EXECUTIVE SUMMARY

Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foams (F3)

SERDP Project WP18-1519

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ACRONYMS AND ABBREVIATIONS

AA	L-ascorbic acid
AFFF	aqueous film forming foam
APS	3-aminopropylmethylbis(trimethylsiloxy)silane
DoD	Department of Defense
F^3	fire-fighting foams
g/mL	grams per milliliter
mN/m	millinewtons per meter
NMR	nuclear magnetic resonance spectroscopy
NRL	Naval Research Laboratory
OTMAP	octa(tetramethylammonium)polyhedral oligomeric silsequioxane
PEG	polyethyleneglycol
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonate
POSS	polyhedral oligomeric silsequioxanes
wt%	mass fraction, percent by weight

1.0 INTRODUCTION

The Tri-services of the Department of Defense (DoD) use enormous quantities of highly flammable substances, particularly high vapor pressure hydrocarbon liquids (such as gasoline, diesel, and jet fuel), which pose serious risks of fire. Even though personnel have excellent training with appropriate procedures and safeguards in place to minimize the risks of fire from these substances, fires can and do happen. Extinguishing such fires as fast as possible must be accomplished to minimize damage to infrastructure, vehicles, and equipment, as well as to keep personnel safe from harm on ships or airfields. Fire-fighting foams (F^3) were developed to combat hydrocarbon liquid pool fires as early as 1902 and these are referred to as Class B foams. F^3 are based on surfactants (surface active agents) that can be added to water, typically at the nozzle of a hose by a mixing head inlet, which creates a thick foam spray (see Figure 1). The F^3 is sprayed onto the pool fire, similar to a wide blanket, and in this way the fire is covered over with a stable mass of small air-filled bubbles.

Figure 1. Navy Personnel in Full Fire Suits to Fight High Temperature Jet Fuel Fire with Aqueous Film Forming Foam (AFFF)

The burning fuel is thus starved from atmospheric oxygen and is extinguished. Because the aqueous foam is composed mostly of air, it is light and able to rest on top of the hydrocarbon, for example gasoline, whose density is typically less than water (e.g. octane: d = 0.7 g/mL), but also has a very low surface tension of 20.7 mN/m (see Table 1). Gasoline is a much harder fuel to form a film on than diesel on account of its lower surface tension.

Table 1. Surface Tensions of Various DoD Hydrocarbon Fuels

FUEL	Surface Tension mN/m (24 C)
Diesel	28.3
Jet	26.7
Gasoline	20.7

Not all surfactants work well as F^3 and many types have been tried. The best surfactants for F^3 are the perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) (see Figure 2) and related perfluoroalkyl brethren, whose fire-fighting applications were discovered and developed by the US Navy.

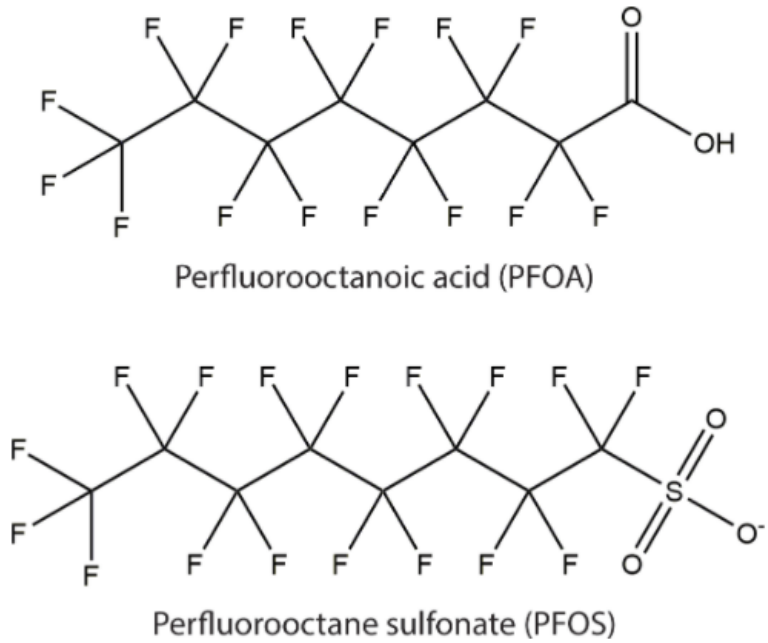


Figure 2. Chemical Structure of Perfluorooctanoic Acid (PFOA), a Typical Ingredient Used in AFFF Concentrates Highly Effective at Putting Out Liquid Hydrocarbon Fires (https://doi.org/10.1371/journal.pbio.2002855.g001)

These perfluoroalkyl surfactants maintain good quality foams and have the unique property of being both hydrophobic *and* oleophobic. This means that the perfluoroalkyl surfactants are resistant to dissolve in both water and non-polar liquids such as the hydrocarbon fuels (see Figure 3).

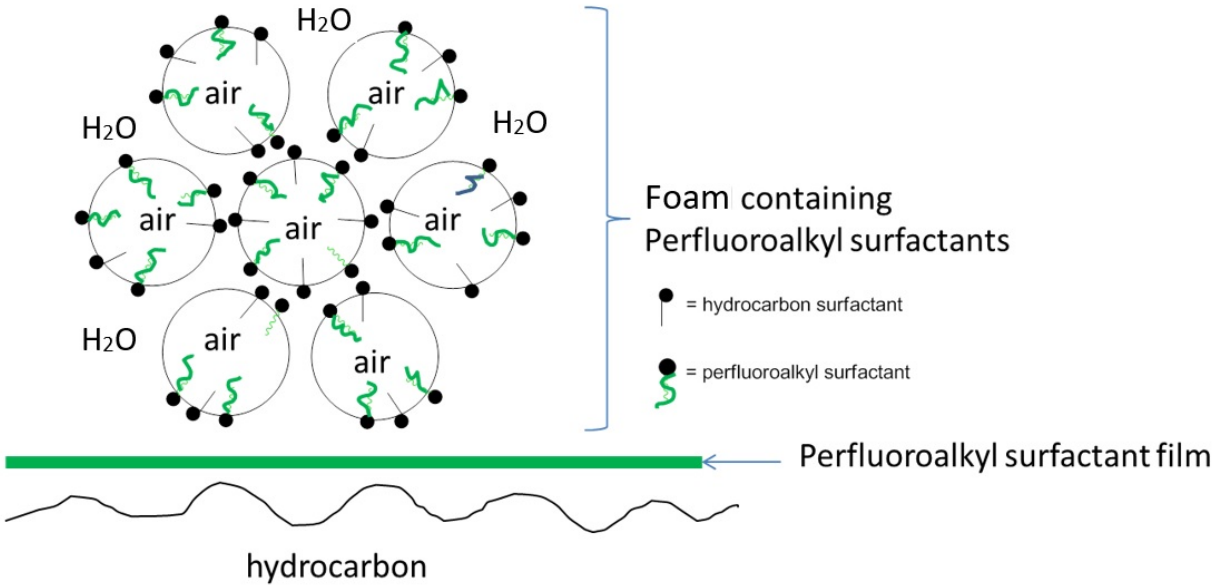


Figure 3. Perfluoroalkyl Surfactant Foam on Surface of Fuel

The specifications for AFFF have been collected in a military specification and the most important criterion of these specifications are shown in Table 2. The AFFF must be able to extinguish a 28 ft^2 pan fire of gasoline in 45 seconds and have a spreading coefficient on cyclohexane of at least 3 or greater.

Table 2. Extinction Times and Spreading Coefficient for AFFF from MIL-F-25485F

	Extinction Times (sec)		
Specification	1.5% Type 3 and 3% Type 6	3% Type 3 and 6% Type 6	Type 3 and Type 6
28 ft^2 gasoline pan fire	45	30	
Spreading Coefficient mN/m			≥3

2.0 OBJECTIVES

The objective of this limited-scope research project was to explore an innovative approach in using polyhedral oligomeric silsequioxanes (POSS) as well as aminoalkylsiloxanes as drop-in replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used by the Department of Defense (DoD) for fire-fighting. Foams containing the new surfactants will be formulated to extinguish small-scale, unleaded gasoline pool fires in 45 seconds or less (1.5% Type 3 and 3% Type 6) as dictated by MIL-F-24385F. In addition, the POSS and aminoalkylsiloxanes may have low acute toxicity to fish and are biodegradable according to measurements of chemical oxygen demand and biological oxygen demand of microorganisms.

3.0 TECHNICAL APPROACH

Silicon is the second most abundant element in the Earth's crust and so new surfactants made from this element might be environmentally-friendly materials. Polyhedral oligosilsesquioxanes (POSS) are thermally stable silicate materials that could be made into surfactants by asymmetric attachment of poly(ethylene)glycol 'tails' to increase water solubility (see Figure 4). Aminopropylsiloxanes (e.g., APS) were another platform that could be chemically modified by salt formation or quaternization to create fluorine-free surfactants.

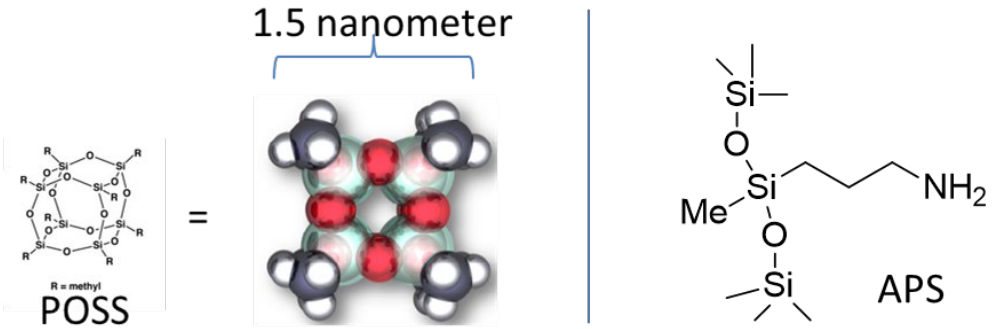


Figure 4. Chemical Structures of OctamethylPOSS and 3-aminopropyl-methylbis(trimethylsiloxy)silane (APS)

The surfactant properties of these new silicon-containing materials will be measured such as surface and interfacial tensions against cyclohexane, specified by MIL-F-24385F. Silicon-based surfactants with spreading coefficient > +3 mN/m will be tested for extinguishing small-scale hydrocarbon pool fires.

4.0 RESULTS AND DISCUSSION

The commercially available heptaisobutyl POSS trisilanol, an incompletely condensed POSS cage, was reacted with dimethylchlorosilane to cap the three free silanol corners (see Figure 5). The incomplete POSS trisilylhydride was reacted with methoxy-allyl-PEG$_{550}$ in a platinum-catalyzed hydrosilylation reaction to form the desired incomplete PEGylated POSS in modest yield.

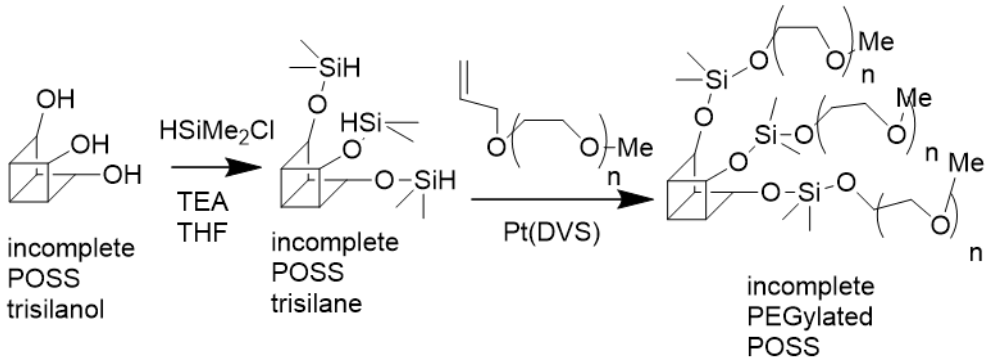


Figure 5. Chemical Synthesis of a Surfactant Made from POSS

The incomplete PEGylated POSS had NMR spectra consistent with the target structure and the product was water soluble with surface tension in air of 48 mN/m at 9 wt% loading which was well above the value for dilute Phos-Chek (~ 27 mN/m), an AFFF product (see Figure 6).

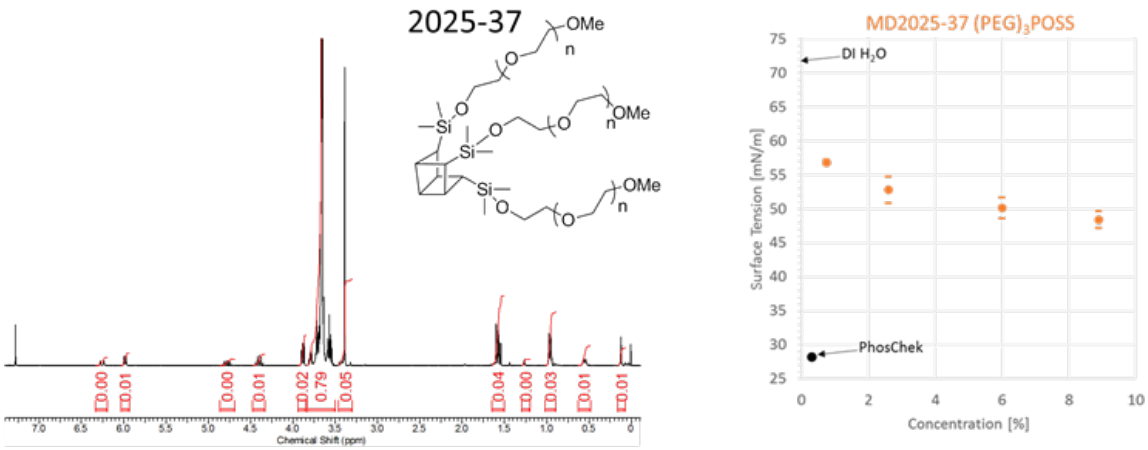


Figure 6. Proton NMR Spectrum of tri(PEGylated) Incomplete POSS 2025-37 (right); Plot of Surface Tension in Air of the POSS Surfactant in Air

The interfacial tension of the incomplete PEGylated POSS versus cyclohexane was also measured by the pendant drop method which gave a value of 18.49 mN/m. Thus the incomplete PEGylated POSS had a spreading coefficient of –49.8 mN/m on cyclohexane which is typical of non-fluorinated surfactants. We tried to improve the water solubility of the incomplete PEGylated POSS by making the methyl rather than isobutyl version but had difficulty preparing the incomplete heptamethylPOSS. Other avenues to water solubilize the POSS, such as making phosphonates, failed owing to the platinum-catalyzed coupling step. Also, sugar acid amides of aminoisobuty POSS and the ascorbic acid salt of the latter were insoluble in water. Generation of surfactants by metathesis of octa(tetramethylammonium)POSS with dodecyltrimethyl-ammonium bromide appeared to work best at 1:1 ratio and gave surface tension of 37.53 mN/m, although dilute Phos-Chek was ~ 27mN/m (see Figure 7).

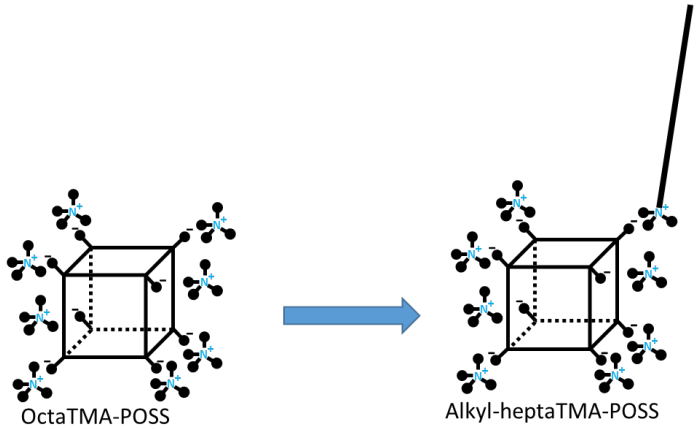
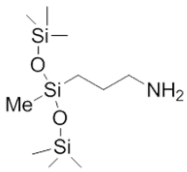


Figure 7. Cartoon Showing the Displacement or Metathesis of One Corner Trimethylammonium Ion by One Dodecyltrimethylammonium Ion

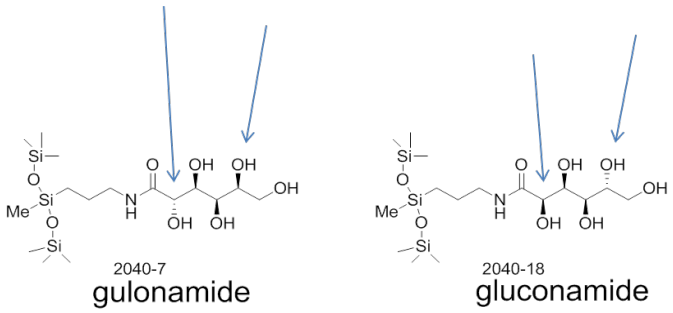
Metathesis of octa(tetramethylammonium)POSS with phosphonium salts were also attempted since phosphorus is a known fire retardant. Reaction of OTMAP with tetrakis(hydroxymethyl)phosphonium chloride generated hydrogen gas by an undesired side reaction. With tetrabutylphosphonium hydroxide, exchange of the ammonium cations occurred and the surface tension was measured at 40 mN/m before precipitation of the complex at high concentration.



3-aminopropyl-methyl-bis (trimethylsiloxy)silane

'APS'

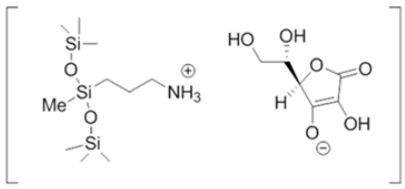
Studies with 3-aminopropylmethylbis(trimethylsiloxy)silane (APS) were also made whose sugar acid amide gluconic acid lactone was appeared to be a surfactant. Yet, the isomeric sugar acid amide of APS with gulonic acid lactone had poor solubility in water (see Figure 8).



WATER SOLUBLE: NO YES

Figure 8. Remarkable Stereochemical Power of Two Hydroxy Groups, and the APS Sugar Amide Went from Water Soluble to Water Insoluble

A stoichiometric mixture of APS and ascorbic acid made a powerful surfactant with a spreading coefficient of +4.6 mN/m on cyclohexane and +0.74 mN/m on heptane, Figure 9. Yet, this apparently good surfactant could not extinguish a heptane pool fire (see Figure 10).



'APS/AA surfactant'

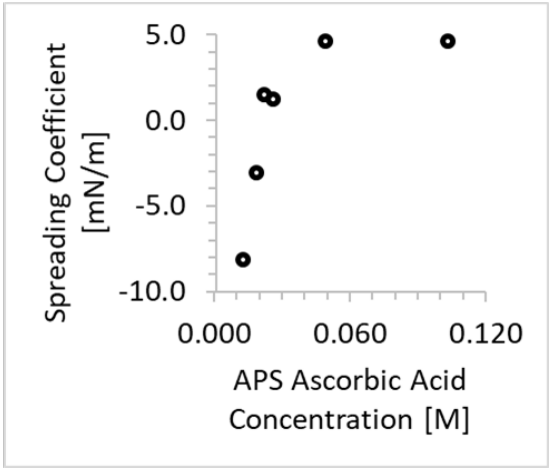


Figure 9. Salt Formation Between APS and AA in Water (*left*); and Plot of APS/AA Surfactant Concentration Versus Spreading Coefficient on Cyclohexane (*right*)

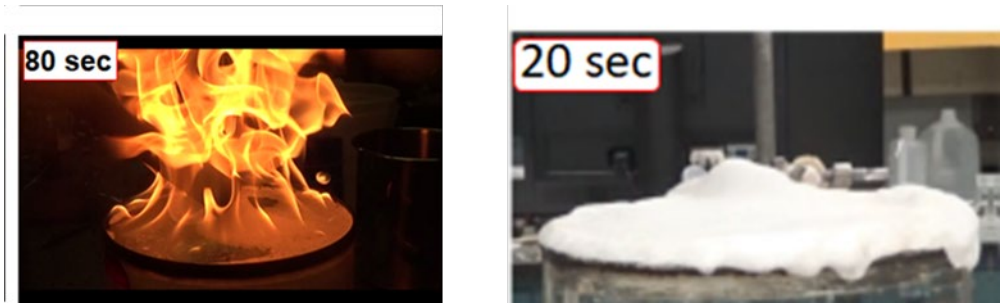


Figure 10. The APS/AA Surfactant (*left*) Could Not Extinguish Heptane Pool Fire While AFFF (*right*) Could Do So in Just 20 Seconds

The APS readily underwent quaternization with alkyl halide to form ammonium salts that were surfactants with low surface tensions but may also suffer from stability issues like the APS carboxylate surfactants (see Figure 11). Apparent surfactants were also made that were structurally similar to the natural product choline by coupling new chlorosilylalkylsiloxanes to dialkylaminoethanol.

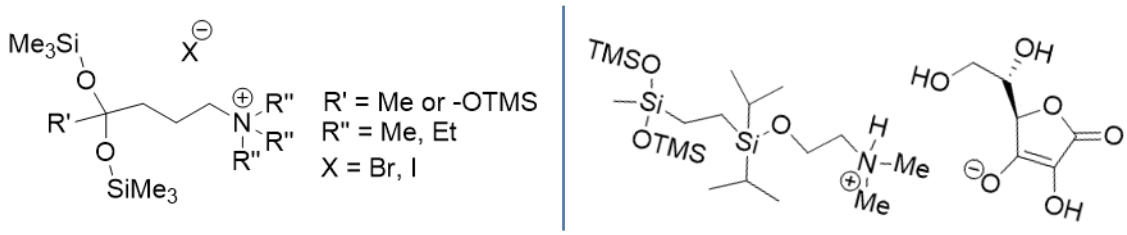
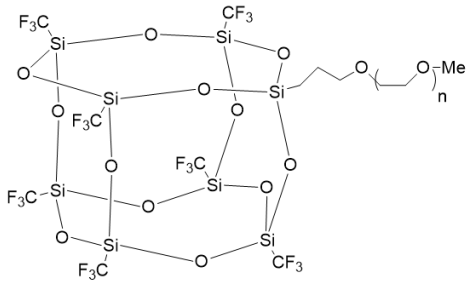


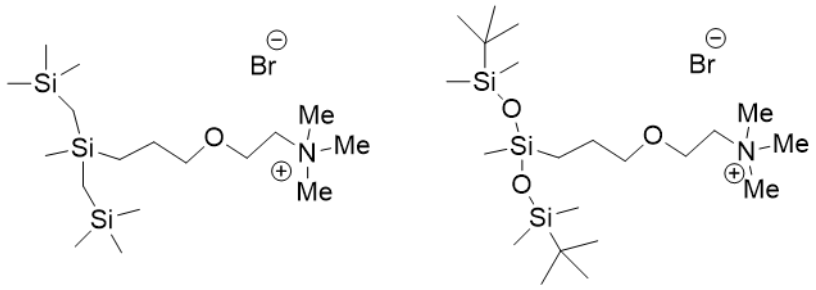
Figure 11. Surfactants Made by Quaternization of APS (*left*); and Choline-like Surfactants from a New Chlorosilylalkylsiloxane Reagent (*right*)

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

POSS can be made into surfactant but would need more synthetic manipulation to achieve lower surface tension. This could be achieved by decreasing the hydrophobicity of the silicate cage by starting from octamethylPOSS but the latter has solubility issue making derivatization difficult. A high-risk idea was to make a perfluorooctamethylPOSS into a surfactant. The compound would have the fluoroalkyl content 'spread out' over the molecule rather than 'concentrated' in long-chain perfluoroalkyls. Such a compound would likely have omniphobic properties similar to AFFF, but may be much more susceptible to breakdown in the environment to potentially less toxic products.



Strong surfactants could be made from stoichiometric neutralization of aminoalkylsiloxanes with simple carboxylic acids. There appears to be much synthetic possibilities with aminoalkylsiloxanes by quaternization since they have low surface and interfacial tension measurements. The aminoalkylsiloxane surfactants appear to have significant stability issues when stored in water solution, something that requires further study. However, one simple example of these, APS/AA, did not extinguish a heptane pool fire. This result was disappointing since tensiometry indicated the surfactant would form a layer. These data showed that favorable tensiometry measurements do not always equate to a good fire-fighting foam. Our NRL colleagues agree that more study should be made of the APS surfactants by making mixtures with alkylpolyglycosides, since the latter tend to have a synergistic effect. The stability issues of the siloxanes could be eliminated by making siloxane surfactants with bulky groups (e.g., *tert*-butyl) to slow down or even prevent hydrolysis, which is the suspected mode of decomposition. Alternatively, carbosilanes with structures similar to the siloxanes could be synthesized that would not hydrolyze readily.



Considering all the careful experiments and expensive instruments that are necessary for collecting tensiometry data, a simple empirical test of a large number of a variety of surfactants against pool fires might be a useful method to identify new lead surfactants. There are so many more surfactants available today as opposed to the early days (1960s) of foam fire-fighting research that a cheap and fast screen might uncover surfactant phenomenon that one could not predict beforehand.