

Fluorosilicone Antifoams

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Synopsis

Antifoam compositions for aqueous surfactants are usually emulsions of insoluble oils containing hydrophobic solids. The emulsion allows easy access to the aqueous environment. The oil droplets carry the solid particles to the foam interfaces by spreading, which also contributes to foam rupture. The particles provide a disruptive dewetting surface and may also adsorb the foam stabilizer. This theory requires both oil and solid to have lower surface tension than the foaming surfactant and explains the ineffectiveness of conventional silicone antifoams based on polydimethylsiloxane against silicone and fluorocarbon aqueous surfactants. Some fluorosilicones have lower surface tensions than polydimethylsiloxane and should produce more effective antifoams. To test this idea the liquid surface tensions of a series of fluorosilicone-containing copolymers were measured. These fluids were formulated into antifoam compounds and emulsions and tested against selected surfactants. Equilibrium and dynamic surface tensions of these test surfactants were also measured. The new antifoams are more effective than conventional silicones against silicone surfactants but are ineffective against fluorosurfactants. The implication of these results on the spreading/dewetting theory is discussed.

INTRODUCTION

Certain fluorosilicone materials are among the most surface active (low surface tension) substances known, see Table I for examples. This surface activity has led to a variety of surface applications including antifoams, lubricants, sealers, and release agents. Pierce⁶ has reviewed the properties and commercial uses of fluorosilicones. The most common commercially available fluorosilicone is poly(3,3,3-trifluoropropylmethylsiloxane) (PTFPMS). Unfortunately it has an insufficient aliphatic fluorocarbon content to be one of the more surface active fluorosilicones. This is particularly so in the liquid state where PTFPMS has a higher surface tension than the more familiar and cheaper polydimethylsiloxane (PDMS).⁷

Our aim was the development of economic silicone antifoams in systems where conventional PDMS could not be used. The best known such application is the defoaming of organic liquids such as crude oil, lubricating oils, hydrocarbon fuels, solvents, etc., where PDMS is too soluble to be effective. Pierce⁶ gives an example of the prevention of foaming in dry cleaning machines. Our interest was the antifoaming of aqueous systems. Highly active surfactants, notably those with silicone and fluorocarbon hydrophobes, cannot be effectively treated with conventional PDMS antifoams. This is because although they have one of the basic prerequisites for antifoam behavior, insolubility, they lack the other, a lower surface tension than the foaming medium. The key to successful aqueous antifoaming is a carrier polymer of lower surface tension than the foaming surfactant that will enter and spread at the foam film surfaces together with a

dispersed hydrophobic solid whose role is still debated but could provide a dewetting surface from which the foam film would retract or might be a site for surfactant removal by adsorption.⁸

Lower surface tension antifoam fluids can be attained by increasing the perfluorocarbon content of the pendent side chains in the fluorosilicone polymer. It is also important to retain the $-\text{CH}_2\text{CH}_2-$ link between the fluorocarbon portion and the silicon atom to preserve adequate hydrolytic stability.⁹ This was done in the form of fluorosilicone-dimethylsiloxane copolymers for economic reasons. These same fluids were used to treat silica particles *in situ* to produce the dispersed hydrophobic solid. These fluid/solid compounds were evaluated in this form and in the form of an emulsion in line with normal aqueous antifoam practice.

EXPERIMENTAL

Copolymer Synthesis

Perfluoroalkyl-substituted chlorosilanes were produced by reacting $\text{CF}_3(\text{CF}_2)_n\text{CH}=\text{CH}_2$ and $\text{H}(\text{CH}_3)\text{SiCl}_2$ catalyzed with chloroplatinic acid. There were three sources of olefins used in this study; Du Pont's Telomer B olefins where n is a mixture of 5, 7, 9, . . . , averaging 7, Du Pont's perfluorobutylethylene and Hoechst's perfluorohexylethylene. Chlorosilanes where $n = 3, 5, \text{ and } 7$ were isolated in greater than 97% purity. These were cohydrolyzed with varying amounts of dimethyldichlorosilane and further equilibrated with dimethylsiloxane cyclics and hexamethyldisiloxane end blocker to give the nine copolymer compositions listed in Table II.

TABLE I
Low Surface Tension Fluorosilicones^a

	Surface tension (mN/m)	Reference
Liquid:		
$(\text{Me}_3\text{CO})_2[\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}]_2\text{Si}$	18.4	1, 2
$\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{Si}(\text{OMe})_3$	18.1	3
$\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2\text{Me}_2\text{SiOSiMe}_2\text{H}$	16.4	This work
Solid (critical surface tension of wetting):		
$\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SiO}_{3/2}$	15	3
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2)_3\text{SiO}_{3/2}$	14	4
Aqueous surfactant solution (1.0% concentration):		
$\ominus \oplus$ $[\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2(\text{CH}_2)_3\text{Me}_2\text{Si}]_2\text{O}$		
$\ominus \oplus$	12.5	5
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2(\text{CH}_2)_3\text{-}$ $\text{Me}_2\text{SiOMe}_2\text{Si}(\text{CH}_2)_3\text{OH}$	13.0	5

^a Me = CH_3- .

TABLE II
Copolymer Composition and Properties

	n	$\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_2\text{MeSiO}$ (mol %)	Me_2SiO (mol %)	$\text{Me}_3\text{SiO}_{1/2}$ (mol %)	Viscosity (mm^2/s) (25°C)	Refractive index (25°C)	Surface tension (mN/m) (22°C)
A	3	15	80	5	82	1.383	19.7
B	3	35	60	5	109	1.366	19.7
C	3	55	40	5	128	1.357	19.8
D	5	15	80	5	134	1.374	19.8
E	5	35	60	5	114	1.377	19.9
F	5	55	40	5	151	1.346	19.8
G	7	15	80	5	132	1.369	19.7
H	7	35	60	5	273	1.353	19.8
I	7	55	40	5	400	1.345	19.6

Equipment

The copolymers were sufficiently free flowing to allow the Wilhelmy plate technique to be used for equilibrium liquid surface tension determination. A Rosano tensiometer based on a manual Roller-Smith precision balance with platinum Wilhelmy blade was used. The instrument was used at laboratory temperature 22°C and calibrated with distilled water and 50 mm^2/s viscosity polydimethylsiloxane fluid (interpolated surface tensions at 22°C of 72.4 and 21.0 mN/m , respectively).

Dynamic surface tensions were obtained using a Chem-Dyne Research Corp. SensaDyne 5000 differential bubble pressure surface tensiometer at a fixed setting that gave a bubble rate of about one bubble per second, depending on surface tension of the test liquid. This instrument was calibrated with distilled water and ethanol.

A Burrell "wrist-action" laboratory shaker was used for antifoam efficiency testing. Length of the clamp support arm, shaking rate, and size of sample and container were all standardized. Antifoams were tested at a concentration of 500 ppm active compound against 0.1% of various foaming surfactants listed in Table III. These were chosen to provide a variety of surfactant types and an adequate challenge for the new fluorosilicone antifoams. The two foamiest of eight fluorocarbon surfactants available to us were selected together with two silicone surfactants of current commercial interest and two hydrocarbon surfactants, of which one (Triton X100) is a very common standard for antifoam testing and the other (WAQE) is known to be very difficult to defoam with silicone materials. Antifoaming efficiency was judged by measuring collapse time and break time as a function of shake time. Collapse time is the time for the foam to fall to less than 5 mm; break time is the time for a clear area free from foam bubbles to appear on the surface.

Antifoam Preparation

Compounds were prepared by mixing 95 parts silicone fluid, 5 parts silica (Syloid 244 FP), and 0.02 parts sulfuric acid (treatment catalyst) and heating

TABLE III
 Foam Test Surfactants

Source and name	Type	Structure	Foaminess (0.1%) (30-s shake)	
			Initial foam height (cm)	Collapse time (h)
WAQE Du Pont	Hydrocarbon anionic	$\ominus \oplus$ $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_3\text{Na}$	> 7.5	> 163
Triton X100, Rohm and Haas	Hydrocarbon nonionic	$\text{Me}_3\text{C}(\text{CH}_2)_5 \text{C}_6\text{H}_4(\text{EO})_n\text{H}$	0.91	1.3
Development surfactant, Dow Corning (DCSN)	Silicone nonionic	$(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{EO})_7\text{H}$	3.0	10
Laboratory surfactant, Dow Corning (DCSC)	Silicone cationic	$\oplus \ominus$ $(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3\text{NMe}_3\text{Cl}$	0.88	1.2
Zonyl FSB, Du Pont	Fluorocarbon amphoteric	$\oplus \ominus$ $\text{CF}_3(\text{CF}_2)_n\text{NMe}_2(\text{CH}_2)_2\text{CO}_2$	> 7.5	> 167
FC 129, 3M	Fluorocarbon anionic	$\ominus \oplus$ $\text{CF}_3(\text{CF}_2)_n\text{CO}_2\text{K}$	> 6.5	> 188

at 60°C for 3 h. A PDMS reference comparison was prepared using Dow Corning DC 200 fluid of 100 mm²/s viscosity. The compounds were also prepared as 10% oil-in-water emulsions using a standard emulsifier system based on non-ionic emulsifiers, chiefly ethoxylated stearic acid, and thickeners such as hydroxyethylcellulose.

RESULTS AND DISCUSSION

Copolymer Surface Tension

Equilibrium surface tensions of the new fluorosilicone copolymers are given in Table II. As the precision of this method is of the order of ± 0.1 mN/m, all these copolymers have essentially the same surface tension. Equilibrium was established in all cases within 30 min, typical of viscous drainage effects with polymers in this viscosity range. Dynamic surface tensions measured where possible on the Chem-Dyne apparatus were about 3 mN/m higher than the equilibrium value (bubble rate ca. 1.2/s). Quantitative figures were impossible to obtain with most of the copolymer fluids because of their tendency to wet the interior of the bubble jets and give fluctuating values.

The similarity of the surface tensions is somewhat surprising. They are lower than that of PDMS of similar viscosity, see Table IV for comparison, but not so low that they should completely wet and spread over polytetrafluoroethylene (PTFE), which has a critical surface tension of wetting with *n*-alkanes of 18.6 mN/m.¹⁰ This was confirmed by the small but finite contact angle that each of these fluids exhibited on PTFE; 5°–10° on a PTFE block, 10°–15° on PTFE

TABLE IV
Comparative Commercial Homopolymers (Dow Corning Corporation Data Sheet Values)

	Viscosity (mm ² /s) (25°C)	Refractive index (25°C)	Surface tension (mN/m) (25°C)
$n = 0$, i.e. PTFPMS	300	1.381	25.7
	1000	1.381	26.1
	10,000	1.381	28.7
PDMS	100	1.403	20.9
	350	1.403	21.1
	1000	1.404	21.2

tape—the systematic variation being most likely due to sample roughness differences.

According to Zisman,¹¹ the order of increasing intrinsic surface activity (decreasing London dispersion force interaction) for the four entities in the pendent side chains is $-\text{CH}_2- > -\text{CH}_3 > -\text{CF}_2- > -\text{CF}_3$. Thus when a methyl group in PDMS is replaced with a partly fluorinated alkyl group, both higher and lower surface energy entities are introduced so it is not axiomatic that very low surface tensions will result. Fluorine and silicon have a strong affinity¹² and possibly the terminal CF_3 associates with the silicon giving a surface that is mostly $-\text{CF}_2-$ groups from the fluoroalkyl side chain and CH_3- groups from the PDMS component. The surface energy of liquids based on $-\text{CF}_2-$ and CH_3- groups are quite close, and this accounts for the lack of dependence of surface tension on copolymer composition. This similarity of surface energy is shown by a plot of liquid surface tension against boiling point for fluoroalkanes and PDMS oligomers (such as Fig. 1 in ref. 13). At the higher boiling points for the longest fluoroalkanes, where the effect of the terminal CF_3- groups is least, the two curves come very close together. This proposed orientation, with the CF_3- coordinated to the silicon leads to the pendent fluoroalkyl group forming a loop rather than sticking straight out from the surface. Thus the unresolved dipole at the $-\text{CF}_2-\text{CH}_2-$ link is not so effectively buried by increasing degrees of fluorination as is the case with other fluoropolymers,¹¹ and this removes another reason for a dependence of surface tension on composition. Further speculation on surface orientation is unwarranted. Computer modeling of these structures might be a useful future direction.

We are confident that the copolymer-treated silica surfaces will also have a lower solid surface tension than PDMS. This is anticipated not only because the least fluorinated fluorosilicone, PTFPMS, has a lower solid surface tension⁷ but also because of some measurements not reported here in detail. Copolymers with n equal to 3 were modified with a minor amount of crosslinker and formed as films on Mylar substrates. Using the method of Owens and Wendt¹⁴ and water and methylene iodide as contact angle test liquids, the solid surface tension was found to be in the 15–20 mN/m range, average 18.5 mN/m. As with the liquid values there was no dependence on composition (mol % fluorosilicone component). PDMS measured by the same technique¹⁵ gives values in the 19–

25 mN/m range, average 21.1 mN/m. The corresponding value for PTFE¹⁴ is 14.0 mN/m.

Antifoam Tests

As the copolymer fluids have similar surface tensions, antifoams were prepared from two representative materials, copolymer E (35 mol % fluorosilicone, $n = 5$) and copolymer I (55 mol % fluorosilicone, $n = 7$). Antifoams containing PDMS of 100 mm²/s and PTFPMS of 300 mm²/s were also prepared for comparison.

Antifoaming data were obtained after 10, 30, 60, and 90 s shaking of the antifoam with the foaming surfactant solution. Data were acquired on increasingly longer shake times. Once a stable foam was evident, longer shake times were not studied so higher shake times indicate better antifoam performance. Tables V and VI list only the longest shake times used to illustrate the trends; thus a shake time of 90 s implies other unreported data at 60, 30, and 10 s. Collapse times and break times longer than 2 min were not quantified.

With the odd exception that sodium dodecyl sulfate (WAQE) is extremely resistant to antifoaming by silicone/silica compounds (but not emulsions of these compounds), the data follow expectations based on equilibrium surface

TABLE V
Antifoam Compound Performance^a

Silicone used in antifoam	Foaming surfactant	Shake time (s)	Collapse time (s)	Break time (s)
Copolymer E (35 mol % fluorosilicone $n = 5$)	WAQE	10	> 120	> 120
	Triton X100	90	7	30
	DCSN	60	34	> 120
	DCSC	—	—	—
	Zonyl FSB	10	> 120	> 120
Copolymer I (55 mol % fluorosilicone $n = 7$)	FC 129	10	> 120	> 120
	WAQE	10	> 120	> 120
	Triton X100	90	1	2
	DCSN	90	1	42
	DCSC	60	12	> 120
PTFPMS (300 mm ² /s viscosity)	Zonyl FSB	10	> 120	> 120
	FC 129	10	> 120	> 120
	WAQE	10	> 120	> 120
	Triton X100	90	1	2
	DCSN	10	> 120	> 120
PDMS (100 mm ² /s viscosity)	DCSC	90	13	> 120
	Zonyl FSB	10	> 120	> 120
	FC 129	10	> 120	> 120
	WAQE	10	> 120	> 120
	Triton X100	90	1	4
PDMS (100 mm ² /s viscosity)	DCSN	60	> 120	> 120
	DCSC	90	3	> 120
	Zonyl FSB	30	> 120	> 120
	FC 129	10	> 120	> 120

^a 0.05% compound, 0.1% foaming surfactant.

TABLE VI
Antifoam Emulsion Performance^a

Silicone used in antifoam compound	Foaming surfactant	Shake time (s)	Collapse time (s)	Break time (s)
Copolymer E (35 mol % fluorosilicone <i>n</i> = 5)	WAQE	90	1	81
	Triton X100	90	< 1	1
	DCSN	90	8	> 120
	DCSC	90	1	3
	Zonyl FSB	10	> 120	> 120
Copolymer I (55 mol % fluorosilicone <i>n</i> = 7)	FC 129	10	> 120	> 120
	WAQE	90	2	> 120
	Triton X100	90	2	7
	DCSN	90	5	> 120
	DCSC	90	1	5
PDMS (100 mm ² /s viscosity)	Zonyl FSB	10	> 120	> 120
	FC 129	10	> 120	> 120
	WAQE	90	1	18
	Triton X100	90	< 1	1
	DCSN	10	> 120	> 120
	DCSC	90	1	3
	Zonyl FSB	10	> 120	> 120
	FC 129	10	> 120	> 120

^a 0.05% compound, 0.1% foaming surfactant.

tension of the foaming surfactant solutions. Values at the test concentration of 0.1% (1000 ppm) are given in Table VII. The hydrocarbon surfactants and one of the silicones, DCSC, have higher equilibrium surface tensions at this concentration than all the silicone antifoams used here. All of the antifoams are effective. The other silicone surfactant, DCSN, has an equilibrium surface tension equal at the test concentration to that of the PDMS antifoam. Neither this antifoam nor the higher surface tension PTFPMS antifoam are effective, but the lower surface tension new fluorosilicone copolymer antifoams are very effective. The general effectiveness of these fluorosilicone copolymers against several commercially available nonionic silicone surfactants was also confirmed.

TABLE VII
Surface Tension of Foaming Surfactants^a

	Equilibrium surface tension (mN/m)	Dynamic surface tension (bubble rate ~ 1/s) (mN/m)
WAQE	25.6	47.3
Triton X100	29.8	36.1
DCSN	21.0	33.9
DCSC	28.2	50.5
Zonyl FSB	17.0	36.4
FC 129	16.5	37.9

^a 0.1% concentration, 22°C ± 1 temperature.

The two fluorosurfactants resist antifoaming by all the antifoams, having lower surface tension than even the new fluorosilicone materials.

The dynamic surface tensions of the foaming surfactants do not relate to antifoaming performance. This is unexpected as all mobile foaming/antifoaming systems are dynamic. Even at a moderate bubble rate of circa one per second, the surfactant surface tensions rise considerably. This data is also shown in Table VII. If dynamic surface tensions at this bubble rate were of any significance, we should anticipate good antifoaming of all the surfactants including the fluorosurfactants. This is not the case.

The idea that a low antifoam surface tension is important is central to most mechanisms of antifoaming and begins with Ross's first mechanism of antifoaming¹⁶: "The agent dispersed in the form of fine drops enters the liquid film between bubbles and spreads as a thick duplex film. The tensions created by the spreading duplex film lead to the rupture of the original liquid film." The spreading process is controlled by the spreading coefficient S , given by¹⁷

$$S = \sigma_F - \sigma_{AF} - \sigma_A$$

where σ_F is the surface tension of the foaming surfactant solution, σ_A that of the antifoam, and σ_{AF} the interfacial tension between them. A positive spreading coefficient should allow spreading. Note that small differences in surface tension evidently matter as a fluorosilicone of $\sigma_A = 19.7$ mN/m can antifoam a silicone surfactant at $\sigma_F = 21.0$ mN/m. This also implies that the interfacial tension between these materials is low, probably less than 1 mN/m. Even though the fluorosurfactants exhibit large rises in surface tension under dynamic conditions, it may be that the interfacial tension rises similarly to keep the spreading coefficient negative.

The resistance of sodium dodecyl sulfate to antifoaming by the silicone/silica compounds is unexplained. The compounds are more difficult to disperse than the emulsions, and this accounts for the general better antifoam behavior of the latter (compare Tables V and VI), but it is not clear why this is particularly so for sodium dodecyl sulfate. Kulkarni and co-workers have speculated on the role of charge in the details of antifoam droplet entering and spreading.¹⁸ They have shown that foam prevention using silicone antifoams is significantly inhibited by the interaction between antifoam droplets and the foaming surfactants. The charge on the antifoam droplets as a result of surfactant adsorption is believed to be the primary cause of the inhibition of antifoam activity. Kulkarni observed it with both anionic and cationic surfactants, including sodium dodecyl sulfate and silicone emulsions, whereas we experience the problem more with antifoam compounds than emulsions and particularly with the anionic sodium dodecyl sulfate rather than the cationic silicone surfactant. As Kulkarni and co-workers say, "the propensity towards defoaming and foam ability are not simply related." More work on charge repulsion effects and on specific foaming surfactant-antifoam component interaction is needed.

CONCLUSIONS

Fluorosilicone copolymers composed of $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_2\text{MeSiO}$, Me_2SiO , and $\text{Me}_3\text{SiO}_{1/2}$, where $n = 3, 5,$ and 7 have surprisingly similar liquid surface

tensions of ca. 19.8 mN/m, lower than that of PDMS of similar viscosity but not low enough to wet PTFE. This is a higher value than might be expected for such species and a looped orientation, with the terminal CF_3 — group coordinating to the Si atom is suggested rather than an extended configuration to explain the data.

These new fluorosilicone copolymers can be formulated into antifoam compounds and emulsions that are more effective at defoaming aqueous silicone surfactants than either PDMS or PTFPMS based materials. However, they are not effective against very low surface tension fluorosurfactants. This rather unexpectedly implies that equilibrium surface tensions are more important in the action of such antifoams than dynamic surface tensions.

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