Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes

Project Number WP18-1638

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14. ABSTRACT
The primary technical objective was to develop a fluorine-free surfactant formulation as a “drop-in” replacement for AFFF.
•Identification of specific carbohydrate functionalized siloxanes and evaluate their use in AFFF that could potentially replace fluorinated surfactants.
•Spreading coefficient and Benchtop fire suppression testing to downselect the formulations and additives.
•28-ft² fire performance to demonstrate the potential of the formulation to meet the MIL-F-24385F standard and biodegradability.

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Project Team

- Kris Rangan- Materials Modification Inc.
- Jerry Back – Jensen Hughes
- John Farley – NRL
- Ramagopal Ananth - NRL

Background

- **Project Period: September 2018- September 2019**
- **Statement of Need (SON) Number #: WPSON-18-L**

➢ **Aqueous film forming foams (AFFFs) containing perfluoro octanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been traditionally used by the Department of Defense in fuel fire suppression operations.**

➢ **These chemicals have strong chemical bonds and are considered as persistent, bio-accumulative and toxic (PBT) substances. PFOS/PFOS chemicals have been detected around the world in the food chain, drinking water, animals and human blood.**

➢ **Environmental Protection Agency, (EPA) is regulating the chemical industry for the complete elimination of PFOA and PFOS chemicals by 2015. Therefore, the Department of Defense is seeking fluorine-free compounds to replace PFOA/PFOS in firefighting foam formulations.**

➢ **In this effort, siloxane-based surfactants were synthesized, and their chemical stability, physical and fire suppression abilities were evaluated. The tests included the evaluation of spreading coefficient, Benchtop fire testing, 28-ft² pool fire performance, and biodegradation.**

Technical Objectives

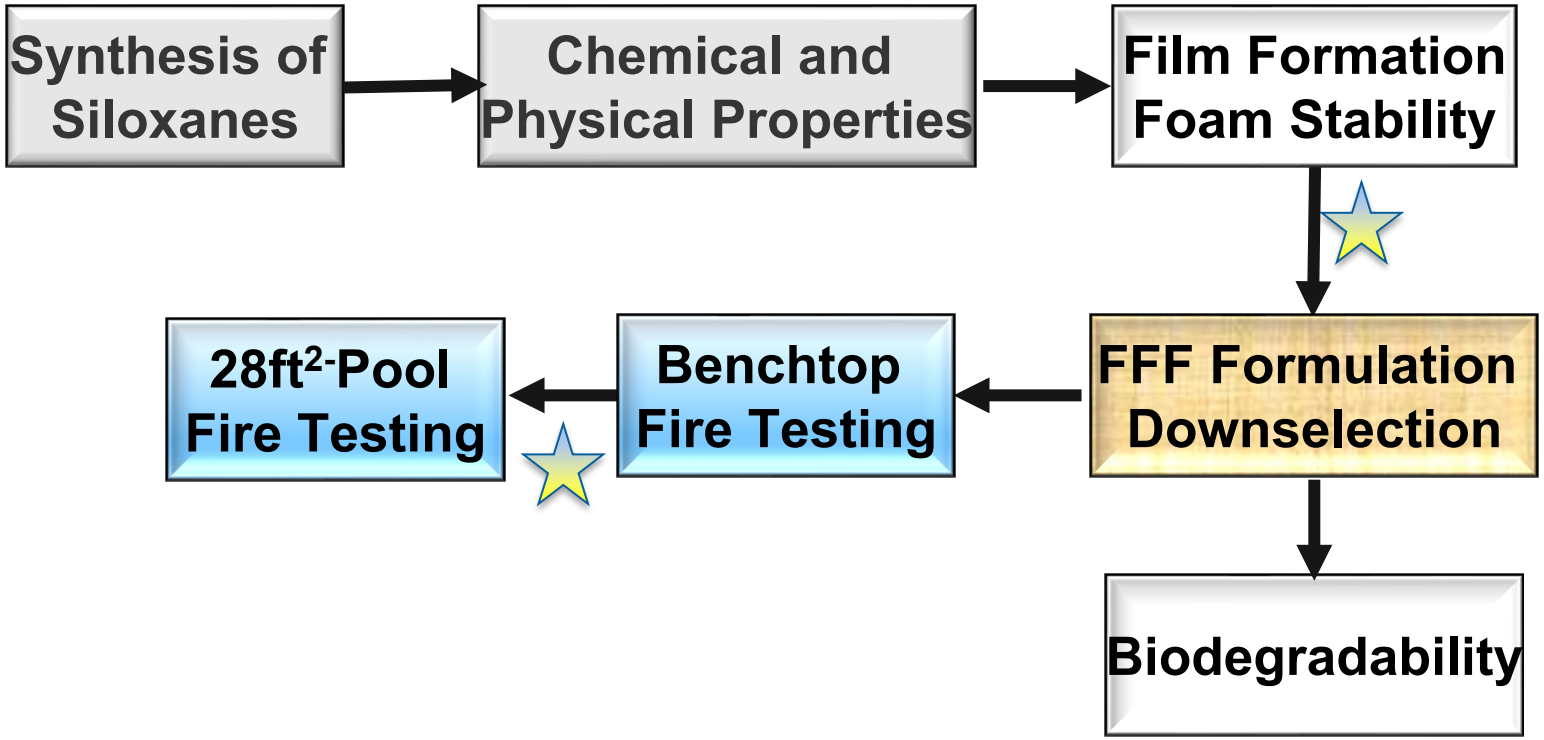
The primary technical objective was to develop a fluorine-free surfactant formulation as a "drop-in" replacement for AFFF.

- **Identification of specific carbohydrate functionalized siloxanes and evaluate their use in AFFF that could potentially replace fluorinated surfactants.**

- **Spreading coefficient and Benchtop fire suppression testing to downselect the formulations and additives**

- **28-ft² fire performance to demonstrate the potential of the formulation to meet the MIL-F-24385F standard., and biodegradability**

Technical Approach



Results

- **Methods and Techniques used**
  - **Surface Tension**
  - **Spreading Parameters on cyclohexane**
  - **Foam formation and Stability over hot heptane**
  - **Benchtop (19-cm) pool fire testing**
  - **28ft^2 pool fire testing**
  - **OECD 301B - Biodegradability**
- **Trisiloxane surfactants have been synthesized and the best surfactant was down selected based on their hydrolytic stability.**
- **Demonstrated the spontaneous formation of a water film on top of the fuel.**
- **Additives to siloxane play a role in the extinction of fire and water stability.**
- **The performance of trisiloxane surfactants are encouraging (extinction time 59s vs 30s for AFFF @ 2 gal/min) and has the potential as a "drop-in" replacement for AFFF.**
- **Further optimization of additive formulations will yield a fluorine-free formulation that can replace current AFFF**

Next Steps

- Completed all the tasks proposed originally in the proposal including 28ft^2 fire testing.
- All future work will be conducted using Gasoline instead of heptane as a fuel.
- Sealing the edges of the pool fire and opening of the foam seal from the quenched area needs to be addressed closely with better seal forming additives, without compromising on the other physical properties such as viscosity and surface tension.
- Economics of large scale production and long term stability of formulations need to be evaluated.

Technology Transfer

- **Present the results of our findings at all meetings and conferences related to elimination of PFOA/PFOS.**
- **Prepare a Technology Fact Sheet that highlights the key findings of our work**
- **Provide the contents of the fact sheet including video of our 28ft^2 test as a weblink on the matmod.com website for easy access.**
- **Publish a technical paper with our findings in a journal that focuses on the chemistry issues associated with the development of fluorine free compounds for AFFF applications**

Key Points

- MMI clearly demonstrated that it was possible to develop a fluorine free formulation based on siloxanes for AFFF applications
- MMI was able to provide a foam for testing that used the standard 2 gpm nozzle
- MMI clearly demonstrated that the materials developed were non toxic and met the requirements for biodegradability
- MMI demonstrated that it can put out the flame in 59 seconds during the 28 ft^2 test
- MMI demonstrated that the foam formulations are stable enough to withstand fire and seal the fuel by passing of burn back test.

Future Research

- Based on our SEED project, MMI believes that further research is warranted to reduce the time of fire suppression from 59 sec to 30 seconds.
- MMI proposes that this reduction can be achieved by the use of appropriate surfactants and additives and their ratios within the synthesized formulation without compromising on the spreading characteristics .
- Conduct all the fire testing experiments with Gasoline instead of heptane and saltwater
- MMI needs to evaluate the long term stability of the system for use after long periods of storage.
- ROM for this effort or 24 months will be about $ 1.2 million including scale up and field testing.

Publications

- K. Rangan, N. Patel, J. Coppage-Gross and T.S. Sudarshan, Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes, Poster # 109, SERDP & ESTCP Symposium, November 28, 2018.
- K. Rangan, J. Terrazas and T.S. Sudarshan Eco-Friendly Aqueous Film Forming Foams, Poster # 244 SERDP & ESTCP Symposium, December 4, 2019
- Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes, Project Number, SERDP WP18-1638, Final Project Report, 2019.

Supporting Material

Project Funding

	FY18		
Funds received to date ($K)	158073		
% Expended	199970		
Funds Remaining ($K)	-41897		

WP18-1638: Fluorine Free Aqueous Film Forming Foams Based on Functional Siloxanes

Performers: Materials Modification Inc

Technology Focus

- *Development of fluorine-free foams for "drop-in" replacement for AFFF*

Research Objectives

- **The primary technical objective of this proposal was to develop a fluorine-free surfactant formulation for use in AFFF.**

Project Progress and Results

- **Specific functionalized siloxane surfactants that could potentially replace AFFF were synthesized. The fire suppression performance of the proposed siloxanes were to meet the performance requirements of the MIL-F-24385F standard. The testing ncluded lab-scale physical properties measurement and fire-test, t28-ft² fire performance, spreading coefficient, and bio-persistency.**

Technology Transition

- *Optimization of the fluorine-free formulation for gasoline fuel pool fire suppression with in 30 seconds.*