FINAL REPORT

Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes

SERDP Project WP18-1638

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14. ABSTRACT
Aqueous film-forming foams (AFFFs) containing perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been used for the past 5-6 decades by the Department of Defense in fuel fire suppression operations. These chemicals have the strongest chemical bonds and are considered as persistent, bio-accumulative, and toxic substances. PFOA/PFOS chemicals have been detected around the world in the food chain, drinking water, animals, and even in human blood. Therefore, the Environmental Protection Agency, EPA, has regulated the chemical industry for the complete elimination of PFOA and PFOS chemicals along with certain C6 substances (containing six fluorinated carbons) by 2015. Therefore, the Department of Defense is seeking non-toxic fluorine-free alternatives to replace PFOA/PFOS in firefighting foam formulations.

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AFFF, Biopersistance, C-8, Fire, foam, fuel, PFAS, PFOA, PFOS, Siloxanes

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List of Acronyms

Acronym	Expanded Form
AFFF	Aqueous Film Forming Foam
COD	Chemical Oxygen Demand
DoD	Department of Defense
EPA	Environmental Protection Agency
FFFC	Fire Fighting Foam Coalition
MMI	Materials Modification, Inc.
NMR	Nuclear Magnetic Resonance Spectroscopy
NRL	U.S. Naval Research Laboratory
OECD	Organization for Economic Co-operation and Development
PFAS	Per/polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PI	Principal Investigator
POC	Point of Contact
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
WP	Weapons Systems and Platforms

Keywords

AFFF, Biopersistance, C-8, Fire, foam, fuel, PFAS, PFOA, PFOS, Siloxanes.

Acknowledgments

Abstract

Objective:
Aqueous film-forming foams (AFFFs) containing perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been used for the past 5-6 decades by the Department of Defense in fuel fire suppression operations. These chemicals have the strongest chemical bonds and are considered as persistent, bio-accumulative, and toxic substances. PFOA/PFOS chemicals have been detected around the world in the food chain, drinking water, animals, and even in human blood. Therefore, the Environmental Protection Agency, EPA, has regulated the chemical industry for the complete elimination of PFOA and PFOS chemicals along with certain C6 substances (containing six fluorinated carbons) by 2015. Therefore, the Department of Defense is seeking non-toxic fluorine-free alternatives to replace PFOA/PFOS in firefighting foam formulations.

Technical Approach:
In this project, specifically, functionalized siloxane-based surfactants were synthesized, and their chemical stability, physical properties, and fire suppression abilities were evaluated. The tests included benchtop testing, 28-ft² fire performance, spreading coefficient, and aquatic toxicity of the foam formulations.

Results:

A number of trisiloxane surfactants have been synthesized and successfully tested for its AFFF capabilities, to enable the spontaneous formation of a water film on top of the fuel. The additives play a critical role in the extinction of fire and stability in water. The performance of trisiloxane surfactants are encouraging and has the potential to replace fluorine-containing AFFF. Further optimization of additive formulations will yield a fluorine-free formulation that can replace current AFFF.

Benefits:
Fluorine-free formulations developed in this effort have potential as "drop-in" replacement for AFFF products and can meet the performance specifications of the fire extinguishing agent, based on MIL-PRF-24385F standard with further optimization of the formulations. The formulations also are capable of complying with environmental regulations and safe by military personnel.

Executive Summary

Introduction

Aqueous film-forming foam, most commonly known as "AFFF" was developed by the US Navy in the mid-1960s. AFFF formulation containing fluorochemical surfactant is the gold standard in firefighting against liquid fuel fires. This traditional AFFF formulation has a low viscosity (>94% water) and can rapidly spread on the surface of hydrocarbon fuels and thereby stop the formation of flammable vapors. The lowering of surface tension by fluoro-surfactants allows the creation of

foam and increase the coverage of water film on hydrocarbon fuel and provide dramatic fire suppression.

AFFF products containing perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were used by multiple DoD installations. Biopersistence and the resulting toxicity of these chemicals (Commonly known as C-8 chemicals) led to new government regulation and a prohibition on PFOA and PFOS chemicals. Starting in 2006, the EPA and the Fire Fighting Foam Coalition (FFFC) initiated the voluntary global 2010/2015 PFOA Stewardship Program that resulted in the termination of these C-8 chemical productions by the manufacturers [1]. This situation created the necessity for the development of new fluorine-free formulations.

Per/polyfluoroalkyl substances (PFAS) were added to AFFF formulations to lower the surface tension below that of the fuel. This helps in the spontaneous spreading of water on top of organic fuels. Therefore, the straightforward approach for replacing C-8 chemicals is to find compounds with low surface tension. New AFFF formulations with short-chain fluorosurfactants (C6 or shorter) have been shown to be less bio-persistent. However, still there exists an uncertainty of these chemicals and suspected of containing a small amount of C-8 substances.

The industry has identified potential fluorine-free non-toxic foams; however, none of these technologies meet the performance required for military applications. For example, an environment-friendly foam based on a betaine surfactant was demonstrated by Shika Bo [23]. A mixture of alkali metal carboxylates such as potassium acetate, potassium citrate, sodium acetate, and sodium citrate and natural surfactants selected from lecithin, saponin, and casein in water was shown to act as a fire suppressing foams [4]. These biomaterials [5] are environmentally friendly; however, their high cost prevents their commercial viability. New industrial fluorine-free foams that are introduced as alternatives are not efficient enough to replace AFFF [6].

Siloxanes

Guoyong *et al.* synthesized new carbohydrate-modified siloxane surfactants and studied their behavior in aqueous solution [7]. Their work demonstrated that siloxane surfactants could exhibit surface tensions as low as 20.54 mN/m, which is much lower than most of the organic fuel liquids and closer to 15 mN/m of perfluoro surfactants. Recently, Blunk *et al.* demonstrated the potential of carbohydrate-modified siloxane surfactants in AFFF fire suppression applications [8]. Among various siloxanes reported in their study, chemicals in which hydrophobic siloxane groups linked by amido group (NH-C=O) spread readily on organic fuels [8]. In this project, we have synthesized and evaluated siloxanes containing specific structural features for the AFFF application.

Objectives

In this effort, a new material system that has: (1) functional groups to reduce the surface energy and (2) ability to form stable foam over the flammable fluids was investigated. The primary technical objective of this effort was to synthesize novel carbohydrate functionalized siloxane surfactants and evaluated their applicability in AFFF fire suppression operations.

The resulting siloxanes have the potential to form a stable foam layer on top of liquid hydrocarbon fuels and act as a barrier for combustible liquids from supplying fuel vapor to the fire. Hydrophobic trimethyl siloxane groups present in these compounds lowered the surface energy and allowed the wetting of hydrocarbon fuels. Hydrophilic carbohydrate moieties increased the solubility of the surfactant in water. Amino (-NH) groups present in the middle of the siloxane surfactant structure are expected to form hydrogen bonding with water and stabilize the water layer on liquid fuel. The location of the nitrogen in the middle of the siloxane chains anchors the molecules to more stable configurations. This can further help in water film formation and hence increase the secondary burn time.
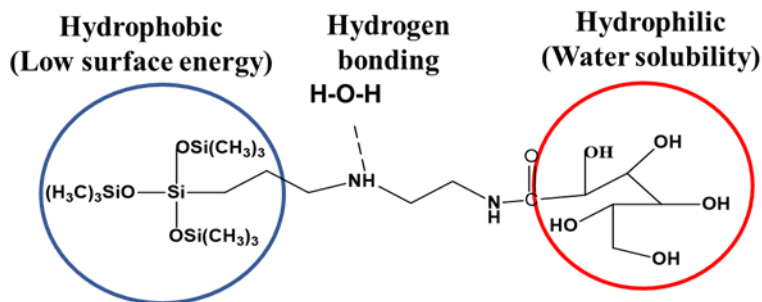

Figure 1. Structure of a typical trifunctional molecule with hydrophobic/hydrophilic ends

Materials and Methods

Materials Procurement

Chemicals for the synthesis of siloxane surfactants were procured from Gelest Inc. and Tokyo Chemical Industry (TCI). Additional compounds to prepare AFFF solutions were provided by BASF and Dow Chemicals. Parts for the benchtop fire testing was purchased from Chemglass Inc. and Ace Glass.

Synthesis of Carbohydrate Functionalized Siloxane Surfactants

Preparation of lower surface tension siloxane surfactants entailed a two-step process using a silane precursor. In a typical setup, an amine-functionalized silane with 2 or 3 hydrolyzable groups (aminopropyltrimethoxysilane, for example) was placed in a flask along with excess hexamethyldisiloxane (HMDS) and a small amount of tetramethyl ammonium hydroxide as a catalyst. The mixture was heated under nitrogen until reflux occurred (typically near the boiling point of the silane) and held at that temperature for two hours. Afterward, the solution was heated to 130 °C to deactivate the catalyst and remove a majority of the remaining HMDS solvent. The final product was rotary evaporated in the range of 100-150°C at 6 mbar to yield the final siloxane material.

Spreading Parameters

The spreading parameter is an essential tool to use in order to determine the viability of aqueous film formation. The spreading parameter should be positive in order for film formation to be possible. A positive spreading parameter does not guarantee film formation; it only confirms if it

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is theoretically possible [9]. To ensure film formation, it should be observed optically. The equation of the spreading parameter is:

$$S = \gamma_{LA} - \gamma_{SA} - \gamma_{SL}$$

where,

- γ_{LA} is the surface tension of the fuel in the air
- γ_{SA} is the surface tension of the surfactant solution in air
- γ_{SL} is the interfacial tension between the surfactant solution and the fuel

In order to achieve a positive spreading parameter, the surface tensions of the surfactant solution and interfacial tension between it and the fuel should be sufficiently low. Surface tension values were measured using a model 250 Ramehart goniometer. For each measurement, an amount of siloxane surfactant was dissolved in distilled water at a 1, 3, or 6% concentration. The solution was loaded into a syringe connected to a needle just above the measurement stage. A droplet of the solution was suspended within the field of view of the camera, and a program was initiated to measure the surface tension based on the drop profile. The measurements were calibrated through the surface tension measurement of common liquids such as cyclohexane and oils. Interfacial tension measurements were taken using a contact angle method. In this method, a flat sheet of Teflon is placed at the bottom of a beaker containing cyclohexane fuel. A syringe containing the surfactant solution with a needle attached is immersed in the liquid, and a drop is slowly dispensed onto the Teflon surface. A similar program then evaluated the drop profile to calculate the interfacial tension value.

Aqueous Film Formation

A positive spreading parameter gives the potential for the surfactant to form an aqueous film over a low surface tension hydrocarbon fuel. Formation of such a film can be observed optically or through ignition tests [10]. However, it is not possible to measure the speed at which the film spreads on fuel because of the transparent nature of the fuel and the foam. Therefore, a new method was devised in this project to track the speed of foam spreading. The proprietary powder available from MMI was placed on cyclohexane in a petri dish since the particles can repel low surface tension liquids (even hexane with surface tension 18.43 mN/m at 20 °C) they float on cyclohexane. When the drop of the surfactant placed on cyclohexane, the surfactant foam pushes the particles as they spread.

A comparison of the film formation between different surfactants was evaluated using Kinovea video software. This software is specially used for motion tracking. Video of the film formation tests was taken and uploaded to the video software. Then three specific points on the video were marked in order to track the pixel movement. Once the video is played and the movement was tracked, the program exports X and Y coordinates of the designated point every 3.33 milliseconds. This movement through the coordinate system was used to calculate maximum velocity and average velocity of the film formation.

Foam Expansion Testing

A bench-scale apparatus based on prior literature [11] was assembled to evaluate the properties of foam produced from a surfactant solution. The design for this apparatus is shown in Figure 2.

Figure 2. Schematic of foam generator apparatus

Two holes were drilled into a plastic jar (product 6702T75 from McMaster-Carr) on the side and cap, approximately 1.5cm and 0.5cm, respectively. A glass dispersion tube sparger (Sigma Aldrich part Z507660) with 25-50 µm porosity was inserted into the top hole, and a 1.5 cm diameter vinyl tube was connected to the side hole. Nitrogen gas at a predetermined flow rate (~5 ft^3/hr) was fed through the dispersion tube into a solution filled to a 9 cm depth in the bottle, with the sparger submerged 4 cm from the bottom of the vessel. The flow rate of nitrogen was adjusted with a flow meter to obtain a foam production rate of approximately 1000mL/min.
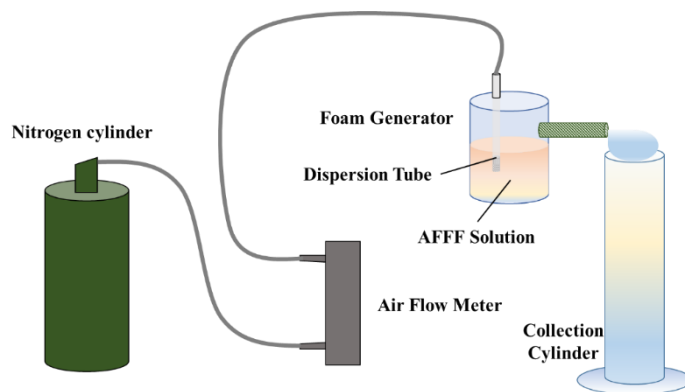
Foam Stability Testing

Foam stability testing was conducted according to the method described by tested by Hinnant *et al.* [10]. A layer of foam was applied onto a 50 mL of heptane in a 100 mL glass beaker. The foam was generated from the surfactant solution. The heptane was heated to 60ºC before the foam was applied. Once the foam occupied the entire available volume on top of hot heptane, a timer was started. The time taken for the foam to completely dissolve into the heptane was recorded as the foam stability time.

Benchtop Fire Testing

The fire extinction performances of the siloxane surfactants were measured using an in-house built benchtop pool fire apparatus (19 cm diameter). This experimental setup was initially developed by the U.S. Naval Research Laboratory (NRL) [[12]]. The setup for the 19cm diameter pool-fire extinction testing is illustrated in Figure 3 [11].
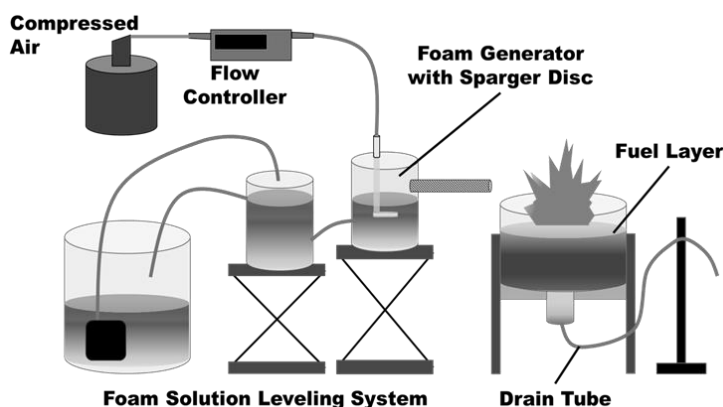

Figure 3. Benchtop foam generation and pool fire suppression [11]

The foam solution was placed in a reservoir where an aquarium pump was used to supply the solution into a second reservoir whose height was adjusted relative to a third solution container in which is immersed a glass frit (sparger) to generate the foam by controlled air flow rate passage.

These three containers required a volume of about 2.5 L of foam formulation. The foam was supplied through a sidearm in the container cap to a connected glass tube that deposited the flowing foam on to the burning pool. The pool was filled to a level 2cm below its lip with water followed by a 1cm layer of the heptane fuel. The extinction experiments were conducted using a range of foam flow rates between 400 and 2000 mL/min. Immediately before and after the extinction time experiment, foam flow rate and expansion ratio measurements were made by measuring the time needed for the generated foam to fill a 500 mL beaker and the foam's mass. The extinction time measurement is conducted by giving the pool a 60-sec pre-burn, then delivering the dispensing nozzle to the tip of the pool fire and observing the times needed for coverage of the pool by the foam and for the extinction of the fire. If extinctions are observed, these data are expressed in a plot of foam flow rate vs. extinction time. A Reference AFFF composed a fluorosurfactant (Capstone 1157), an alkyl polyglycoside surfactant (Glucopon 215UP), and a solvent (diethylene glycol monobutylether) were used as the reference formulation which has passed MilSpec extinction evaluation [11].

28 ft^2 fire performance

Large-scale fire testing was conducted according to the method described in the MIL-PRF-24385F standard, albeit with heptane as the fuel. This task was performed at Chesapeake Bay Detachment, U.S. Naval Research Laboratory, Chesapeake Beach, MD. The test was performed using a circular pan 6 ft in diameter, as provided in Figure 4.

(A) **(B)**

Figure 4. 6 ft diameter pool fire pan with (A) Fuel and (B) Foam on top of fuel after the extinction of fire

The foam produced from the siloxane formulation was sprayed on the heptane fuel using an aspirated nozzle at a rate of 2 gals/min. 10 gallons of heptane was used as test fuel in this task. The fire was started by igniting the fuel. After 10 seconds of a pre-burn period, the foam was sprayed on the fuel, and the fire extinguishing time was recorded using a video camera.

Biopersistance Testing

The anticipated superiority of the siloxane-based surfactants over fluorinated chemicals is their non-persistence in the environment. Therefore, in this task, the biodegradability of the siloxane as a pure material was tested for its biodegradation properties in an aquatic environment. This testing was conducted in accordance with the guidance 301B provided by the Organization for Economic Co-operation and Development (OECD) at Situ Biosciences LLC., Wheeling, IL. The OECD 301B method is designed to provide a screening of chemicals for ready biodegradability in an aerobic aqueous medium. Total carbon was determined analytically for each sample and used as the reference for the determination of the percentage of carbon dioxide (%ThCO$_2$) produced by microbiological degradation. Test of samples using OECD 301 301B was conducted for 28 days with daily analysis of CO$_2$ production. The second level of biological degradation can be

determined for material that does not achieve ready biodegradability; Inherent Biodegradation is determined when the biodegradation rate results in removal of 20% or greater $ThCO_2$ within the total timeframe.

Results and Discussion

Synthesis of carbohydrate functionalized siloxane surfactants

Four siloxane surfactants, namely aminopropylmethyl disiloxane, aminopropyl trisiloxane, diaminopropylmethyl disiloxane, and diamino propyl trisiloxane modified with glucose were synthesized using a two-step reaction, as shown in Figure 5. Aminosiloxanes were reacted with D-(+)-gluconic acid δ-lactone to attach a glucose component on the end of the molecule opposite the siloxane. In this procedure, equimolar amounts of the aminosiloxanes and D-(+)-gluconic acid δ-lactone were dissolved in methanol and refluxed with stirring. Methanol was removed via rotary evaporation to yield the final surfactant. The phase purity of the materials was confirmed using the proton NMR spectroscopic data.
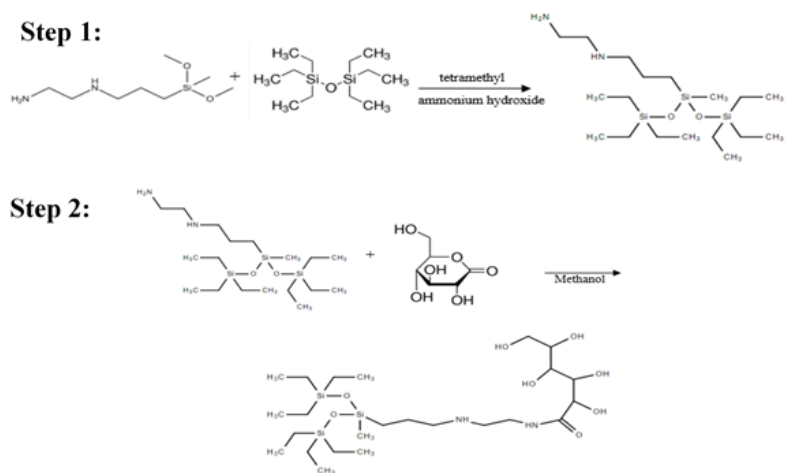

Figure 5. Synthesis of a typical siloxane carbohydrate

Hydrolysis of trisiloxane groups ($-O-Si(CH_3)_3$) has been a concern in literature studies of siloxane-based surfactants [13]. Glucose-based surfactants synthesized in this effort were unstable in water and separated into two layers within 24 hours. Due to instability and water solubility issues faced with the glucose functionalized trisiloxanes, a polyhydroxy group was used to replace glucose moiety. We expected that increasing the number of hydroxyl groups would increase the solubility of siloxane surfactants in water. The proprietary siloxane surfactant prepared with a large number of hydroxy groups was named "MMI-Siloxane." At a 1% concentration, the surfactant had a surface tension of 19.78±0.04 mN/m initially, which slowly rose to 20.94±0.23 mN/m after a week. This rise in surfactant was not as significant as the glucose-based siloxane surfactants, and there was no separation of layers, suggesting improved water stability. In this project, MMI-Siloxane was examined extensively to determine its applicability in replacing AFFF.

Improving Chemical Stability of MMI-Siloxane with Additives

In Figure 6, the effect of various additives on the stability of the MMI-Siloxane surfactant solution is provided. Glucopon, polysaccharide, and tributyl aminopropyl phosphonium bromide (TBAP) were able to stabilize the siloxane surfactants in water for over 20 days. On the other hand, diethylene glycol monobutyl ether (DGME) was not able to stabilize the MMI-Siloxane in water.

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Figure 6. Effect of additives on the stability of MMI-Siloxane

Film Formation

Representative data for Glucose modified siloxanes on spreading on cyclohexane is provided in Table 1, along with a commercial AFFF (C-6) solution.
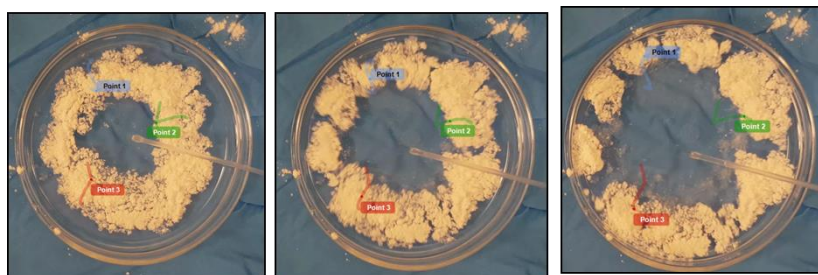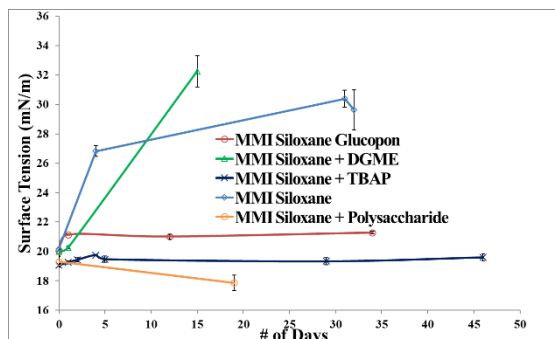

Figure 7. Motion Tracking of 3% DAPMDS-G Film Formation

Table 1. Kinovea Film Formation Data

Surfactant Solution	Average Maximum Velocity (px/ms)	Average Velocity (px/s)
3% Glucose modified diaminopropylmethyldisiloxane	2.76	1.13
3% Glucose modified diaminopropylmethyldisiloxane + Sea Water	4.91	1.92
3% Glucose modified diaminopropylmethyldisiloxane	16.41	6.71
3% AFFF (C-6 Fomtec)	10.25	5.59

Foam Stability

Foam stability of a formulation containing 3 wt% MMI-siloxane surfactant, 1.5 wt% polysaccharide, and 1 wt% Glucopon 215 hydrocarbon surfactant was tested over hot heptane fuel (60 °C). The foam produced from this solution was able to last a total of 96 minutes, as shown in Figure 8. In comparison, a typical C-6 fluorinated foam exhibited foam stability for 33 minutes under similar conditions.
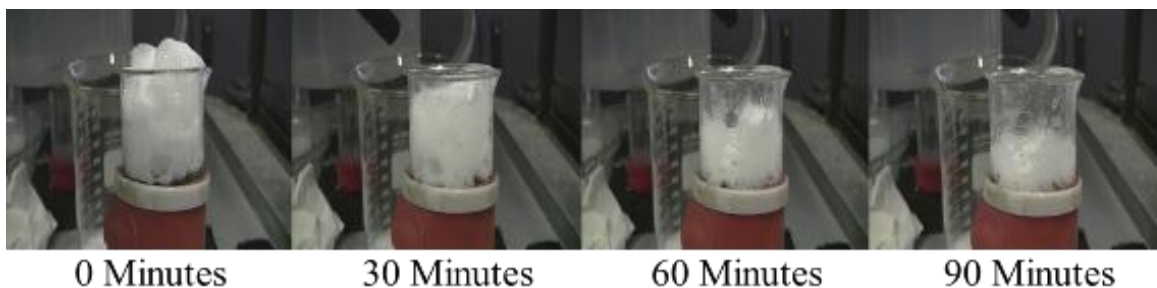
Figure 8. Effect of polysaccharide additive on the stability of siloxane surfactant-based foam over hot heptane

The polysaccharide added siloxane formed a thick free-flowing foam and showed extraordinary persistence over hot heptane, almost three times longer than C-6 foam. Unfortunately, this formulation was not amenable for fire foam application due to the viscosity of the foam, reducing the spreading ability of the foams over the heptane fuel surface. In comparison, pristine MMI-Siloxane, and Glucopon215-added MMI-Siloxane, foams lasted for 1 min., and 3 min., respectively, on top of the hot heptane.

The above-discussed results demonstrate that there is a significant effect of additives added to siloxane foams on the foam stability and hence, on the fire extinction performance. Therefore, optimization of the type and concentration of additives in the foam formulation can lead to a fluorine-free formulation that meets all the military-standard requirements.

Benchtop Fire Testing

In the test apparatus, the MMI-Siloxane solution generated a nice foam, and we started the testing with an airflow rate of 400 mL/min. The foam spread very quickly under 10 s to cover the pool thoroughly. Unfortunately, no extinction was observed in 2 min because of burning at the edges for MMI-Siloxane at this flow rate. We decided to increase the airflow rate to 1000 mL/min, but again, no extinction. We the airflow rate was increased to 1500 ml/min, MMI-Siloxane was able to extinguish the fire. We increased the airflow to 2000 mL/min, MMI-Siloxane extinguished the heptane fire in 78 s. The results are shown in Figure 9. These observations, along with expansion ratio data, are summarized in Table 2. Some still shots from a video of this experiment are provided in Figure 10.

By adding a polysaccharide foam stabilizer ("MMI-Siloxane with additive"), the fire suppression rates of the MMI-Siloxane solution dramatically increased (20 seconds at 1.7 L/min). Further, the polysaccharide added MMI-Siloxane foam was able to quench the fire in 22 seconds compared to 18 seconds for C-6-based Reference AFFF formulation ("RefAFFF") at the same flow rate of 1.5 L/min. Further optimization of MMI-Siloxane formulation will be carried out in the future efforts to improve the performance of fluorine-free AFFF near to that of C6-RefAFFF foams.
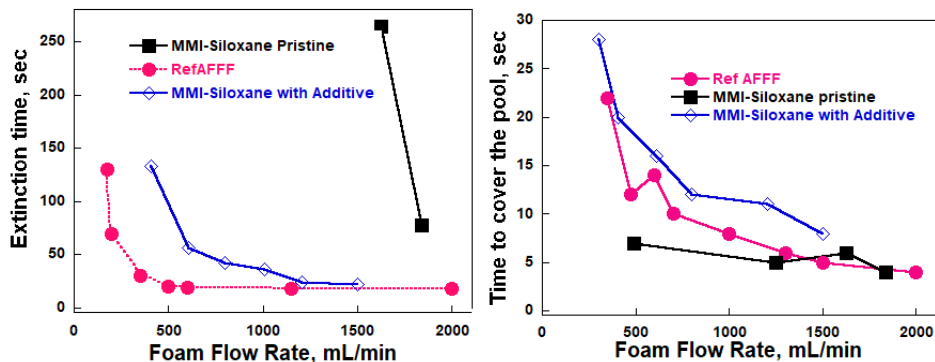
Figure 9. (A) Extinction time versus foam application rate (B) Time to cover the pool versus foam application rate.

The MMI-Siloxane solution showed a negative spreading coefficient over heptane and a positive spreading coefficient over cyclohexane. But still, the foam was able to flow over the heptane fuel and quench the heptane pool fire, albeit at a higher foam application rate compared to RefAFFF.

Table 2. Surface Tension Results

Parameter	MMI-Siloxane
Surface Tension	20.36
Interfacial Tension Heptane	0.58
Spreading Coefficient Heptane*	-1
Interfacial Tension Cyclohexane	0.60
Spreading Coefficient Cyclohexane*	4

*Calculated using measured surface tension values of 19.9 mN/m for heptane and 24.9 mN/m for cyclohexane at 19°C

Figure 10 shows MMI-Siloxane is able to knock down the fire significantly in **20 seconds,** but it could not seal the edges of the pool and extended time for complete extinction.
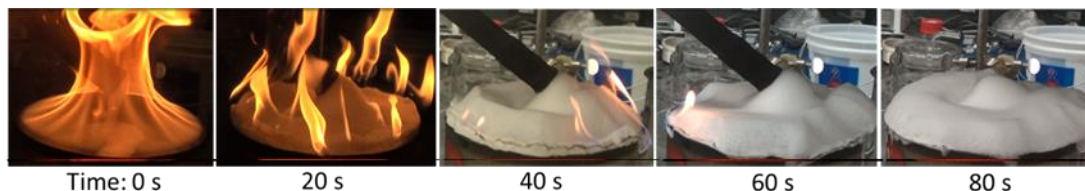

Figure 10. Comparison of heptane fire being extinguished by MMI-Siloxane foams at different times.

28-ft² fire suppression testing

28-ft² pool fire test was conducted using heptane as the fuel. After 10 seconds of a pre-burn period, the MMI-Siloxane with additive foam was sprayed on the fuel, and the fire extinguishing time was recorded. The snap-shots of the video as a function of time are provided in Figure 11. The data

showed that MMI-Siloxane formulation with additive was able to quench the flame in 59 seconds as compared to 31 seconds for C-6 AFFF formulation under the same application rates (2 gal/min).
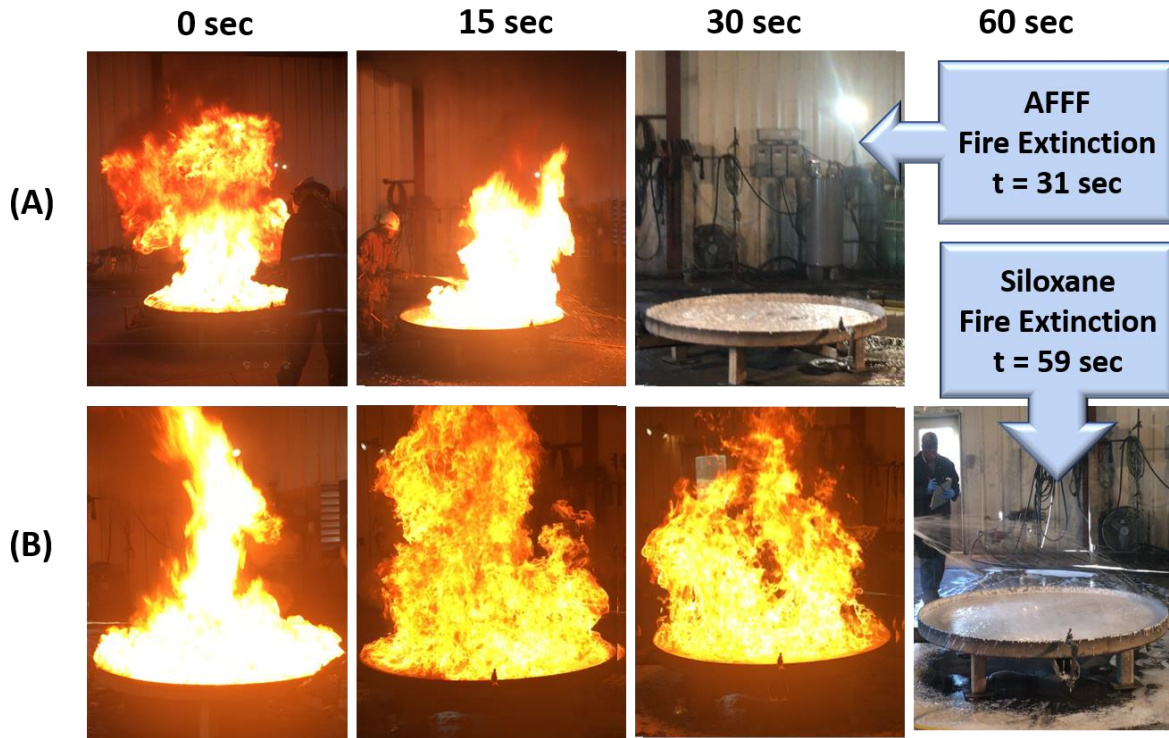

Figure 11. Time-lapse images were taken during large scale 1.83m (6 ft) diameter heptane pool fire suppression tests of (A) AFFF and (B) MMI-Siloxane with additive.

Within 60 seconds of the completion of the MMI-Siloxane solution (A total of 4 gallons) application, a burning pan was placed in the center of the pan ("ad hoc method"). The burn-back time was measured.

Figure 12. Burn-back testing images (A) AFFF and (B) MMI-Siloxane with additive after 2 minutes of the start of the testing. Siloxane formulation passed the "*ad hoc*" test with stability over 6 minutes.

The data were compared with AFFF formulation, and the potential of the proposed siloxanes to replace PFOA-based AFFF products was demonstrated in Figure 12. Figure 12 shows the burn back rates of AFFF and MMI-Siloxane with the additive formulation. The burn-back time for siloxane formulation was comparable to that of AFFF formulation (6 minutes).

The large scale 28 ft^2 fire performance data clearly demonstrated the potential of *siloxane surfactants with additives as a "drop-in" replacement* for bio-persistent AFFF formulations.

Biopersistance testing

The MMI-SILOXANE sample achieved **45% inherent biodegradation by day 28.** The test data are provided in Table 11.

Table 3. OECD 301B Test Data

pH	0 day	7.3 pH
Sample TOC determination	0 day	24.2 ppm
pH	28 day	7.0 pH
Bacterial concentration	28 day	370000 CFU/mL

The graph in Figure 13 provides the test chamber carbon dioxide measurement as the percent of theoretical maximum (%ThCO$_2$).
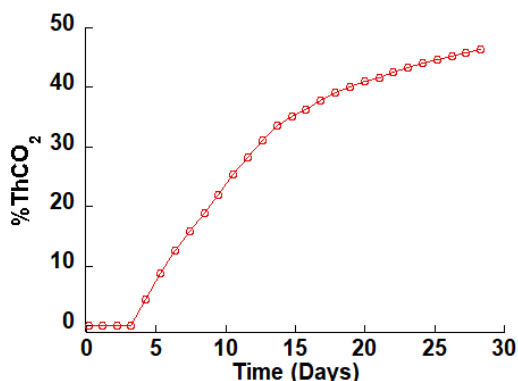

Figure 13. OECD 301B inherent biodegradation data

Conclusions and Implications for Future Research

➢ Trisiloxane surfactants have been synthesized and successfully tested for its AFFF capabilities, to enable the spontaneous formation of a water film on top of the fuel.
➢ The additives play a critical role in the extinction of fire and stability in water.
➢ The performance of trisiloxane surfactants are encouraging and has the potential to replace fluorine-containing AFFF.
➢ Further optimization of additive formulations will yield a fluorine-free formulation that can replace current AFFF.
➢ Future fire testing will be conducted with gasoline fuel (with and without alcohol).
➢ Future work will also involve long term stability test according to the MIL-STD.

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