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Additive Enhanced Siloxane Surfactants for Fire Fighting Foams

SERDP Project WP20-1540

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14. ABSTRACT

Polyfluorinated aqueous film-forming foams (AFFF) are typically used in the suppression of liquid fuel pool fires such as tank fires with crude oil or other hydrocarbon fuels. Since the polyfluorinated chemicals are stable to degradation, they have contaminated the soil and groundwater surrounding the site of application including military sites. In this seed project, a siloxane-based fluorine-free foam formulation was developed and its capability to quench gasoline pool fires was demonstrated. The data obtained in this effort indicated that the addition of selective foam stabilizing chemicals could enhance the fire fighting performance of siloxane surfactants. The fluorine-free formulations developed in the prior efforts have been optimized to meet the performance specifications of the fire extinguishing agent, aqueous film-forming foam (AFFF) liquid concentrate based on MIL-PRF-24385F standard specifications. The performance of siloxane surfactants were encouraging (extinction time 38s vs 30s for AFFF @ 2 gal/min). Further optimization of additive formulations will yield a fluorine-free formulation that can replace current AFFF.

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AFFF, Pool fire, surfactants, foams, siloxanes

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List of Acronyms

Acronym	Expanded Form
AFFF	Aqueous Film Forming Foam
APG	AlkylPolyGlucosides
COD	Chemical Oxygen Demand
DGME	Diethylene glycol monoethyl ether
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

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Abstract

Introduction and Objectives:

The objective of this project is to improve the fire-fighting efficiency of the siloxane surfactants based foam formulations towards meeting the performance of per and poly fluorinated alkyl substances (PFAS) containing Aqueous Film Forming Foam (AFFF) products.

Technical Approach:

In this project, low surface tension, fire quenching, and fluorine-free siloxane surfactants were developed. The siloxane surfactants produced stable foams when combined with selective additives. The feasibility of using siloxane surfactants for AFFF applications was assessed through benchtop trials using gasoline pool fire. Selective formulations were evaluated for large scale Mil-spec 28ft^{-}fire testing and aquatic toxicity.

Results:

Numerous commercial and proprietary siloxane surfactants (prepared in-house) were tested and the best performing surfactants were selected based on their firefighting performance and foam stability. It was determined that low surface tension of the surfactant alone does not guarantee foam formation or foam stability. The foam stability can be significantly improved with selective additives. The best performing foam formulations were selected from benchtop pool fire testing studies for 28ft^2 gasoline pool fire testing. The firefighting performance of siloxane surfactants was encouraging (extinction time 38s vs 30s for AFFF @ 2 gal/min with mil-spec aspirated nozzle) and has the potential as a “drop-in” replacement for AFFF.

Benefits:

PFAS-free firefighting foams have considerable financial, socio-economic, public health, and environmental advantages over bio-accumulative and toxic fluorochemical-based AFFFs. The new formulations developed in this effort will comply with environmental regulations while meeting the military-standard requirements. The initiative will eliminate the use of traditional AFFF formulations and provide the operational capabilities to military and first responders with a fluorine-free Class B foams in fighting against liquid fuels.

Executive Summary

Polyfluorinated aqueous film-forming foams (AFFF) are typically used in the suppression of liquid fuel pool fires such as tank fires with crude oil or other hydrocarbon fuels. Since the polyfluorinated chemicals are stable to degradation, they have contaminated the soil and groundwater surrounding the site of application including military sites. In this seed project, a siloxane-based fluorine-free foam formulation was developed and its capability to quench gasoline pool fires was demonstrated. The data obtained in this effort indicated that the addition of selective foam stabilizing chemicals could enhance the fire fighting performance of siloxane surfactants. In the proposed effort, the performance of siloxane surfactants developed in the prior SERDP effort was improved by optimizing the type and amount of foam stabilizing additives in the foam formulation. This work specifically addressed the FY 2020 STATEMENT OF NEED (SON) topic Number: WPSON-20-A1 of the Strategic Environmental Research and Development Program (SERDP) under the Weapons Systems and Platforms (WP) Program Area. The fluorine-free formulations developed in the prior efforts have been optimized to meet the performance specifications of the fire extinguishing agent, aqueous film-forming foam (AFFF) liquid concentrate based on MIL-PRF-24385F standard specifications. The performance of siloxane surfactants were encouraging (extinction time 38s vs 30s for AFFF @ 2 gal/min). Further optimization of additive formulations will yield a fluorine-free formulation that can replace current AFFF.

Introduction

Polyfluorinated aqueous film-forming foams (AFFF) are typically used in the suppression of liquid fuel pool fires such as tank fires with crude oil or other hydrocarbon fuels. Since the polyfluorinated chemicals are stable to degradation, they have contaminated the soil and groundwater surrounding the site of application including military sites [1,2,3]. Materials Modification, Inc. (MMI) has developed a siloxane-based fluorine-free surfactant-based fire fighting foam formulation capable of matching the performance of C-6 based AFFF albeit at a higher foam application rate (1 L/min vs 0.5 L/min) in a SERDP funded project (WP18-1638) [4]. The data obtained in this effort indicated that the addition of selective foam stabilizing chemicals could enhance the fire fighting performance of siloxane surfactants. In this project, the performance of siloxane surfactants developed in the prior SERDP effort was further improved by optimizing the type and amount of foam stabilizing additives in the foam formulation. This work specifically addressed the FY 2020 STATEMENT OF NEED (SON) topic Number: WPSON-20-A1 of the Strategic Environmental Research and Development Program (SERDP) under the Weapons Systems and Platforms (WP) Program Area [5]. The fluorine-free formulations developed in the prior efforts were optimized towards meeting the performance specifications of the fire extinguishing agent, aqueous film-forming foam (AFFF) liquid concentrate based on MIL-PRF-24385F standard specifications [6].

Objectives

The primary research objective of this project is to enhance the fire suppression efficiency of the selective siloxane surfactants with the help of a variety of foam stabilizing additives. The fire suppression performance of the additive mixed siloxane surfactants was tested to meet the performance requirements of the MIL-F-24385F standard. The improvement in the foam stability over hot gasoline was evaluated as a function of type and concentration of additives. Best performing additive-containing formulations were then used in lab-scale fire testing, and their fire suppression abilities were measured. Based on the lab-scale tests, the potential additives mixed siloxane formulation were evaluated using $28ft^2$ pool fire testing.

Background:

Aqueous film forming foam (AFFF) is the conventional method used by military and first responders to fight against hydrocarbon fuel fires. AFFFs formulation uses polyfluorinated chemicals to reduce the surface tension of water and forms a stable foam [1-5] on top of the burning fuels. Polyfluorinated surfactants have inert chemical-bonds (carbon-fluorine) and are not degraded in the environment (“forever chemicals”). Their bio-persistence in the atmosphere has increased the potential of them turning into health hazards. Therefore, the chemical industry and the US Government are focusing on reducing exposure of humans and animals to these AFFF chemicals [7] through regulations and stopping production of these chemicals. The fluorinated surfactants (PFOA and PFOS) that were used in the traditional AFFF formulations which are explicitly mandated by MIL-F-24385F have been discontinued by the manufacturers and banned by Environmental Protection Agency under EPA’s 2010/15 PFOA Stewardship Program [8].

Therefore, MMI and other groups are working to develop safe alternatives to polyfluorinated AFFFs [9].

The most critical issue in finding a fluorine-free solution is that any AFFF used by the US military must meet the requirements provided in Military Specification MIL-F-24385F. Developing new formulations that will satisfy the fire protection standard requirements and be environmentally friendly will require improvement of the stability of fluorine-free foams. In this project, siloxane surfactants developed in the prior SERDP funded effort were mixed with selective foam stabilizers and enhancement in their fire suppression efficiency were evaluated.

Siloxane-based surfactants

The siloxane-based surfactants have been used to form low surface energy aqueous solutions. They are typically used in the aqueous wetting of hydrocarbon surfaces [10,11,12]. Specifically, trisiloxane surfactants were able to reduce the surface tension of water down to 20 mN/m. In comparison, typical hydrocarbon chain surfactants could reduce the surface tension of water only to 30-45 mN/m range [10].

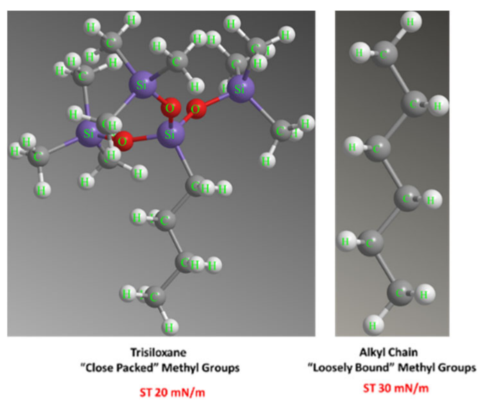

Figure 1. Chemical structure of trisiloxane (cluster of methyl groups) and long alkyl chain group (Single methyl group) of surfactants

The low surface tension value of siloxane surfactants is achieved by the close-packed array of methyl groups, as shown in Figure 1 [10]. The siloxane backbone is flexible and is amenable to orient the molecules to form flat layers on the surface of the water, exposing the low surface energy methyl groups to the air or gasoline. Such a parallel orientation of the molecules with respect to the water allows for a relatively large surface area coverage with low critical micelle concentrations (cmc) [10]. Guoyong *et al.* synthesized new carbohydrate-modified siloxane surfactants and studied their behavior in aqueous solution [13]. Their work demonstrated that siloxane surfactants could exhibit surface tension 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. Blunk *et al.* demonstrated the potential of siloxane containing formulations use in pool fire suppression applications [14].

However, in order to meet the MIL-STD requirement, the organosilicon surfactant should have oleophobicity (low surface tension), high surface activity, foamability, foam stability and be environment-friendly. These aspects need to be investigated further to arrive at a formulation that can satisfy all the requirement of AFFF Milspec MIL-F-24385.

MMI has synthesized several siloxane surfactants and procured commercially available siloxane wetting agents such as Dowsil®, SilRes® and Silwet® L-77, and evaluated their surface tension, stability in water, spreading parameters, film formation ability, foam formation, and stability on top of hot heptane (60°C) [15]. In this project, low surface tension trisiloxane groups containing precursors were reacted with the various hydrophilic groups (marked as 'X' in Figure 2) containing compounds, including glucuronic acid, glucosamine hydrochloride, and glycidol. All these compounds exhibited lowering of surface tension of water <20 mN/m. However, their foam stability was poor when applied onto hot gasoline. These results and other published literature suggested that surface tension reduction is not the only criteria for achieving superior fire foams. Foam stability on fuel fire is critical in improving the fire suppression efficiency of fluorine-free foams. In this project, a proprietary siloxane surfactant along with selective additives (labeled as "MMI-Siloxane") was selected for fire extinction and foam stability evaluation tests.

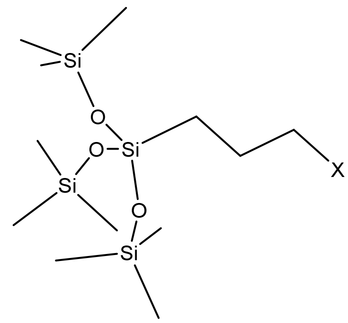

Figure 2. Chemical structure of tris(trimethylsiloxy)silane with hydrophilic group X.

Materials and Methods:

Materials

Siloxane precursors and water-soluble additives were purchased from Sigma Aldrich. Siloxane surfactants were synthesized in-house. Gasoline fuel was purchased from Merrifield Citgo or Costco, Fairfax, VA gas stations.

Surface Tension Measurements

Surface tension and the interface surface tension of the foam formulations were measured using the pendant drop method. Rame-hart Model 250 goniometer/tensiometer was used to collect the surface tension data. About 2 mL of the test liquid was delivered through a Teflon needle into an external atmosphere (air), and the liquid drop image was recorded and analyzed using DROPimage Advanced software. The surface tension of the test formulation will be obtained from the data collected from a drop in air.

Benchtop Fire Testing

Benchtop fire testing experiments were conducted following the method developed by Hinnant *et al.* [16] as provided in Figure 3. A 25-micron sparger was used as a controlled foam generating system with a dish containing water and a gasoline (procured from a local gas station) fuel layer. The foam can be generated at a rate of 0.5-2 L/min with an airflow controller and was applied to a 1 cm layer of gasoline on the 19 cm diameter glass dish. The flame was lit and allowed to preburn for 1 minute before applying the fluorine free foam. A video was recorded, and the extinguishing time was measured in seconds.

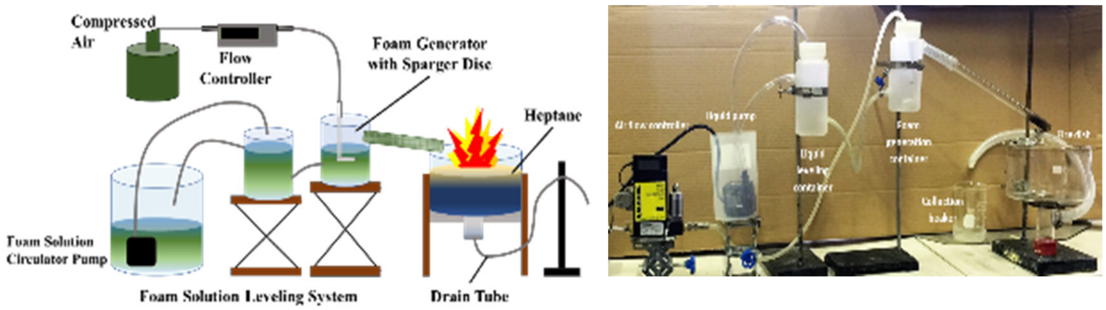

Figure 3. Experimental setup of small scale pool fire testing foams

In-house design and construction of aspirated foam sprayer

MMI's siloxane foams were able to quench both heptane and gasoline fuels within 60 seconds in benchtop fire testing. Based on the 28ft^2 fire testing performance data, efforts were focused on reducing the quench time by fine-tuning the formulations for foamability, foam expansion ratio, and concentration of the active ingredients in the foam formulations.

The quality and properties of the foam generated from the in-house benchtop using sparger for foam generation and 28-ft^2 fire testing are very different and influenced the firefighting results. Therefore, we were interested in developing form generation in-house mimicking the foam generation using a Mil-Spec aspirating nozzle.

A typical Mil-spec aspirated foam sprayer nozzle comprised of 6 parts: the foam solution body, a jet, a receiver, an air-inlet, and a porous aluminum disc. The foam solution was pressurized and pushed through the jet and receiver, where it then becomes aerated in the air-inlet. Once the solution becomes aerated, it comes into contact with the porous disc causing turbulent flow. The combination of aeration and turbulent flow generates foam. A similar foam spray system was built from a Pressurized Beer Mini Keg System. Figure 4 displays the nozzle attached to a pressurized vessel, which ws used for measuring the expansion ratio of foam solutions as well as bench-scale fire testing instead of using the sparger to generate foams.

Figure 4. Foam sprayer apparatus.

The foam sprayer apparatus was tested with a baseline AFFF foam solution of 3% PHOS-CHEK C6 and used with all fluorine free foams evaluated in this effort.

Large scale Mil-spec Fire Testing

Large-scale fire testing was conducted according to the method described in the MIL-PRF-24385F standard. This task was performed at Chesapeake Bay Detachment, U.S. Naval Research Laboratory, Chesapeake Beach, MD. The typical fire test was conducted using a circular pan 6 ft in diameter as provided in Figure 5.

Figure 5. Photograph of 28 ft^2 pool fire testing pan with burnback fire in the middle

The fluorine free foam was applied on the burning fuel using a Mil-spec aspirated nozzle at a rate of 2 gal/min. 10 gallons of unleaded alcohol-free gasoline was used as the test fuel. The fire was started by igniting and allowed to burn for 10 seconds. After 10 seconds of a preburn period, the foam was applied, and the fire extinguishing time was recorded. Within 60 seconds of the completion of the application of our foam, a burning pan was placed in the center of the pan. The burn-back time was recorded.

Technical Approach

Several fluorine-free foams (F3) are available in the market today for a variety of fire-fighting applications [3] and they degrade quickly in the environment. However, they do not meet the performance goals of MIL-PRF-24385 standard [17]. In this project, a promising foam formulation based on siloxane surfactant was evaluated for performance enhancement using specific additives with the aim of meeting the military standard.

Results and Discussion

Preparation of foam formulations with additives

The foam solutions were prepared by dissolving MMI-Siloxane surfactant and selective additives such as commercially available trisiloxanes (wetting agents), chitosan, APG-Glucopon, Xanthan gum and polyethylene glycol in distilled water. 1% acetic acid was added to chitosan-based formulations to keep the chitosan in solution. The formulations were left to stir until they were ready for fire testing. The surface tension of 1% solution of the siloxane surfactant was 19-20 mN/m. The surface tension was increased up to 26 mN/m upon the addition of selective additives.

Mixing of MMI-Siloxane with commercial trisiloxanes did not fill the dish during fire testing and was discontinued from further testing. Benchtop fire testing of several additives with MMI-Siloxane are provided in Table 3. The data clearly indicate the strong influence of additives on the fire quenching performance of the MMI-Siloxanes.

Table 1. Benchtop fire testing data of MMI-Siloxane with various additives

Sample #	Formulation	Expansion Ratio	Dish fill time (s)	Quench time (s)	ST (mN/m)	pH
Ref.	3% C6 on GAS	7.5	5	14	16.54	6.5
1	MMI-SILOXANE 0.2% Xanthan gum	16.1	7	135	18.99	6.0
2	MMI-SILOXANE	14.7	8	300	19.61	6.0
3	MMI-SILOXANE 0.1% Chitosan	8.1	7	142	19.71	4.0
4	MMI-SILOXANE 0.2% Chitosan	7.1	8	182	19.73	4.0
5	MMI-SILOXANE 0.4% Chitosan	8.6	9	280	19.35	5.0
6	MMI-SILOXANE 0.8% Chitosan	9.6	9	304	19.77	5.5
7	MMI-SILOXANE 0.2% Polyethylene Glycol	12.5	12	184	19.50	6.5
8	MMI-SILOXANE 0.8% Polyethylene Glycol	13.2	10	216	19.80	6.0
9	MMI-SILOXANE + Proprietary additives	12.5	7	42	18.94	7.0
10	MMI-SILOXANE + Proprietary Additives	11.6	6	32	20.01	7.0

In addition to above additives, four foam solutions containing MMI-siloxane solution were also prepared using Glucopon (AlkylPolyGlucosides, APG) as additive. The compositions (labeled as APG-n) of each solution are shown in

Table 2. Each foam solution was submitted to bench scale fire testing on gasoline at a foam flow rate of 1 L/min. The extinction times data is compiled in Table 3. From the data provided in Table 1 and Table 3, the best formulation was selected for large scale 28ft^2 fire testing at the NRL facility.

Table 2. Compositions of Alkylpolyglucosides (APG) Additive foam solutions.

Solution	MMI-Siloxane %	Glucopon %	DGME %	Cellulose Derivative
APG-1	3	0.8	-	-
APG-2	3	0.8	0.6	-
APG-3	3	0.8	-	0.1
APG-4	3	0.8	-	0.2

Table 3. Fire testing data for Alkylpolyglucosides (APG) Additive foam solutions

Solution	Expansion ratio	Dish fill time (s)	Extinction time (s)
APG-1	11.6	6	87
APG-2	12.2	6	142
APG-3	11.9	7	27
APG-4	10.4	18	213

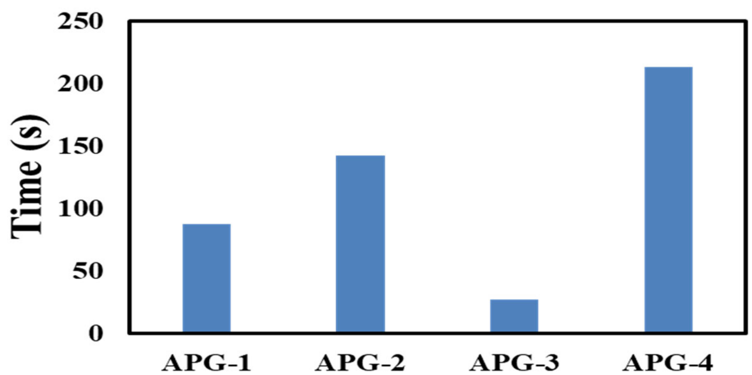

Figure 6. Extinction time for APG foam solutions.

The time lapse images of the fire testing are provided in Figure 7.

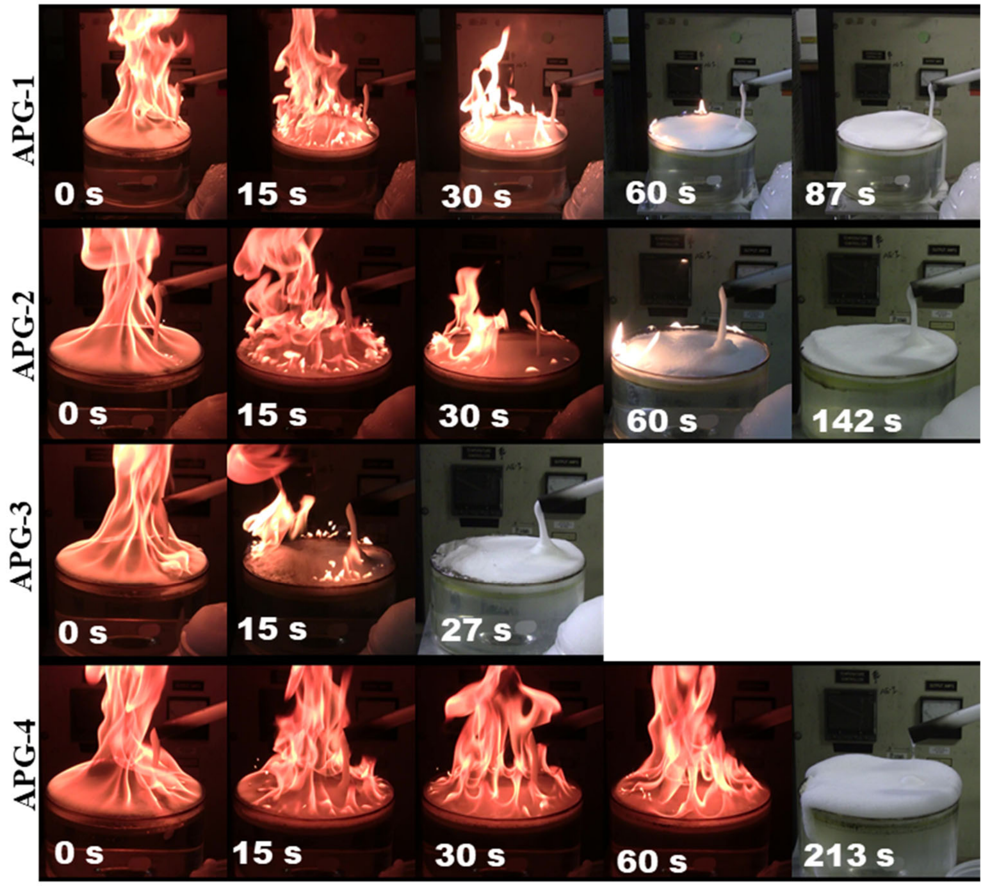

Figure 7. Time-lapse photographs of APG foam fire testing

28ft^2 Fire Testing with Gasoline Fuel

28-ft^2 fire test was conducted using gasoline as the fuel at Naval Research Laboratory-Chesapeake Bay Detachment (NRL-CBD) in Chesapeake Beach, MD. After 10 seconds of a pre-burn period, the MMI-siloxane-based foam formulation was sprayed on the burning gasoline fuel, and the fire extinguishing time was recorded. The snap-shots of the video as a function of time are provided in Figure 8. Time-lapse images were taken during 28ft^2 gasoline pool fire suppression tests of (A) AFFF and (B) MMI foam. The data showed that MMI-Siloxane formulation with additive was able to quench the flame in 57 seconds as compared to 30 seconds for C-6 AFFF formulation under the same application rates (2 gal/min).

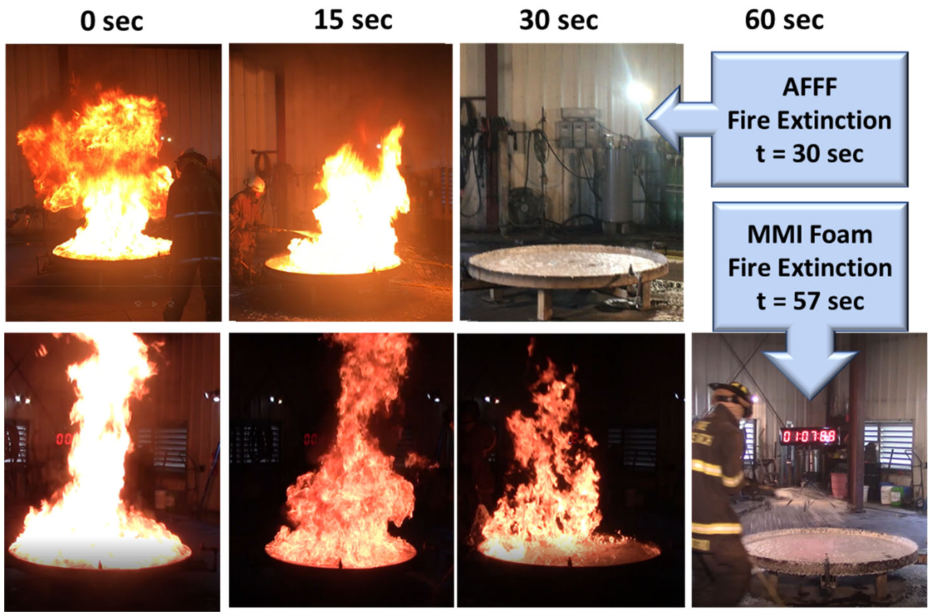

Figure 8. Time-lapse images were taken during 28ft^2 gasoline pool fire suppression tests of (A) AFFF and (B) MMI foam

Large scale fire testing using optimized formulations

Further development of formulations and additives along with the fire extinction data are provided in Table 4. Fluorine Free Foam Formulations and 28-ft2Fire Testing Data. The new formulations were tested against both Gasoline and Jet fuels. Photographs of the fire testing on Gasoline fuel are provided in Figure 9. Time-lapse images were taken during 28ft^2 gasoline pool fire suppression tests of AFFF and MMI-Siloxane foams (38 seconds quench time)

Table 4. Fluorine Free Foam Formulations and 28-ft^{2}Fire Testing Data

Composition	MMI-Siloxane /Additive Ratio	Expansion Ratio	Fuel	Extinction Time (s)	25% Burnback Time (min)
1-1	4	3.5	Gasoline	**57**	**11.09**
2-1	4	3.7	Gasoline	**45**	**12.28**
2-2	4	3.7	Jet Fuel	**21**	**12.05**
2-3	6	4.3	Gasoline	**38**	**12.21**
2-4	12	5.2	Gasoline	**60**	**4.56**

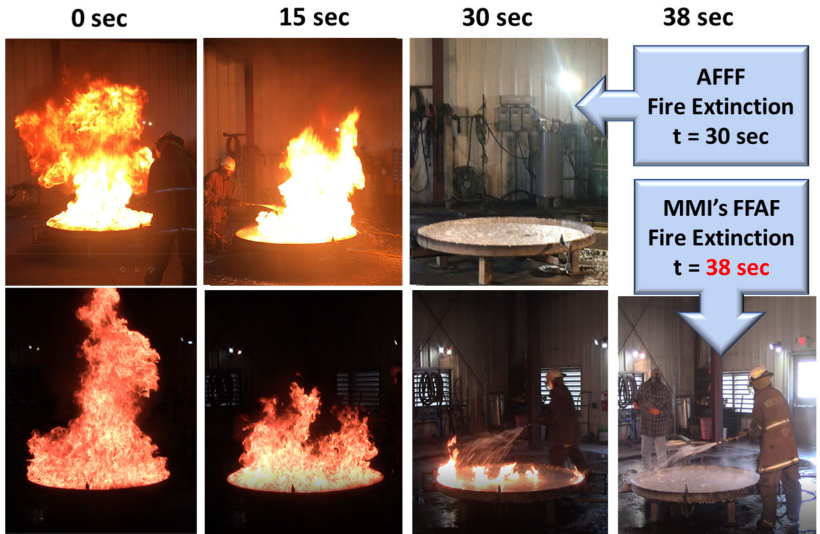

Figure 9. Time-lapse images were taken during 28ft^2 gasoline pool fire suppression tests of AFFF and MMI-Siloxane foams (38 seconds quench time)

The fire extinction time was much less for Jet Fuel (21 s) compared to Gasoline fuel (45 s) for the same MMI-Siloxane formulation as expected. Increasing the expansion ratio of the foams from 3.7 to 4.3 decreased the fire quenching time from 45 seconds to 38 seconds. This was achieved by changing the MMI-Siloxane to the additive ratio. The siloxane-to-additive ratio has to be optimum to achieve higher firefighting performance. For example, increasing the ratio to 12 detrimentally affected the firefighting performance (60 seconds). In future efforts, further optimization of the formulation will be conducted to reach the goal of 30-sec quenching with gasoline fuel. Interestingly, all the formulations exhibited excellent burnback performance with a maximum 12 minutes (720 seconds) for 25% of the flash fire.

Toxicity Testing

Plant and animals in water are the ones that are most likely to be affected by exposure of fire-fighting foam formulations. Therefore, analyzing the aquatic toxicity is an good indicator of the relative toxicity of newly developed foam formulations. OECD 203 is an acute toxicity test similar to ASTM E729 tested using different fish species [18,19]. This test was conducted at EnviroScience Inc, Stow, OH. According to standard testing for OECD 203, a selected species of fish was exposed to the foam formulation for a period of 96 hours. Mortalities of fish was recorded at 24, 48, 72, and 96 hours, and the concentrations that kill 50% of the fish was determined. Acute (short term) and chronic (long term) toxicity are typically expressed as EC50 (Effective Concentration 50), LC50 (Lethal Concentration 50). Typical AFFF formulations have LC50 value of 884-1500 mg/L (Practically non-toxic). Commercially available fluorine free formulations exhibited LC50 toxicity in the range 65-180 (slightly toxic to non-toxic) probably due to higher concentrations of hydrocarbon surfactants and solvents in order to compensate for the lack of film formation. MMI-Siloxane-based formulation exhibited LC50 value of 456 mg/L (Practically nontoxic based on Fish and Wildlife Service (FWS) Scale [20]. The MMI-Siloxane LC50 data obtained is from only preliminary data and will require further investigation to determine the long-term toxicity of the formulations.

Conclusions and Implications for Future Research and Benefits

Numerous commercial and proprietary siloxane surfactants (prepared in-house) were evaluated for firefighting performance and foam stability. It was determined that low surface tension of the surfactant alone does not guarantee foam formation or foam stability. The foam stability can be significantly improved with selective additives. The best performing foam formulations were selected from benchtop pool fire testing studies for 28ft^2 gasoline pool fire testing. The firefighting performance of siloxane surfactants was encouraging (extinction time 38s vs 30s for AFFF @ 2 gal/min with mil-spec aspirated nozzle) and has the potential as a "drop-in" replacement for AFFF.

Literature Cited

1. Department of Defense Alternatives to Aqueous Film Forming Foam Report to Congress, https://www.denix.osd.mil/derp/home/documents/alternatives-to-aqueous-film-forming-foam-report-to-congress/
2. X. Lim, Tainted water: the scientists tracing thousands of fluorinated chemicals in our environment, Nature **566**, 26-29 (2019) doi: 10.1038/d41586-019-00441-1
3. Fluorine-Free Firefighting Foams (F3) Viable Alternatives To Fluorinated Aqueous Film-Forming Foams (AFFF) Ipen Stockholm Convention POPRC-14RomeSeptember 2018 https://cswab.org/wp-content/uploads/2018/09/Fluorine-Free-Foams-IPEN-Paper-POPRC-14-Sept-2018-FINAL.pdf
4. Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes, Materials Modification Inc, WP18-1638, https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP18-1638
5. https://www.serdp-estcp.org/content/download/45801/426898/file/FY19 Instructions SEED BAA.pdf
6. R.S. Sheinson, B.A. Williams, C. Green, J.W. Fleming, R. Anleitner, S. Ayers, A. Maranghides, D. Barylski, The future of aqueous film forming foam (AFFF): Performance parameters and requirements https://www.nist.gov/document-8291
7. Agency for Toxic Substances and Disease Registry,Toxicological Profile for Perfluoroalkyls, Draft for Public Comment, June 2018, ch. 5, https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=1117&tid=237
8. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/pfoa-stewardship-program-baseline-year-summary-report
9. https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Contaminated-Groundwater-SONs/Innovative-Approaches-to-Fluorine-Free-AFFF-2018/(language)/eng-US
10. Snow, S. A.; Fenton, W. N.; Owen, M. J., Synthesis and characterization of zwitterionic silicone sulfobetaine surfactants. *Langmuir* 1990, *6* (2), 385-391.
11. Gentle, T. E.; Snow, S. A., Adsorption Of Small Silicone Polyether Surfactants At The Air/Water Interface. *Langmuir* 1995, *11* (8), 2905-2910.
12. He, M.; Lin, Z.; Scriven, L. E.; Davis, H. T.; Snow, S. A., Aggregation Behavior And Microstructure Of Cationic Trisiloxane Surfactants In Aqueous-Solutions. *Journal of Physical Chemistry* 1994, *98* (24), 6148-6157.

13. W. Guoyong, D. Zhiping, L. Qiuxiao, and Z. Wei, Carbohydrate-Modified Siloxane Surfactants and Their Adsorption and Aggregation Behavior in Aqueous Solution, J. Phys. Chem. B 2010, 114, 6872– 6877
14. D. Blunk, R.H. Hetzer, A. Sager-Wiedmann, K. Wirz, Siloxane-containing fire extinguishing foam, US Patent Application # US 2014/0306141 (2014)
15. Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes, Materials Modification Inc, WP18-1638, https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Waste-Reduction-and-Treatment-in-DoD-Operations/WP18-1638
16. K.M. Hinnant, S.L. Giles, A.W. Snow, J.P. Farley, J.W. Fleming, R. Ananth, An Analytically Defined Fire-Suppressing Foam Formulation for Evaluation of Fluorosurfactant Replacement, *Journal of Surfactants and Detergents*, **21,** 711-722, (2018); DOI: 10.1002/jsde.12166
17. MIL-PRF-24385, Fire Extinguishing Agent, Aqueous Film-Forming Foam (AFFF) LiquidConcentrate, for Fresh and Sea Water https://quicksearch.dla.mil/qsDocDetails.aspx?ident_number=17270
18. ASTM E729 - 96(2014) Standard Guide for Conducting Acute Toxicity Tests on Test Materials with Fishes, Macroinvertebrates, and Amphibians
19. EPA, 2006a. Fathead Minnow (*Pimephales promelas*) Larval Survival and Growth Toxicity Test, EPA-833-C-06-001. December 2006.
20. AFRL-ML-TY-TR-2003-4524, Aquatic Toxicity Screening of Fire Fighting Agents;2003 Report