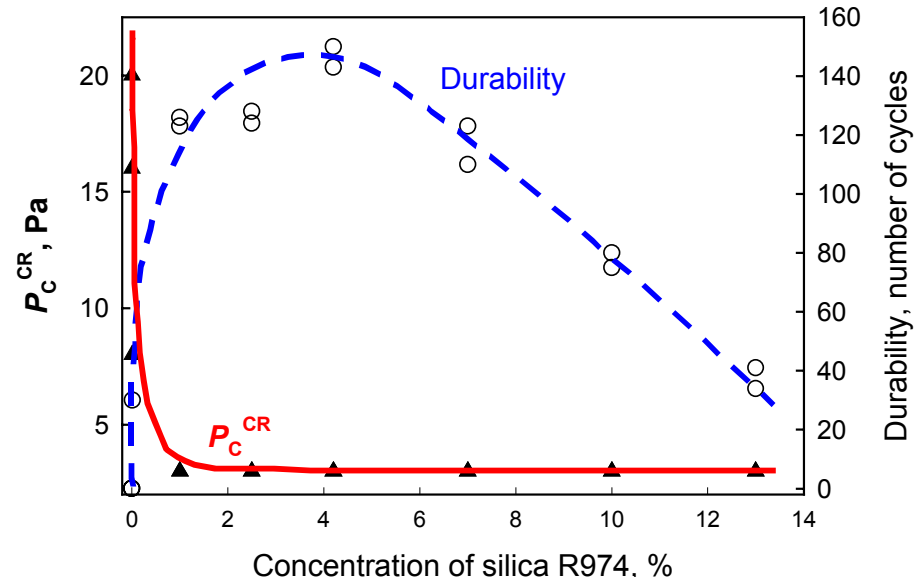
The spread oil on the solution surface decreases the critical pressure for antifoam globule entry (Denkov et al. 2002)

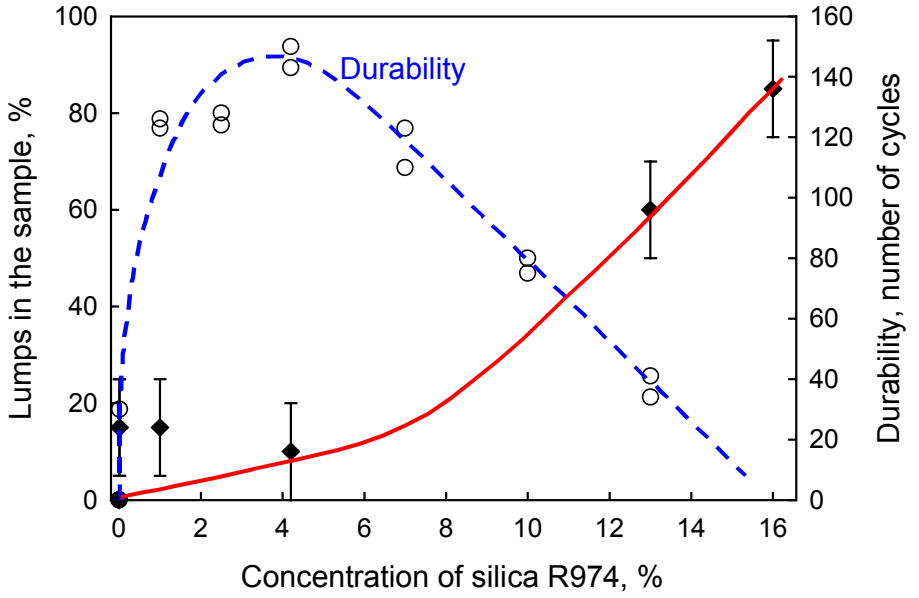
P_c^{CR} for several antifoams in solutions of 10 mM AOT:

Spread oil layer on the solution surfaces	*Antifoam*		
	PDMS	**AF Compound**	**AF Emulsion**
NO	**28 ± 1**	**8 ± 1**	**20 ± 5**
YES	**19 ± 2**	**3 ± 2**	**4 ± 1**

Role of the silica concentration, C_S

(silica-deprived and silica enriched globules in exhausted AF)

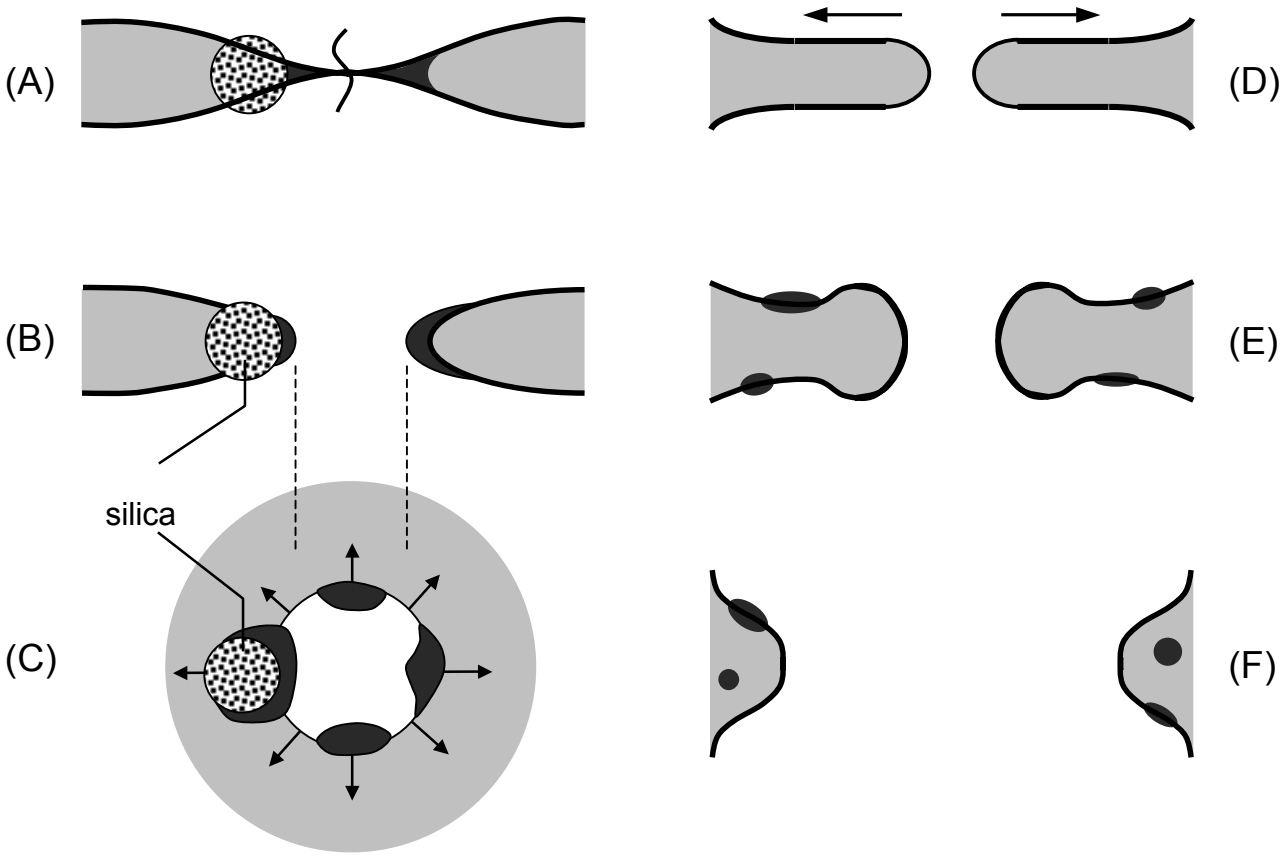




- **P_C^{CR} increases significantly when C_S decreases below 2 wt. %;**
- **The part of non-deformable lumps increases significantly when C_S > 7 wt. %.**

The compounds with very low (< 0.1 wt. %) or very high (> 7 wt. %) concentration of the solid particles represent the two types of globules appearing in the process of exhaustion: deformable with high P_C^{CR}, and non-deformable, which are unable to form unstable oil bridge in the foam films.

Possible mechanisms of antifoam fragmentation



(A) An oil bridge ruptures and forms a hole in the film.

(B) The hole rapidly expands and the ramained oil rim stretches and fragments into several smaller oil droplets

(C) Some of the droplets contain silica, while others are deprived of silica.

Part of the spread, ultra-thin oil layer can be also emulsified in the moment of foam film rupture:

(D) The hole in the film expands, which leads to:

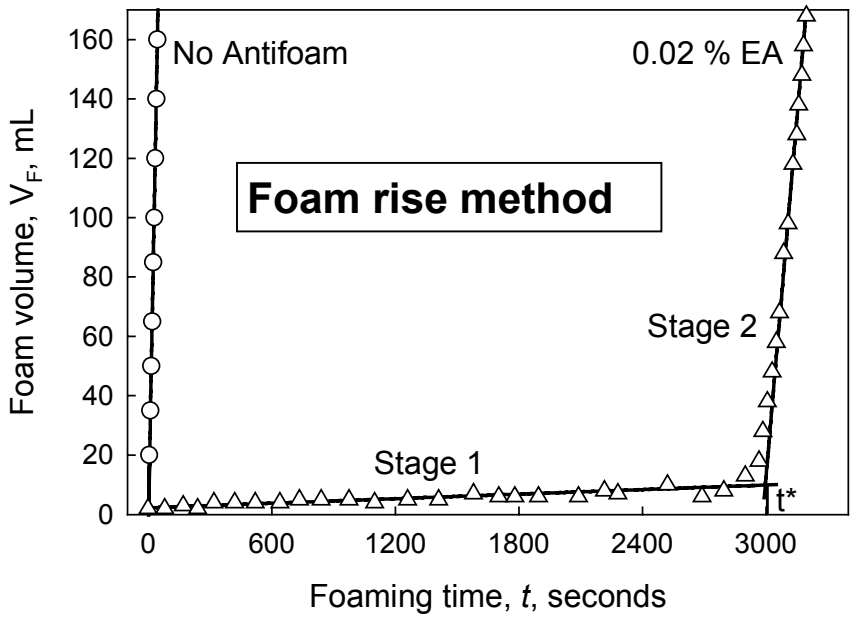
(E) a rapid contraction of film surfaces.

(F) The excess of spread oil forms oil lenses, which are dragged towards the GPB by the perimeter of the expanding hole. The impact of these lenses with the GPB could lead to oil emulsification.

Phenomenological model

(Denkov et al. 2002)

Typical results from the foam tests with 10 mM AOT solutions containing 0.02 wt % of antifoam emulsion:



Stage 1 - the decrease of AF activity is relatively slow.
Stage 2 - a sudden, almost complete loss of antifoam activity.

t* (***N****) - the moment of the break indicates the moment of antifoam exhaustion, i.e. the transition from Stage 1 to Stage 2.

Rate of bubble production, ν_B (number of bubbles per unit time):

$$\nu_B = \frac{1}{V_B}\frac{dV_F}{dt} = \frac{dN_B}{dt} \qquad [1]$$

dV_F/dt - foaming rate in the absence of antifoam.
V_B - mean volume occupied by one bubble in the foam column.

$$\frac{dC_B}{dt} = \nu_B - k_1 C_A C_B \qquad [2]$$

$$\frac{dC_A}{dt} = -k_2 C_A C_B \qquad [3]$$

C_A – concentration of antifoam globules.
C_B – bubble concentration.
k_1 - characterizes the antifoam activity.

Stage 1: the rate of bubble formation is equal to the rate of bubble destruction. $\Rightarrow$ steady-state approximation:

$$\frac{dC_B}{dt} \approx 0 \qquad \text{(Stage 1)} \qquad [4]$$

$$\Rightarrow \quad k_1 C_A C_B \approx \nu_B = \text{const.} \qquad \text{(Stage 1)} \qquad [4']$$

$$\frac{dC_A}{dt} = -\frac{k_2}{k_1}\nu_B = \text{const.} \qquad \text{(Stage 1)} \qquad [5]$$

$$C_A(t) \approx C_{A0} - k_3\, t \qquad \text{(Stage 1)} \qquad [6]$$

The solution:

$$C_B(t) \approx \frac{\nu_B}{k_1 C_A} \approx \frac{\nu_B}{k_1\left(C_{A0} - k_3 t\right)} = \frac{1}{\left(k_1/\nu_B\right)C_{A0} - k_2 t} \qquad \text{(Stage 1)} \qquad [7]$$

$$\text{where } k_3 \equiv \frac{k_2}{k_1}\nu_B \qquad [8]$$

Stage 2:

C_A^* - a critical concentration, below which the antifoam is unable to suppress efficiently the foam,
i.e. Eqs. 4 to 7 are not satisfied at $C_A < C_A^*$.

The parameters characterizing the antifoam performance:

$\boldsymbol{k_1}$ - characterizing the antifoam activity,

$\boldsymbol{k_2/k_1}$ and $\boldsymbol{C_A^*}$ - both characterizing the antifoam durability.

If $\boldsymbol{C_A^* << C_{A0}}$ - the antifoam durability might be characterized by:

$$\boxed{Dr = \frac{\nu_B\, t^*}{C_{A0}} = \frac{k_1}{k_2}}$$

Dr = number of bubbles destroyed by the antifoam for time t* before its exhaustion, normalized by the antifoam concentration.

It allows quantitative comparison of antifoams.

Conclusions

The quantitative characterization of the process of exhaustion of mixed PDMS-silica antifoam by several experimental methods has revealed that:

- The spread oil gradually disappears from the solution surface upon the exhaustion process.
- The critical pressure for antifoam globule drop entry increases with the number of shaking cycles and approaches the value for pure oil (without of silica).
- The above two processes are interrelated, because the presence of spread oil reduces the entry barrier for mixed silica-silicone oil antifoams.
- A gradual decrease of the number of deformable antifoam globules at the expense of non-deformable, enriched in silica lumps is observed along the exhaustion process.

A phenomenological model for description of the performance of mixed PDMS-silica antifoams is proposed.

- Foam test is characterised by the rate of bubble generation, ν_B.
- During the initial period, when the antifoam is very active (Stage 1), the rate of bubble coalescence is practically equal to the rate of bubble generation, ν_B (steady-state approximation).
- The antifoam properties are described by three parameters: k_1 characterises the initial antifoam activity; k_2/k_1 shows how rapidly the antifoam looses its activity in the course of foam destruction; and threshold concentration, C_A*, below which the antifoam is unable to suppress efficiently the generated foam.

The model is supported by the results from several preliminary experiments with two different foam tests.