FINAL REPORT

Hollow Microspheres Based Fire Fighting Foams

SERDP Project WP20-1533

APRIL 2022

Krishnaswamy Rangan
Materials Modification Inc.

SERDP
DOD ▪ EPA ▪ DOE

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 15/04/2022	**2. REPORT TYPE** SERDP Final Report	**3. DATES COVERED** *(From - To)* 12/9/2020 - 12/9/2022

4. TITLE AND SUBTITLE Hollow Microspheres Based Fire Fighting Foams	**5a. CONTRACT NUMBER** 21-P-0009
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Krishnaswamy Rangan	**5d. PROJECT NUMBER** WP20-1533
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Materials Modification Inc.
2809-K MERRILEE DR
FAIRFAX, VA 22031

8. PERFORMING ORGANIZATION REPORT NUMBER
WP20-1533

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and Development Program (SERDP)
4800 Mark Center Drive, Suite 16F16
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
WP20-1533

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The use of firefighting foam containing per- and polyfluorinated alkylated substances (PFAS) led to the contamination of soil, ground and surface water across the US including manufacturing sites and Department of Defense bases. PFAS and their degradation products are bio-accumulative and toxic. PFAS chemicals are difficult to remove from contaminated water or soil, because there is no known degradation for perfluorinated substances in these sites. The objective of this Limited Scope Research work was to develop a PFAS-free formulation based on hollow glass microspheres and evaluate their application in extinguishing pool fire that could potentially replace polyfluorinated aqueous film forming foams (AFFF).

15. SUBJECT TERMS
AFFF, bio-accumulative, C-8, Fire, foam, fuel, hollow glass microspheres, persistant, PFAS, PFOA, PFOS, Siloxane, surfactant

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Krishnaswamy Rangan
UNCLASS	UNCLASS	UNCLASS	UNCLASS	39	**19b. TELEPHONE NUMBER** *(Include area code)* (703) 560-1371

Table of Contents

List of Tables

List of Figures

List of Acronyms

Acronym	Expanded Form
AFFF	Aqueous Film Forming Foam
APS	Ammonium persulfate
DoD	Department of Defense
EPA	Environmental Protection Agency
FAA	Federal Aviation Authority
HGM	Hollow Glass Microsphere
MMI	Materials Modification, Inc.
MTMS	Methyltrimethoxysilane
NMR	Nuclear Magnetic Resonance Spectroscopy
NRL	U.S. Naval Research Laboratory
OECD	Organization for Economic Co-operation and Development
PBT	Persistant, Bio-accumulative, Toxic
PFAS	Per/polyfluoroalkyl substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PI	Principal Investigator
POC	Point of Contact
PVA	Poly Vinyl Alcohol
PVB	Poly Vinyl Butyral
PVP	Poly Vinyl Pyrrolidone
PEG	Poly Ethylene Glycol
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
TEMED	N,N,N′,N′-tetra methyl ethylene diamine
TEOS	Tetraethyl Silicate
WP	Weapons Systems and Platforms

Keywords
AFFF, bio-accumulative, C-8, Fire, foam, fuel, hollow glass microspheres, persistant, PFAS, PFOA, PFOS, Siloxane, surfactant

Acknowledgments

We thank the support of program manager Dr. Robin Nissan, Strategic Environmental Research and Development Program (SERDP) of the U.S. Department of Defense, for having faith in us to deliver a better understanding of PFAS-free foams that could be a potential replacement for AFFF. We acknowledge the assistance of Braxton V. Lewis and various members of the Noblis team for always responding to queries and providing valuable advice in executing the programs in a timely manner. *The opinions or assertions contained herein are the private views of the authors and are not to be construed as official or as reflecting the views of the DoD.*

Abstract

Introduction and Objectives

The use of firefighting foam containing per- and polyfluorinated alkylated substances (PFAS) led to the contamination of soil, ground and surface water across the US including manufacturing sites and Department of Defense bases. PFAS and their degradation products are bio-accumulative and toxic. PFAS chemicals are difficult to remove from contaminated water or soil, because there is no known degradation for perfluorinated substances in these sites. The objective of this Limited Scope Research work was to develop a PFAS-free formulation based on hollow glass microspheres and evaluate their application in extinguishing pool fire that could potentially replace polyfluorinated aqueous film forming foams (AFFF).

Technical Approach

AFFF products used in fuel fire-fighting are made up of air bubbles dispersed in a continuous aqueous medium. The AFFF replacement PFAS-free products lack the foam stability which is critical for the functioning of fire quenching foams. If the air bubbles of PFAS-free products are made up of solids, they can form "extremely stable" foams on top of hot fuel. Hollow glass microspheres are stable solids which are also of low density like air bubbles. Therefore, PFAS-free foam formulations can be made using HGMs. In this project, the fire suppression performance of the HGM containing formulations were tested to meet the firefighting performance requirements of the MIL-F-24385F standard. The film-forming and fire suppression abilities of the hollow microsphere foams were evaluated. The tests included foam stability over hot fuel and benchtop fire suppression test. Based on the lab-scale tests, the potential formulation were down-selected for further research work.

Results

Hydrophobic and hydrophilic hollow glass microspheres were prepared using surface coatings. Hydrophobic microspheres sank to the bottom of gasoline layer while hydrophilic microspheres floated on top of the gasoline fuel, though both types of microspheres had similar density lower than that of gasoline. The spray application of glass microspheres on top of burning fuel was complicated by their floating on top of water layer due to their low density. Addition of surfactants and additives to homogeneous microspheres in water was not successful. Application of dry HGM powders on hot fuel did not result in fire quenching, because they are not able to form tight seal. Interestingly, the hydrophilic glass microspheres could seal the gasoline from evaporating. Therefore, glass microspheres could be used in the firefighting to prevent the burnback along with other PFAS-free foams. When glass microspheres are applied, after quenching of the fire using PFAS-free foams, they could seal the fuel layer and can increase the burnback time response to meet the MilSpec.

Benefits

Per and polyfluorinated fire-fighting foams need to be replaced immediately because they are not environmentally sustainable due to the growing awareness on the social impacts and enormous cost expected from cleaning the contaminated environment. The safe alternate to polyfluorinated chemicals must reduce the water and soil contamination and will help in improving the human health caused by the AFFF used in firefighting.

Executive Summary

Per- and polyfluorinated alkylated substances (PFAS) containing aqueous film forming foams (AFFF) are not environmentally sustainable. PFAS chemicals have contaminated soil, groundwater, drinking water, and surface water worldwide. The objective of this Limited Scope Research work was to investigate a spray formulation based on hollow microspheres as an alternative approach to replace polyfluorinated Aqueous Film Forming Foams (AFFF). AFFF products used in fuel fire-fighting are made up of air bubbles dispersed in a continuous aqueous medium. The AFFF replacement PFAS-free products lack the foam stability which is critical for the functioning of fire quenching foams. If the air bubbles of PFAS-free products are made up of solids, they can form "extremely stable" foams on top of hot fuel. Hollow glass microspheres are stable solids which are also of low density like air bubbles. Therefore, PFAS-free foam formulations made using HGMs can behave similar to AFFF foams on top of gasoline. The primary research objective of this project was to evaluate HGMs' application in extinguishing pool fire that could potentially replace AFFFs. Both hydrophilic and hydrophobic glass microspheres were prepared and tested in firefighting foams. The film-forming and fire suppression abilities of the hollow microsphere foams was evaluated. HGMs when mixed with surfactants in water was unable to quench the fuel fire. However, the hydrophilic glass microspheres could seal the gasoline fuel from evaporating. Therefore, glass microspheres could be used in the firefighting to prevent the burnback. When glass microspheres are applied, after quenching of the fire using PFAS-free foams, they can seal the fuel layer and prevent the fuel from catching fire again.

1. Introduction

The use of firefighting foam containing perfluorooctane sulfonic acid (PFOS) and other per- and polyfluorinated alkylated substances (PFASs) has resulted in the contamination of soil, groundwater, drinking water, and surface water, across the US including manufacturing sites and Department of Defense bases [1]. PFAS and their degradation products are bio-accumulative and toxic and are more difficult to remove from contaminated water or soil because there is no known degradation for perfluorinated substances at these sites [2,3]. In this project, a novel fluorine-free formulation based on hollow glass microspheres were developed as an alternative product to replace polyfluorinated Aqueous Film Forming Foams (AFFF). This project 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 [4]. New fluorine-free formulations for AFFF developed in this project is expected to meet the performance specifications of the fire extinguishing agent, aqueous film-forming foam (AFFF) liquid concentrate based on MIL-PRF-24385F standard specifications [5].

2. Technical Objective

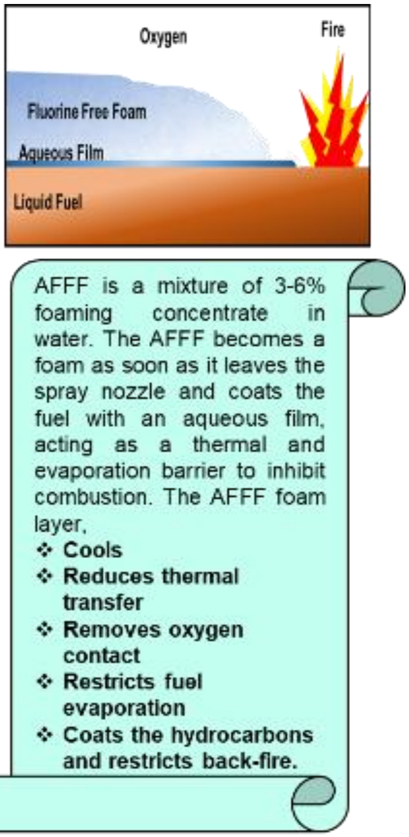
The primary research objective of this project was to develop a fluorine-free formulation based on hollow glass microspheres (HGMs) and evaluate their application in extinguishing pool fire that could potentially replace polyfluorinated AFFFs. The fire suppression performance of the HGM containing mixtures were evaluated to meet the performance requirements of the MIL-F-24385F standard. The film-forming and fire suppression abilities of the hollow microsphere foams were evaluated. The tests included the evaluation of foam stability over hot fuel, and lab-scale fire suppression testing. Based on the lab-scale tests, hydrophilic microspheres were down-selected as a potential product to assist in pool firefighting, especially in improving burnback time.

3. Background

Aqueous film forming foam (AFFF) is the primary technology available today to military and first responders to fight against liquid fuel pool fires. Conventional AFFFs contain perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) [1-5]. These chemicals have the most robust chemical (carbon-fluorine) bonds and are considered persistent, bio-accumulative, and toxic (PBT) materials. PFOS and the family of chemicals have leached into groundwater and were detected around the world in the food chain, drinking water, animals, and even in human blood. Due to their ubiquitous presence in the environment and the increasing concern of their toxicological effects, efforts have been focused on reducing exposure to these chemicals [6]. The regulation on PFOA/PFOS chemicals has directly affected the AFFF industry. Therefore, MMI and other groups are working on environmentally acceptable alternatives such as fluorine-free siloxane-based AFFF, for use on militarily relevant fuels, to meet the performance requirements of the MIL-F-24385F standard [7].

The functioning of AFFF firefighting foams is schematically described in Figure 1. The AFFF applied forms a layer of foam on top of the liquid fuel [5]. The foam spreads across the fuel surface and acts as a thermal and fuel evaporation barrier to inhibit and eventually extinguish the flame. The film formed also cools the fuel surface, reduces thermal transfer, and removes oxygen contact with the fuel. Therefore "film-forming" characteristics of the AFFF is critical for an AFFF formulation.

AFFF that is used by the U.S. military follows the MilSpec (MIL-F-24385) and are effective against liquid fuel fire threats [6]. The formulations are typically used as either a 3% or a 6% concentrate. The foam forms as the concentrate/water mix come out of the nozzle. The AFFF concentrates are 97-94% water, with other components such as glycol ethers and ethylene or propylene glycol that are added to increase the stability of the foam [8]. The lowering of surface tension is accomplished by the use of fluorocarbon surfactants (typically PFOA/PFOS and currently by C-6 fluorochemicals). This allowed the formation of foam and coverage film of water on fuel [8].



AFFF is a mixture of 3-6% foaming concentrate in water. The AFFF becomes a foam as soon as it leaves the spray nozzle and coats the fuel with an aqueous film, acting as a thermal and evaporation barrier to inhibit combustion. The AFFF foam layer,

- **Cools**
- **Reduces thermal transfer**
- **Removes oxygen contact**
- **Restricts fuel evaporation**
- **Coats the hydrocarbons and restricts back-fire.**

Figure 1. Mechanism of AFFF action

The fluorinated surfactants (PFOA and PFOS) that were used in the traditional AFFF formulations are explicitly mandated by MIL-F-24385F and have been discontinued by the manufacturers and eliminated by Environmental Protection Agency under EPA’s 2010/15 PFOA Stewardship Program [8]. US Military and fire protection industry have moved towards using short-chain (C-6) perfluorochemicals as a stop-gap measure until a non-toxic alternative can be established. The current trend in the US and international environmental agencies in restricting perfluorochemicals has severely impacted the options available to firefighters [3]. This situation is a strong impetus to the development of new fluorine-free AFFF formulations. In order to accommodate the fluorine-free AFFFs, the US Congress recently passed legislation (FAA Reauthorization Act of 2018 (HR 302)), directing the Federal Aviation aircraft manufacturers and airports to remove the requirement of the use of fluorinated chemicals to meet the performance standards after three years [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 Mil-Spec requirements and be environmentally friendly will require improvement of the stability of PFAS-free foams. In this project, surface functionally modified hollow glass microspheres were evaluated as foam additives of low surface tension surfactants such as polysiloxanes [10,11,12].

Siloxane based surfactants

Silicone-based surfactants have been used to form a low surface energy aqueous solution. They are typically used in the aqueous wetting of hydrocarbon surfaces [13,14]. Many of these wetting agents are nonionic, cationic or zwitterionic siloxane monomers and polymers with a range of molecular weights and side-chain linkages. They have demonstrated excellent ability to reduce the surface tension of water to approximately 20 mN/m [15]. By comparison, typical hydrocarbon chain surfactants can reduce the surface tension only to 30-45 mN/m range [15]. The low surface tension value of silicone surfactants is achieved by the close-packed array of methyl groups [14]. The siloxane backbone is flexible and is amenable such that the molecules can be oriented to form flat layers on the surface of the water, exposing the low surface energy methyl groups to the air. Such a parallel orientation of the molecules with respect to the water allow for relatively large surface area coverage with low critical micelle concentrations (cmc) [14]. Guoyong *et al.* synthesized new carbohydrate-modified siloxane surfactants and studied their behavior in aqueous solution [16]. 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 carbohydrate-modified siloxane surfactants in AFFF fire suppression applications [17].

However, in order to meet the MIL-STD requirement, the organosilicon surfactant should have oleophobicity (low surface tension), high surface activity, foamability, and environmentally-friendly. These aspects need to be investigated further to arrive at a formulation that can satisfy all the requirements of AFFF Milspec MIL-F-24385. In this project, efforts were focused on the application of surface modified hollow microspheres with a variety of coatings along with polysiloxane surfactant in increasing the foam stability and reducing the fire suppression time and foam application rate of the fluorine-free formulation.

Ananth *et al.* have recently demonstrated that trimethyl siloxy silane polymers (Dow 502W additive) along with hydrocarbon surfactants (Glucopon family of surfactants from BASF) were able to quench the heptane pool fire at a reasonable time when mixed in appropriate ratios [6]. The chemical structures of these products are provided in Figure 2.

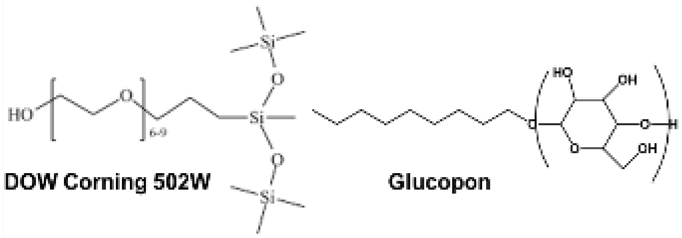


Figure 2. Chemical structure of siloxane surfactant and additives used in the AFFF formulation by US Naval Research Laboratory (From Ref. [6]).

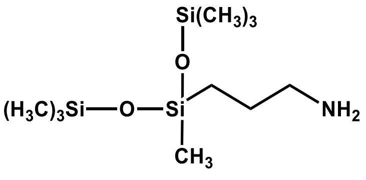


Figure 3. Chemical structure of 3-aminopropyl methyl bis (tri methyl siloxy)silane.

Their results exhibited shorter fire quenching times for these surfactant mixtures. The extinction time was 1.5 times that of an equivalent fluorinated AFFF formulation (60% effectiveness of fluoro AFFF formulation). Similar results were also obtained by MMI using trisiloxane surfactants [18]. In addition, MMI has assisted CertainTech Inc., in a DoD-funded work [19], to produce and test polyoctahedral silsesquioxanes ("POSS") based surfactants, as fire stopping foam materials. In this project, oleophobic 3-aminopropylmethyl bis(trimethylsiloxy)silane (Figure 3) was reacted with the various hydrophilic groups 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 the heptane fire. These results suggest that surface tension reduction is not the only criteria for achieving superior fire foams. ***Foam stability on fuel fire is more critical in improving the fire suppression efficiency of fluorine-free foams.*** Therefore, in this effort a novel approach of using surface treated hollow glass microspheres in foam formulation was investigated as a potential alternative to polyfluorinated AFFFs.

Improving the Foam Stability and Fire Suppression Efficiency of Fluorine Free Foams

Fire-fighting foams are made up of air bubbles dispersed in a continuous aqueous medium [20]. It is difficult to make a stable foam, especially with fluorine-free chemicals in the presence of hot gasoline fuel vapors. Three primary instability factors, namely Ostwald ripening, liquid drainage, and air bubble coalescence, are the causes of the collapse of fire-fighting foams [21]. Smaller air bubbles in the fire foam rapidly disappear turning into bigger ones, by diffusion of gas through the continuous phase. (Ostwald ripening). A foam with large bubbles results in rapid water drainage from the bubble and hence results in the shorter foam stability. These instabilities including Ostwald ripening can be prevented and can result in "**extremely persistent**" foams if the air bubbles can be made up of solids. However, the solid air bubbles (particles) should be able to float on the gasoline fuel surface.

These requirements were demonstrated by MMI in a recent SERDP project on "Fluorine-Free Aqueous Film Forming Foams based on Functionalized Siloxanes" [19]. Foam stability of a formulation containing 3 wt% siloxane carbohydrate surfactant, 1.5 wt% Xanthan gum, 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 4. In comparison, a typical C-6 fluorinated foam exhibited foam stability for 33 minutes under similar conditions. The Xanthan gum formed a thick-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 heptane fuel surface.

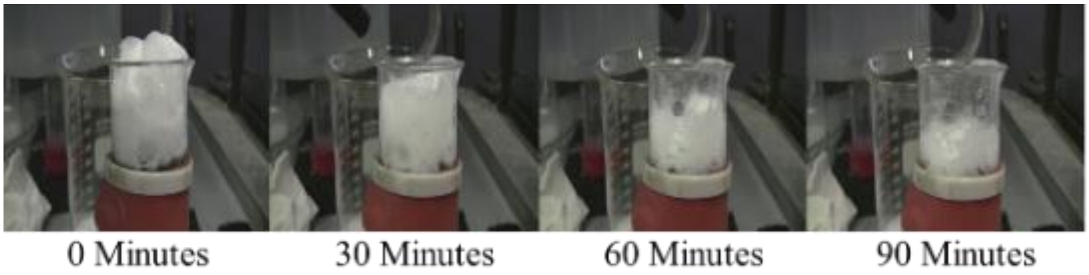


Figure 4. Effect of Xanthan gum on the stability of siloxane surfactant-based foam over hot heptane

Therefore, we were interested in developing alternative approaches to form extremely stable foams. One method was to use hollow glass microspheres (HGM) [21,22,23,24,25]. Hydrophobically or hydrophilically treated HGMs were added to fluorine-free siloxane surfactants to increase the foam stability without the side effects such as increased viscosity issues faced with Xanthan gum.

Hollow Glass Microspheres

Hollow glass microspheres (HGMs) are a well-known additives for high mechanical strength and low density in polymer composites (Syntactic foams). Sadler *et al*. have studied the fire-retardant and mechanical properties of the hollow glass microsphere-based foams [26]. In the past, the HGMs were used as protective surface layers to prevent evaporation of toxic and highly volatile liquids (oil, petroleum products) from open storage basins [27], as insulation foams in cryogenic technology and in the fabrication of acoustic and thermal insulating materials [28].

Hollow microspheres are finely dispersed, free-flowing powders consisting of thin-walled (0.5-2.0 µm) spherical particles 10-200 µm and more in diameter. HGMs consist of an outer stiff glass shell and an inner inert gas. HGMs are therefore of lightweight (low density of order of 0.1 -0.5 g/cc) and have low thermal conductivity. In Figure 5, electron microscopic images of hollow spheres are provided.

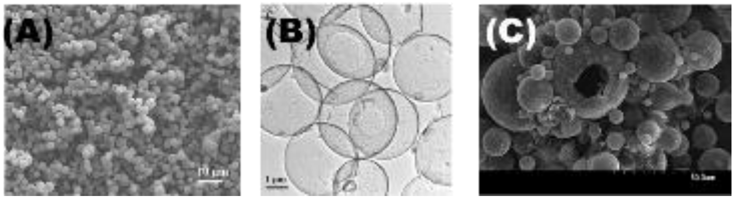


Figure 5. (A) SEM image of hollow microspheres, and (B) corresponding TEM image (From Ref. [30]) and (C) SEM image of glass microspheres showing the hollow structure

Due to the unique combination of the spherical shape, controllable size, low density, relatively high strength in uniform compression, excellent thermal and acoustic insulating and dielectric properties, hollow microspheres are critical technogenic fillers. Hollow microspheres can be made from a variety of materials including glass, ceramic, carbon, and polymers. In this effort, glass microballoons were functionalized with hydrophilic and hydrophobic groups and were evaluated in fire-fighting foam applications.

Weihong *et al.* have shown that by adding hollow glass microspheres to polyfluorinated fire-fighting foams, a stable scaffold of a three-phase foam can be formed and the foam stability over hot fuels can be significantly increased [24]. Tang and Wu have used oleophobic tridecafluorooctyltriethoxysilane coated hollow glass microspheres along with protein foams in the fire foam formulation [23]. The oleophobic hollow glass microspheres significantly increased the foaming capacity and foam stability over hydrocarbon fuel and decreased fire suppression time. The liquid drainage rate from foams also decreased about 8.4 times (half-drainage $t_{25\%}$ value) compared to fire foam without the addition of oleophobic hollow glass microspheres. Further, the addition of oleophobic glass microspheres also increased foam stability. For example, the foam height over the liquid fuel was decreased by 83% in the pristine foam in 5 minutes compared to <3% decrease for oleophobic hollow glass microspheres mixed fire foams. These results clearly demonstrate that the foam foaming and fire suppression efficiency of the fire-fighting foams can be significantly improved by the addition of oleophobic glass microspheres. We investigated a similar approach using oleophobic tris(trimethyl siloxy) $[((CH_3)_3Si)]_3$ groups coated on the microspheres. However, dispersibility of a hydrophobic microsphere in water is a concern. Therefore, both hydrophilic and oleophobic hollow glass microspheres were investigated.

4. Technical Approach

For most firefighting foam applications, fluorine-free foams (F3) are available today [3]. They degrade in the environment and are not a long-term concern for ground and drinking water. However, currently available F3 foams exhibit poor performance compared to polyfluorinated AFFFs on fires such as tank fires with crude oil or other hydrocarbon fuels. Compared to AFFFs, F3 formulations require a higher application rate (and hence higher amount of F3 product) to achieve the equivalent fire suppression efficiency [3,29]. This is most likely due to the poor stability of F3 foams on burning fuels and therefore foams with higher stability over burning fuels are required to replace the polyfluorinated AFFFs.

In this effort, a new materials' system based on hollow microspheres capable of forming a stable foam layer over the flammable fluids was investigated. The primary technical objective of the proposed effort was to prepare oleophobic and hydrophilic hollow glass microspheres and evaluate their applicability in fire suppression operations. The commercial glass microspheres with various particle size and density are functionalized with oleophobic tris(trimethyl siloxane) groups as well as hydrophilic polymers. The surface treated hollow microspheres were dispersed in a polysiloxane medium (for example, Dowsil 501W) in various ratios. The HGMs were expected to act as a barrier for combustible liquids from supplying fuel vapor to the fire and reduce the thermal conductivity below the flash point of the fuels.

5. Materials and Methods

Hollow glass microspheres were purchased from Aircraft Spruce & Specialty Co., Corona, CA. Silane products were purchased from Gelest Inc. Gasoline was purchased from local gas stations.

6. Results and Discussion

Preparation of Hydrophobic Hollow Glass Microspheres

Hollow Glass Microspheres (HGMs) are known as high-strength and low-density additives made from water resistant and chemically stable glass. These silica microparticles are being researched in order obtain an oleophobic additive for the siloxane-based surfactants. The oleophobic HGMs should act as a barrier for combustible liquids from supplying fuel vapor and decrease the thermal conductivity of the fuels. Hydrophobic trimethyl siloxane groups are known to lower the surface energy and could possibly increase compatibility with low surface tension fuels. Thus, surface modification of the HGMs to obtain these groups is desired. The HGMs used in particular were 3M's K37 Glass Bubbles. Three routes have been investigated so far.

The first two involved reacting glass beads, hydrolyzed or not, with (3-Aminopropyl) trimethoxy silane using a 1:2 molar ratio and methanol as solvent. The reaction ran under reflux at room temperature for over 24h. Then, the product was dried and reacted with excess hexamethyldisiloxane (HMDSO) and tetramethyl ammonium hydroxide pentahydrate as catalyst in an oil bath at 85°C, under reflux as provided in Figure 6. After 24 hr, the product was dried and tested. The resulting HGMs had both remained hydrophilic.

Figure 6. HGMs being reacted with HMDSO (left), being dried using vacuum filtration (center), and final product obtained (right)

The third path involved starting with the hydrolyzed glass beads and a chlorinated silane. The HGMs were reacted with 3-Trimethoxysilylpropyl Chloride in an oil bath at 85°C, under reflux for 24h. The product was then dried and tested to be hydrophobic. Then, a similar reaction with HMDSO was conducted, and the final product was found to be even more hydrophobic. A comparison of the two types of glass beads obtained is photographed in Figure 7.

Figure 7. Comparison of water droplet behavior over as-purchased HGMs (left) and 3-Trimethoxysilyl propyl Chloride then HMDSO-reacted HGMs (right)

Foam Solutions Preparation

The foam solutions were prepared by mixing a trisiloxane surfactant and hydrophobic glass microspheres. First the siloxane surfactant, (Dowsil 501W) was dissolved in 1L of water. Next, the additives were dissolved separately. Shear mixing was used if necessary. After slowly adding the additives to the solution, the volume was completed to 2L of water. The foam formulation was then left to stir until it was ready for fire testing.

Benchtop Fire Testing

Once each foam formulation was prepared, it was tested in the same day using a small-scale fire testing setup. This apparatus was built with directions provided by the U.S. Naval Research Laboratory and is pictured in Figure 8. It consists of an airflow controller for foam generation between 0.5-2L/min and a 19cm diameter glass dish topped with a 1cm layer of gasoline. During each test, the dish filling and fire quenching times were recorded. Additionally, the mass of 500mL of the foam was measured to calculate the expansion ratio, the pH was taken using pH paper, and finally the surface tension was measured using a Ramé-Hart Goniometer.

Figure 8. Experimental setup of benchtop pool fire testing

A summary of the data collected is presented in Table 1.

Table 1. Summary of Fire Test, Surface Tension and pH Results

Formulation	Expansion Ratio	Dish fill time (s)	Quench time (s)	ST (mN/m)	pH
3% C6 on GAS	7.5	5	14	16.54	6.50
1.5% Dowsil 501W 0.8% hydrocarbon surfacant	13.2	10	68	-	6.50
1.5% Dowsil 501W 0.8% hydrocarbon surfactant 0.2% 3M K37 Glass Bubbles (untreated)	14.3	11	50	22.32	7.00
3% Trisiloxane surfactant + Proprietary additive	15.2	10	56	-	7.00
3% Trisiloxane surfactant + Proprietary additive + 0.2% 3M K37 Glass Bubbles (untreated)	11.6	8	40	-	7.00
1.5% Dowsil 501W 0.8% hydrocarbon surfactant 0.2% Hydrophobic 3M K37 Glass Bubbles	15.6	14	Not Quenched	21.81	6.00

Addition of untreated glass microspheres improved the fire quenching performance of the siloxane foam formulation. The comparison data are provided in Table 1 and Figure 9, ***clearly demonstrating the advantage of adding hydrophilic or untreated microspheres to PFAS-free foam formulations in quenching the pool fire.***

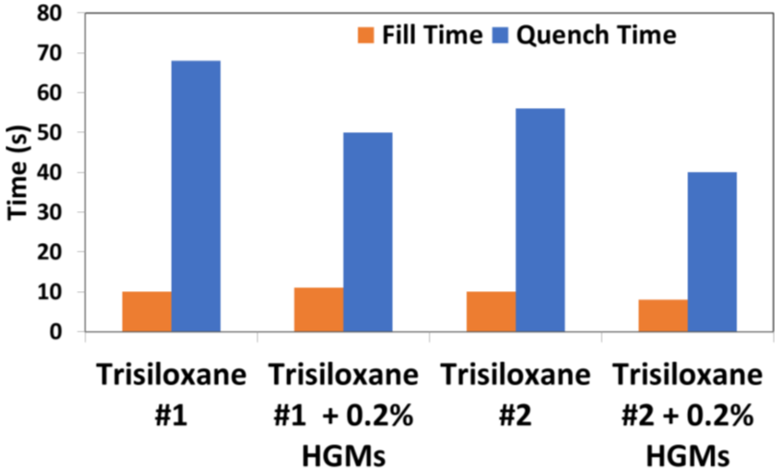


Figure 9. Demonstration of the effect of addition of hydrophilic hollow glass microsphere in PFAS-free foam formulations on the firefighting. Plot shows both dish fill time and fire quench time.

On the contrary, addition of hydrophobic (oleophilic) glass microspheres to the PFAS-free foams was detrimental to the firefighting application. ***The PFAS-free formulation with hydrophobic glass microspheres did not quench the pool fire.***

Synthesis of Surfactant Solutions

A commercial detergent was used as a surfactant and eight different concentrations (0%, 1%, 3%, 5%, 10%, 30%, 50% and 70%) of the commercial detergent were made and assessed. The microspheres used in these solutions were A20/1000 with an average density of 0.18 g/cc. All eight solutions were placed in 20 ml vials. Each vial was shaken for 30 seconds and the time taken for a visible majority of microspheres to rise to the top of the vial was measured. This time is noted as the dispersal time. The times are shown in Table 2**.**

Table 2. Dispersal time in each commercial detergent solution concentration

	0% solution	1% solution	3% solution	5% solution	10% solution	30% solution	50% solution	70% solution
Time (min	3.567	5.600	6.433	7.050	5.650	6.400	21.000	21.717

The general trend seen here is that as the surfactant concentration increases, the time the microspheres stay dispersed in water also increases. However, it is important to note that there is not a significant difference in dispersal times for the solution concentrations ranging from 1% to 30%. The large increase in dispersal time for the 50% and 70% commercial detergent solutions could be attributed to the increased viscosity of the solution compared to the other solution concentrations.

Synthesis of Polymer Coated Glass Microspheres

Synthesis of Polyvinyl Alcohol (PVA) coated microspheres

Three different types of PVA solutions were used to coat the microspheres. The solutions contained the following:

1) PVA Treatment 1
    a) 0.02 g of polyvinyl alcohol (MW: 13000-23000)
    b) 2.00 g of A20 glass microspheres
    c) 50 ml of distilled water
2) PVA Treatment 2
    a) 0.04 g of polyvinyl alcohol (MW: 13000-23000)
    b) 2.00 g of A20 glass microspheres
    c) 60 ml of ethanol
3) PVA Treatment 3
    a) 0.02 g of polyvinyl alcohol (MW: 13000-23000)
    b) 0.02 g of polyvinyl alcohol (MW: 31000-50000)
    c) 2.00 g of A20 glass microspheres
    d) 60 ml of distilled water

PVA was dissolved in water by heating to 80°C with stirring. Once dissolved, the glass microspheres were added to the solution. The solution was then stirred and heated to 100°C in a 100 ml beaker until the water was removed.

Synthesis of Polyethylene Glycol (PEG) coated microspheres

Polyethylene glycol (PEG) was also used as a coating for the microspheres. Similar to the PVA, several solutions with PEG coatings were made to assess which proportion and MW of PEG resulted in the best dispersion. A high molecular weight and low molecular weight of PEG was used. Five different types of PEG solutions were used to coat the microspheres. The solutions contained the following:

1) PEG Treatment 1
    a) 0.04 g of polyethylene glycol (MW: 10000)
    b) 2.00 g of A20 glass microspheres
    c) 40 ml of distilled water
2) PEG Treatment 2
    a) 0.046 g of polyethylene glycol (MW: 980)
    b) 2.00 g of A20 glass microspheres
    c) 40 ml of distilled water
3) PEG Treatment 3
    a) 0.022 g of polyethylene glycol (MW: 10000)
    b) 2.00 g of A20 glass microspheres

    c) 40 ml of distilled water
4) PEG Treatment 4
    a) 0.014 g of polyethylene glycol (MW: 10000)
    b) 2.00 g of A20 glass microspheres
    c) 40 ml of distilled water
5) PEG Treatment 5
    a) 0.035 g of polyethylene glycol (MW: 10000)
    b) 2.00 g of A20 glass microspheres
    c) 40 ml of distilled water

PEG was dissolved in water by heating to 50°C with stirring. Once dissolved, the glass microspheres were added to the solution. The solution was then stirred and heated to 100°C in a 100 ml beaker until the water was removed.

Synthesis of Polyvinyl Butyral (PVB) coated microspheres

One PVB solution was made and it contained the following:

1) PVB Treatment 1
    a. 0.21 g of polyvinyl butyral
    b. 240 ml of ethanol
    c. 12 g of A20 glass microspheres

The PVB was dissolved in ethanol in a 1000 ml round bottom flask. Then the microspheres were added into the solution and the solution was then put on the rotor evaporator until the ethanol was removed.

Synthesis of Polyvinylpyrrolidone (PVP) coated microspheres

One PVP solution was made and it contained the following:

1) PVP Treatment 1
    a. 2.1 g of 10% polyvinylpyrrolidone solution (in water)
    b. 250 ml of distilled water
    c. 12 g of A20 glass microspheres
    d. 0.03 g of ammonium persulfate
    e. 0.5 ml of TEMED
    f. 80 ml of distilled water

The PVP was dissolved in 250 ml of water in a 1000 ml round bottom flask. The microspheres were added into the solution and the solution was then put on the rotor evaporator until the water was removed. The PVP coating was then cured by making a solution containing the ammonium persulfate (APS), N,N,N′,N′-tetramethylethylenediamine (TEMED) and 80 ml of water. This solution was added to the PVP coated microspheres in the 1000 ml round bottom flask and the flask was heated to 50°C and stirred for four hours so the ammonium persulfate could react with the PVP. Afterwards, the water was removed using the rotor evaporator.

Synthesis of Sodium Carboxymethyl Cellulose (CMC) coated microspheres

One CMC solution was made, and it contained the following:

1) CMC Treatment 1
    a. 0.04 g of sodium carboxymethyl cellulose
    b. 40 ml of water
    c. 2 g of A20 glass microspheres

CMC was dissolved in water by heating to 50°C with stirring. Once dissolved, the glass microspheres were added to the solution. The solution was then stirred and heated to 100°C in a 100 ml beaker until the water was removed.

Assessment of Dispersion of Polymer Coated Microspheres in Water

PVA Coatings

0.1 g of each of the PVA treated microspheres were added to 10 ml of distilled water in a 20 ml vial to assess whether they had better dispersal when compared to the uncoated microspheres in water; however, the dispersal time was roughly only a minute longer. Each vial was shaken, and its dispersal was assessed. While the PVA coating did result in the microspheres being dispersed longer than their uncoated counterparts, there was no sizeable difference in dispersal time between the different PVA coatings. The vials are shown in Figure 10 and Figure 11.

Figure 10. From right to left, PVA treated microspheres 1, 2, and 3 in water immediately after being shaken

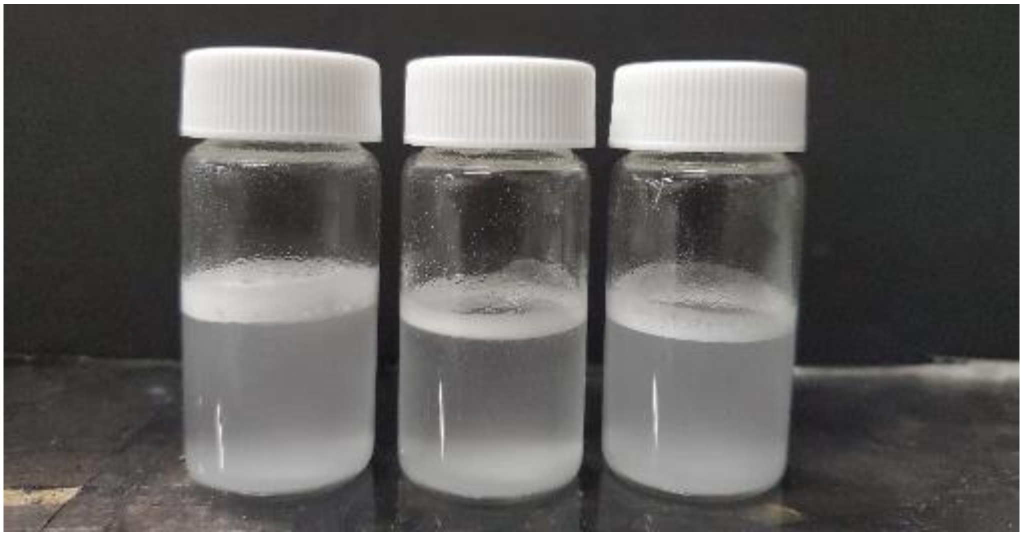


Figure 11. From right to left, PVA treated microspheres 1, 2, and 3 in water 5 minutes after being shaken

PEG Coatings

0.1 g of each of the PEG treated microspheres were added to 10 ml of distilled water in a 20 ml vial to assess whether they had better dispersal when compared to the uncoated microspheres and PVA coated microspheres in water. PEG treatment 1 was the most effective at increasing dispersal time amongst all other coatings with the dispersal time being upwards of 5 minutes, though some of the microspheres sank to the bottom. PEG treatment 5 was also more effective than the uncoated and other polymer coated microspheres, but it was not better than PEG treatment 1. PEG treatments 2, 3, and 4 resulted in more microsphere dispersal than the uncoated and PVA coated microspheres, though the treatments had no significant difference between themselves and were worse than PEG treatment 1 and 5. The vials are shown in Figure 12 and Figure 13.

Figure 12. From right to left, PEG treated microspheres 1, 2, 3, 4 and 5 in water immediately after being shaken

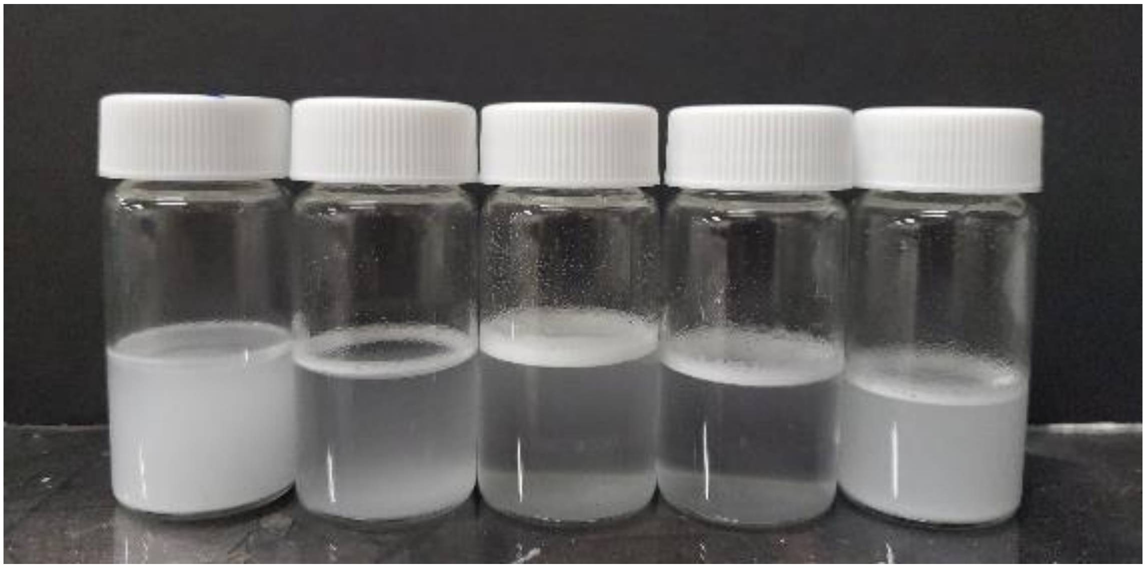


Figure 13. From right to left, PEG treated microspheres 1, 2, 3, 4 and 5 in water 5 minutes after being shaken

PVB Coating

0.1 g of the PVB treated microspheres were added to 10 ml of distilled water in a 20 ml vial to assess dispersal. Since the PVB coating is hydrophobic, the microspheres immediately separated from water after the vial was shaken. Of all the polymer coatings, the PVB coating had the worst dispersion in water. 0.1 g of the PVB treated microspheres were also added to 3 g of gasoline in a 20 ml vial. It was observed that the microspheres floated on top of the gasoline and even after the vial was shaken, all the microspheres rose to the top of the vial. The vials are shown in Figure 14.

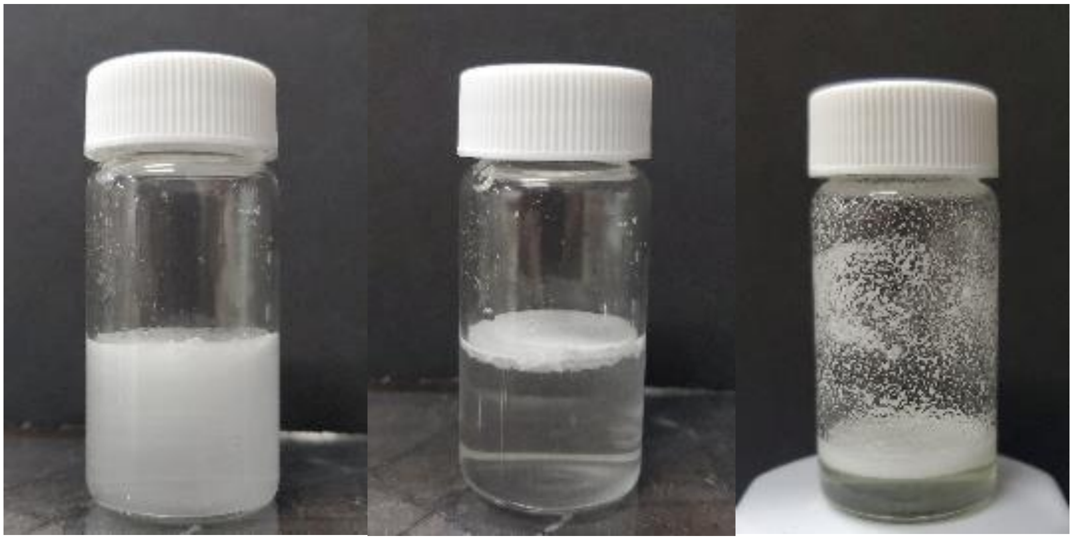


Figure 14. PVB treated microspheres in water immediately after being shaken (left image), PVB treated microspheres in water 5 minutes after being shaken (middle image), and PVB treated microspheres in gasoline immediately after being shaken

PVP Coating

0.1 g of the PVP treated microspheres were added to 10 ml of distilled water in a 20 ml vial to assess dispersal. This coating, despite being cured with ammonium persulfate, was not effective at increasing dispersal. The dispersal time of the PVP coating was shorter than the dispersal time of the PVA coatings. The vials are shown in Figure 15**.**

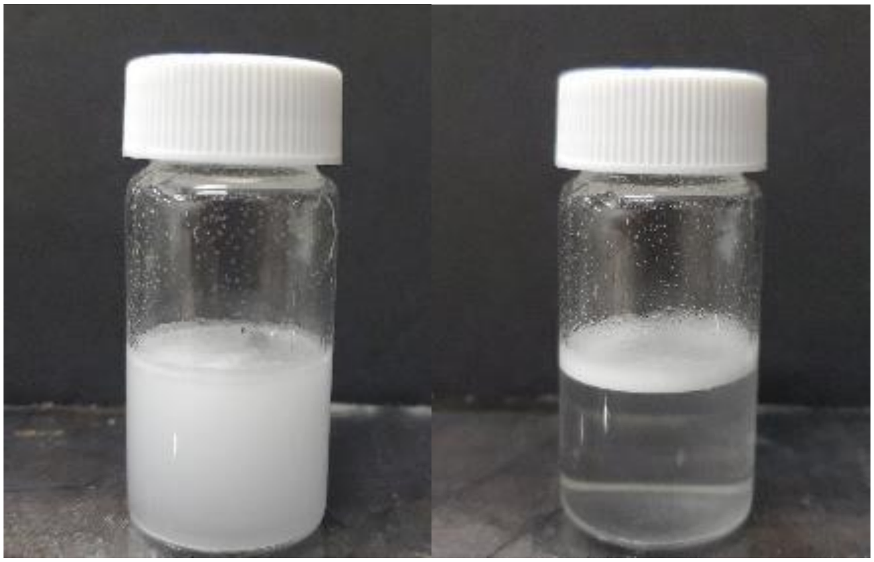


Figure 15. PVP treated microspheres in water immediately after being shaken (left image), PVP treated microspheres in water 5 minutes after being shaken (right image)

CMC Coating

0.1 g of the CMC treated microspheres were added to 10 ml of distilled water in a 20 ml vial to assess dispersal. The CMC coating had the same effectiveness as the PVA coatings. The vials are shown in Figure 16**.**

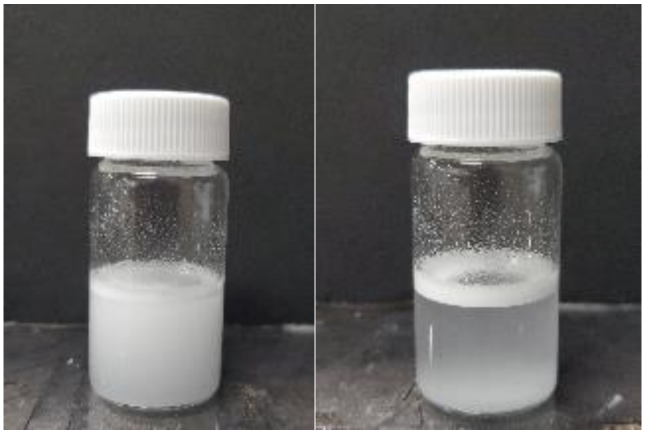


Figure 16. CMC treated microspheres in water immediately after being shaken (left image), CMC treated microspheres in water 5 minutes after being shaken (right image)

Fire Testing

Synthesis of Fire Testing Solutions

Two of the polymer coatings were used in fire testing. The first was PVA treatment 1 and the second was PEG treatment 5. The solutions contained the following:

1) Solution 1: 0.1% PVA-coated microspheres, 5% commercial detergent in water
    a. 2 g of PVA treatment 1 microspheres
    b. 100 g of commercial detergent
    c. 1898 g of distilled water

2) Solution 2: 0.5% PEG-coated microspheres, 0.4 % DOWSIL501W, 0.8% glucopon in water
    a. 10 g of PEG treatment 5 microspheres
    b. 8 g of DOWSIL501W
    c. 16 g of glucopon
    d. 1966 g of distilled water

Each solution was made in a 2L container and each solution was added to the fire testing apparatus. The foam from Solution 1 dissipated quickly on the gasoline and did not fill the dish nor did it quench the flames. The foam from Solution 1 did not visibly seem to contain any microspheres, implying that most of the microspheres floated to the top of the solution and did not stay dispersed in the water. The foam from Solution 2 did contain microspheres and it successfully filled the dish, as seen in Figure 17, and quenched the flames, as seen in Figure 18 and Figure 19; however, after the foam dissipated, it was apparent that the microspheres had sank beneath the gasoline and had formed a layer between that water and gasoline, as seen in Figure 20. The results of all fire tests are summarized in Table 3**.**

Figure 17. Foam from solution 2 completely fills the dish.

Figure 18. Foam from solution 2 gradually quenches the flames

Figure 19. Foam from solution 2 successfully quenches the flames

Figure 20. As indicated inside the red circle, as the foam from solution 2 dissipates, the microspheres can be seen floating between the gasoline and water layers

Based on the fire test, the PEG-coated microspheres stayed better dispersed in water than PVA-coated microspheres, since the PEG coated microspheres were found in the foam and in dish containing the gasoline.

The PEG coating was done using the rotary evaporator; however, the coating did not seem to be as effective as the coating made using the method with the beaker. Therefore, 12 g of A20 microspheres were coated with 0.24 g of PEG in a 600 ml beaker with 200 ml of water (PEG treatment 6). These microspheres were used in a fire test. Additionally, a solution that contained no microspheres was used in the fire test for comparison. The solutions contained the following:

1) Solution 3: 0.4 % DOWSIL501W, 0.8% glucopon in water
    a. 8 g of DOWSIL501W
    b. 16 g of glucopon
    c. 1976 g of distilled water

2) Solution 4: 0.5% PEG-coated microspheres, 0.4 % DOWSIL501W, 0.8% glucopon in water
    a. 10 g of PEG treatment 6 microspheres
    b. 8 g of DOWSIL501W
    c. 16 g of glucopon
    d. 1966 g of distilled water

Each solution was made in a 2L container and each solution was added to the fire testing apparatus. The foam from Solution 3 (without microspheres) had an expansion ratio of 12.2. The fill and quench times were 7 seconds and 41 seconds, respectively. The foam from Solution 4 had an expansion ratio of 10.9 and its fill and quench times were 8 seconds and 57 seconds, respectively. A thin layer of microspheres was between the gasoline and water layers, but most of the microspheres presumably went into the water layer. Since the PEG coating is hydrophilic, its interaction with water most likely results in the microspheres sinking beneath the gasoline, even though their density (0.245 g/cc) is lower than that of gasoline (0.71-0.78 g/cc). The solution containing the PEG-coated microspheres did not quench the fire faster than the solution without the microspheres which suggests that the addition of the microspheres negatively affects the quench time.

A fire test was also conducted with a 1.5% DOWSIL501W, 0.5% PEG-coated A20 microsphere solution (Solution 5). The expansion ratio was 10.9. The foam from this solution dissipated quickly and foam did not fill the dish or quench the flames suggesting that there needs to be some additive to stabilize the foam. Additionally, the PEG-coated microspheres sank below the gasoline layer and stayed in the water layer. There was no layer of microspheres between the gasoline and water layers.

Table 3. Fire test results

	Expansion ratio	Fill Time (sec)	Quench Time (sec)
Solution 1	15.6	N/A	N/A
Solution 2	13.8	9	46
Solution 3	12.2	7	41
Solution 4	10.9	8	57
Solution 5	10.9	N/A	N/A

Effect of the Type of Microsphere

Two additional types of microspheres were used to assess whether the microsphere type affected their dispersion in water. The H50/10000 EPX glass microspheres with a density of 0.5 g/cc and the K37 glass microspheres with a density of 0.37 g/cc were used in addition to the A20 glass microspheres used in previous experiments. 12 g of each type of microsphere were coated with 0.24 g of PEG (MW:10000) in a 600 ml beaker using 200 ml of water. After the microspheres were coated, 0.1 g of each type of PEG-coated microsphere was added to 10 ml of water in a 20 ml vial. Each vial was shaken and compared to discern which type of PEG-coated microsphere stayed dispersed in water the longest. Of the three types of microspheres, the PEG-coated A20 microspheres stayed dispersed the longest, followed by the PEG-coated H50 microspheres. The PEG-coated K37 microspheres stayed dispersed for the least amount of time.

Physical density or Oleophilicity? Which force is higher?

HGMs are lightweight (low density of order of 0.1 -0.4 g/mL) and therefore expected to float on gasoline with a density of 0.7 g/cc. In Figure 21 density of PVB and PEG coated hollow microspheres are provided, indicating all these microspheres should float on gas based on their densities.

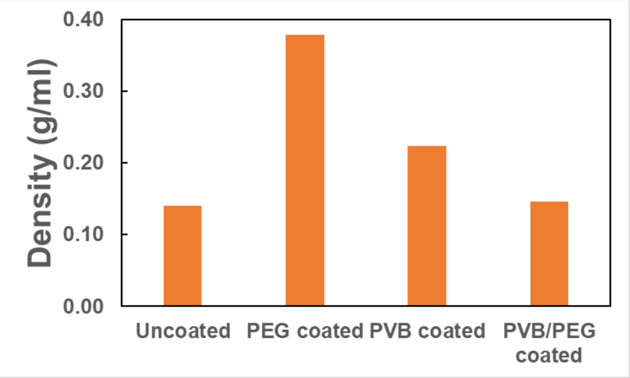


Figure 21. Density of polymer coated hollow glass microspheres

However, only un-treated microspheres floated on top of gas. PEG coated HGMs went into water and PVB/PEG coated HGMs were found to stay on the interface between water and gasoline layers. These observations were schematically represented in Figure 22. ***These observations clearly show that attractive forces between the HGMs and water or gasoline is more critical than the density of particles.***

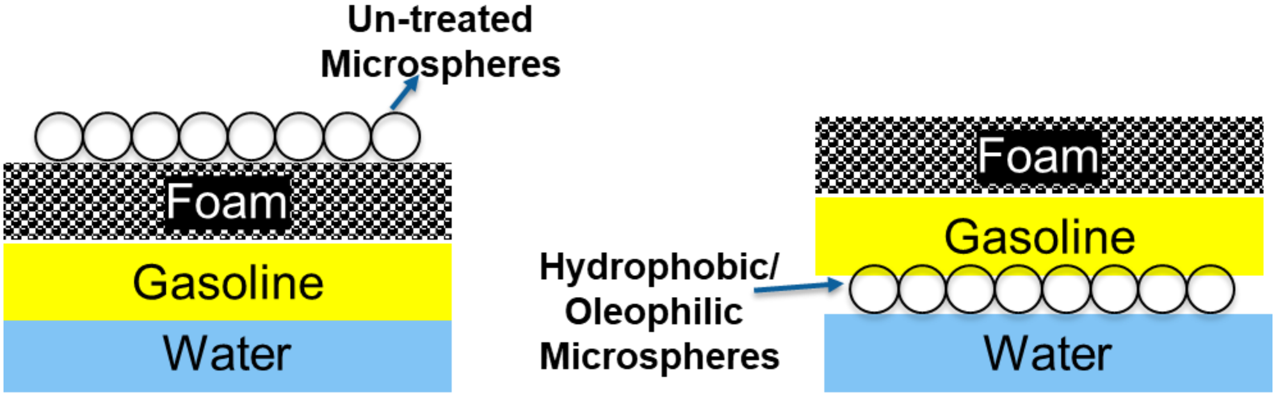


Figure 22. Schematic diagram showing the behavior of hydrophobic, hydrophilic and un-treated microspheres

In order for HGMs to get dispersed in water, the particles need to be hydrophilic. However, when added to fuel, the microparticles are pulled into the gasoline allowing fire to continue.

Modification of Foam Spray System

The benchtop pool fire system provided in Figure 8 using sparger was not suitable for applying HGMs on flames because of floating of HGMs and clogging of sparger pores. Therefore, an alternate sprayer was investigated. The foam was generated using a pump sprayer instead of air flowing through a sparger. The new setup is provided in Figure 23.

Figure 23. Photographs of new HGM foam sprayer setup

The HGMs dispersed in water or a solvent mixture was applied through a glass tube. The glass tube was kept on the edge of the 19-cm diameter gasoline pool. This method allowed us to test both traditional foams and HGM-based foams.

Figure 24. Photographs of (A) fire testing, (B) and (C) uncoated-HGMS on top of gasoline after fire testing

A 10% concentrate of 3M A20/1000 HGMs was prepared in water. The HGMs were tested on a gasoline fuel fire. Image was taken after the fire was manually suppressed using snuffing method. A thick layer of clumped microspheres formed on top of the gasoline layer as shown in Figure 22. The HGM foams were unable to quench the flame because of the voids between the microspheres. It is interesting to note that the HGMs were fused together probably due to melting in the fire. Optical images of the HGMs taken after the first testing is provided in Figure 23 showing fused microspheres.

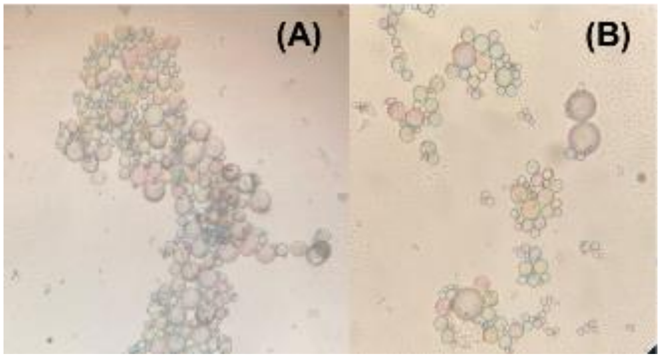


Figure 25. Optical images of HGMs after fire testing.

PVB/PEG-coated HGMs also tested using similar method. In this case, HGMs were found in the water/gasoline interphase.

Exploring Previously Made Coating Behaviors

PEG and PVB coated microspheres and varying amounts of surfactants were tested to observe dispersion time and foam stability. The primary microspheres tested included A20 (uncoated), PVB coated, and PEG coated microspheres. The main surfactants used were Dowsil 501W and Polysorbate 80 (Tween 80). Even with varying amounts of Dowsil 501W and Tween 80, A20 (uncoated) and PVB microspheres showed poor dispersion time in water. PEG-coat stayed suspended in water some microspheres eventually sinking to the bottom. Increasing amounts of Tween 80 did not appear to improve dispersion time.

Figure 26. Microsphere dispersion of 2% PEG, 2% PVB, 2% uncoated, and control in 1% Tween 80 after shaking.

Behavior of microspheres on gasoline was observed. PVB coated and A20 (uncoated) microspheres floated on top of the gasoline before and after shaking. PEG coated sank to the bottom of the gasoline vial before and after shaking. When PVB coated and A20 microspheres (uncoated) were combined with water and added to gasoline, a layer of microspheres appeared between the gasoline and water layer.

Figure 27. Uncoated A20, PEG, and PVB microspheres with gasoline.

Exploring New Coating Behavior

From the dispersion time and gasoline behavior, new coatings for the microspheres were explored. A20 microspheres were coated with PEG (mw: 10000) in order to test performance. The PEG (mw: 10000) microspheres did not show great dispersion time in water and did not float on gasoline before and after agitation. A20 microspheres were also coated with a siloxane surfactant in a 1:2 ratio and 1:10 ratio. The foam from the siloxane surfactant microspheres looked good, but a layer of microspheres formed at the top of the water and under the foam after agitation. When the siloxane surfactant microspheres foam was added to a vial with gasoline, the microspheres appear to negatively impact the foam stability of the siloxane surfactant. A layer of microspheres formed at the top and bottom of the gasoline layer. The microspheres and foam from the top layer appeared to slowly travel to the bottom layer dropwise.

Results using Different Coatings

Based on the research performed by Tang and Wu, an oleophobic coating on the HGM was necessary to improve foaming capacity and stability [30] However, the coating used by Tang and Wu contains fluorine, so a non-fluorinated alternative will need to be explored. Methyltrimethoxysilane (MTMS) is a current compound used for non-fluorinated oleophobic coating development. The process for MTMS oleophobic coating involves hydrolysis of MTMS and coating of the desired substrate. This coating technique has been used to coat steel mesh, paper, and glass slides [31,32,33].

A technique for MTMS hydrolysis and coating microspheres is currently being explored. In *Fabrication of Oleophobic Paper with Tunable Hydrophilicity by Treatment with Non-fluorinated Chemicals,* it is demonstrated that oleophobic/hydrophilic characteristics depend on hydrolysis time of MTMS. [31] Different hydrolysis times and the corresponding characteristics were tested in order to produce an oleophobic and hydrophilic coating for the microspheres. Additionally, coating techniques was explored so the coated microspheres maintain low enough density to float on gasoline and a powder consistency as opposed to clumping.

Cleaning and Coating of Glass Microspheres with MTMS

In order to coat the microspheres with hydrolyzed MTMS, the A20 HGM were stirred in a 1 M solution of HCl for 18 h. The goal of this wash was to remove any impurities or coatings on the microspheres while attempting to ensure the presence of hydroxyl groups on the surface.

MTMS was sonicated with 0.1 M HCl in a 1:4 ratio to induce hydrolysis. The hydrolysis times were 5 minutes, 10 minutes, and 20 minutes. For each hydrolysis time solution, 3 grams of A20 microspheres were combined with 30 mL of the hydrolyzed MTMS to form a slurry. The slurries were then stirred and heated until the solvent completely evaporated. The resulting coated microspheres were clumpy. When pressed between two glass slides and water was dropped on, the microspheres displayed a hydrophobic behavior with water droplets remaining on top of the microspheres and some microspheres appearing to be attracted to the water drops. This hydrophobic behavior is shown in Figure 28 and Figure 29. When water is dropped on uncoated A20 microspheres, the water is easily absorbed.

Figure 28. Behavior of hydrolyzed MTMS coated A20 microspheres.

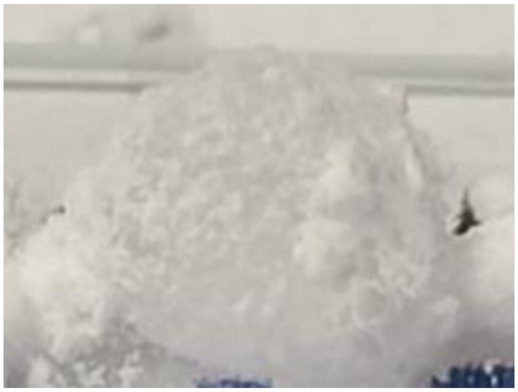


Figure 29. Behavior of hydrolyzed MTMS coated A20 microspheres.

Another coating technique was explored in an attempt to remove excess coating prior to drying. This was done by placing the microspheres in a hand sieve with a piece of cloth. The microspheres and hydrolyzed MTMS were combined and excess MTMS was allowed to drip through the sieve. The microspheres were then added to a petri dish and heated until dry. This resulted in a hard puck of microspheres that had to be broken up in order to test for hydrophilicity. The microspheres displayed hydrophobic characteristics.

The MTMS hydrolysis coating was tested on glass slides in order to see if the MTMS hydrolysis times were producing the desired hydrophilic characteristics. The glass slides were rinsed with methanol, isopropanol, and acetone. MTMS was hydrolyzed with 0.1 M HCl with sonication. The glass slides were then dipped into the hydrolyzed MTMS solution for 2 minutes. The excess hydrolyzed MTMS was combined with A20 microspheres until a consistency of wet sand was achieved. The resulting MTMS coated slides showed hydrophobic characteristics. The resulting microspheres initially appeared hydrophobic with the drops of water remaining on top of the microspheres and then slowly being absorbed after a few seconds. It is unclear if that is the result of some hydrophilic characteristics of the MTMS being present or some microspheres remaining uncoated and therefore able to absorb the water drops.

Zwitterion Coating with Betaine

Betaine is a zwitterion which is a neutral compound which has positively and negatively charged functional groups shown in Figure 30. A20 microspheres were coated with betaine dissolved in water with a rotary evaporator and then dried in a 60 °C oven. Another batch of microspheres were coated with betaine dissolved in methanol and evaporated while stirring on a hot plate. The resulting coated microspheres were added to water and did not stay well dispersed.

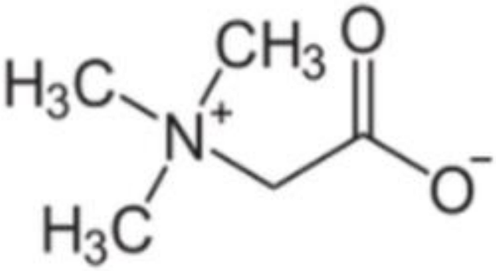


Figure 30. Betaine structure.

Exploration of Different Application Techniques

Dispersion in solution and application techniques of microspheres have been obstacles in testing microsphere-based foam application techniques. One of the problems faced is microspheres were trapped or not passing through evenly with the current small scale testing facilities. The use of a hose attachment which would allow water and liquid concentrate with microspheres to be combined during application was explored. A Miracle-Gro LiquaFeed hose attachment, shown in Figure 31, was modified to allow microspheres and an increased flow of liquid concentrate to pass through. When tested with a hose, the application of microspheres and generation of foam was successful. However, the flow rate and pressure of the hose prevents the use of this approach on the small scale fire testing set up.

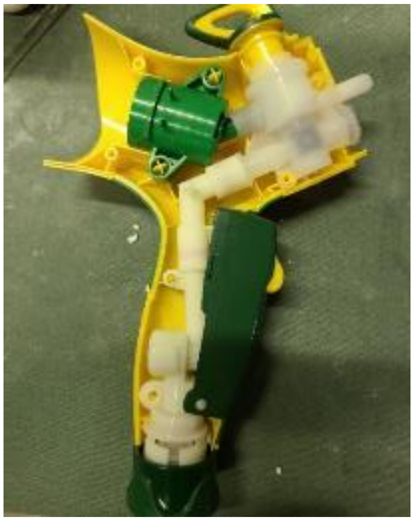


Figure 31. Inside of Miracle-Gro Liquafeed hose adapter.

Dispersion in Higher Viscous Liquid Concentrates

The dispersion of uncoated A20 microspheres in higher viscous liquid concentrates were explored. The solutions used were Rain-X 2-in-1 Windshield Washer Fluid, poly(propylene glycol), Tween 80, ethylene glycol, and tetraethylene glycol dimethyl ether. Good dispersion in liquid concentrates can be useful in finding a medium concentrate to disperse microspheres in without requiring long dispersion time in water.

Sol-Gel Approach

A20 microspheres were tested with a sol-gel approach to improve dispersion in water. In separate bottles, 20 grams and 40 grams of tetraethyl orthosilicate were measured into a plastic bottle. In each bottle, 2 grams of A20 microspheres and 20 grams of ammonium hydroxide were added and slightly shaken. The bottle was repeatedly opened to release any gas accumulation. The mixture was then mixed for at least an hour. This process was repeated with 40 and 60 grams of TEOS with K37 microspheres instead of A20 microspheres. The dispersion time of the sol-gel microspheres in water did not significantly improve as a distinct layer of microspheres rose to the top of the water.

Hydrogel Approach

K37 microspheres were tested with a hydrogel approach to improve dispersion in water. 20 g of 2-acrylamido-2-methyl-1-propanesulfonic acid and 0.04 g of N-N’-methylenebis(acrylamide) were dissolved in 100 mL of distilled water. 3 g of K37 microspheres was mixed into the solution. The resulting mixture was then purged under argon for 115 minutes. 0.20 g of ammonium persulfate was added and the mixture was heated and stirred until a gel formed. This procedure was repeated with 30 g of 2-acrylamido-2-methyl-1-propanesulfonic acid. When small amounts were mixed with water, the microsphere gel suspended in water. However, the mixtures were very viscous and did not contain a significant amount of microspheres.

Fire Testing Attempts

Besides formulation issues, microsphere-based foams pose application technique challenges. Dispersion time in water base solutions have been tested in order to try to prevent microspheres from floating to the top of the solution and not being evenly applied to the fire. Another obstacle in microsphere foam application is microspheres getting trapped or clogging the sparger and sprayer. In order to prevent microspheres from not being able to flow out properly, the nozzle of the microsphere specific pump sprayer was modified. The modification results in less agitation and therefore less foam and a higher flow rate of liquid.

In order to test using the sprayer to apply the microspheres, 75 grams of K37 microspheres were first tested with a 15% commercial sodium lauryl sulfate surfactant solution using the sprayer. The fire was not quenched and sections of the foam appeared to be mixed with gasoline shown in Figure 32.

Figure 32. Foam later of K37 and commercial sodium lauryl sulfate surfactant solution with streaks of gasoline after unsuccessful fire testing.

In order to see if adding K37 microspheres could improve foam performance, 40 grams of K37 microspheres (4%) were added to a 1L solution of 3% siloxane surfactant and 0.5% polysaccharide which by itself quenches the fire in less than a minute. The solution with the K37 microspheres were applied to the fire using the microsphere sprayer. The foam did not quench the fire and appeared to burn parts of the foam shown in Figure 33.

Figure 33. Foam layer of 4% K37 with siloxane surfactant and polysaccharide after unsuccessful fire testing.

Spray application of HGM powders

The sealing efficiency of glass microspheres on top of gasoline was investigated. The solid microsphere powder (3M glass microsphere type K20) was added through a funnel on top of the fuel. The as-received K20 microsphere was floating on top of the gasoline. In Figure 34, various layers are shown, indicating the floating nature of glass microspheres.

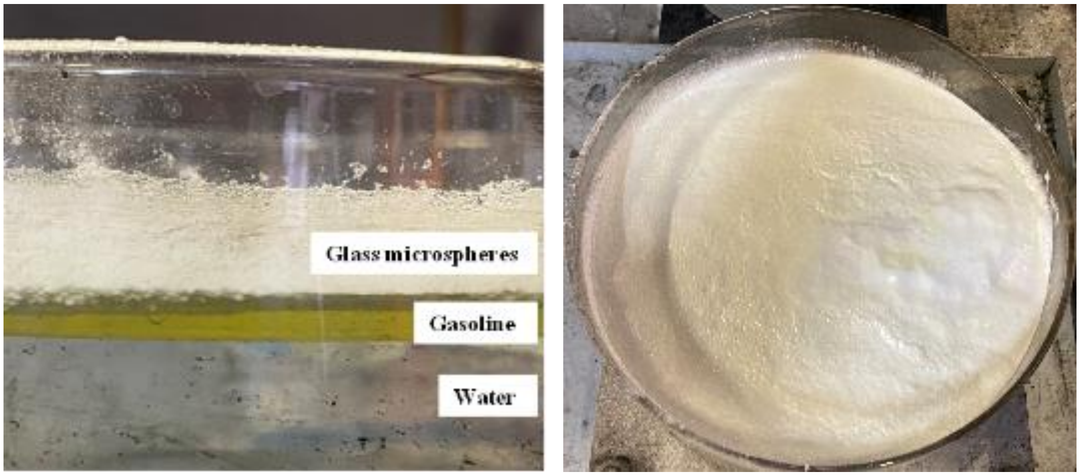


Figure 34. Photographs of solid glass microspheres floating on top of gasoline (A) Side view and (B) Top view

The sealing effect of glass microspheres was tested by moving the flame from a lighter on top of the gasoline layer covered with microspheres. There was no lighting of gasoline observed even after several attempts as shown in Figure 35.

Figure 35. Photograph showing the fire on top gasoline covered with glass microspheres

The results shown in Figures 34 and 35 clearly suggest that glass microspheres can indeed seal the gasoline from evaporating. The glass microspheres cover on top of gasoline remained stable even after 30 minutes. Interestingly, a small fire started on a corner of the pool, ***self-quenched*** immediately as shown in Figure 36.

Figure 36. Self-quenching action of glass microspheres of gasoline pool fire

The issue that remains is the mode of delivery of glass microspheres on top of burning fuel. In future efforts, powder spray process must be investigated for fire quenching.

7. Conclusions and Implications for Future Research and Benefits

1. Hydrophobic, hydrophilic and un-treated glass microspheres were investigated for firefighting foam application, along with PFAS-free foam formulations.
2. Hydrophobic microspheres are difficult to disperse in water due to low density and hydrophobicity. Therefore, they were not suitable for foam formulation in water.
3. Hydrophobic microspheres are also miscible in gasoline fuel and sink into the fuel. Therefore, they were not useful for pool fire quenching.
4. Hydrophilic and un-treated microspheres are relatively easy to disperse in water. However, they float on top of gasoline and form a seal preventing evaporation of the fuel.
5. Dispersion of microspheres and delivery of microspheres in an aqueous medium is challenging because of their low density. One approach could be using viscous concentrates of PFAS-free foam formulations to disperse hydrophilic or un-treated microspheres.
6. Due to particle nature of the microspheres, the nozzles may need to redesigned to prevent clogging of the nozzle.
7. ***Untreated, as-received microspheres improved the firefighting performance of PFAS-free foam formulations. Therefore, they could be considered as additive in the newly developed PFAS-free foam formulations.***
8. Untreated microspheres could be sprayed as powders on top of the quenched fuel to prevent evaporation and can potentially increase the burnback time.

8. 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. https://www.serdp-estcp.org/content/download/45801/426898/file/FY19 Instructions SEED BAA.pdf
5. 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
6. 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
7. https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Contaminated-Groundwater-SONs/Innovative-Approaches-to-Fluorine-Free-AFFF-2018/(language)/eng-US
8. https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/pfoa-stewardship-program-baseline-year-summary-report
9. https://www.congress.gov/bill/115th-congress/house-bill/302/text
10. An Analytically Defined Fire-Suppressing Foam Formulation for Evaluation of Fluorosurfactant Replacement, By: Hinnant, Katherine M.; Giles, Spencer L.; Snow, Arthur W.; Farley, John P.; Fleming, James W.; Ananth, Ramagopal, Source: Journal of Surfactants and Detergents, Volume: 21, Issue: 5, Pages: 711-722, Journal; Online Computer File, 2018, CODEN: JSDEFL, ISSN: 1558-9293, DOI: 10.1002/jsde.12166
11. Measuring fuel transport through fluorocarbon and fluorine-free firefighting foams, Hinnant, Katherine M.; Giles, Spencer L.; Ananth, Ramagopal, Source: Fire Safety Journal, Volume: 91, Pages: 653-661, Journal; Online Computer File, 2017, CODEN: FSJODZ, ISSN: 0379-7112, DOI: 10.1016/j.firesaf.2017.03.077
12. Influence of fuel on foam degradation for fluorinated and fluorine-free foams, Hinnant, Katherine M.; Conroy, Michael W.; Ananth, Ramagopal, Source: Colloids and Surfaces, A: Physicochemical and Engineering Aspects, Volume: 522, Pages: 1-17, Journal; Online Computer File, 2017, CODEN: CPEAEH, ISSN: 0927-7757, DOI: 10.1016/j.colsurfa.2017.02.082
13. Snow, S. A.; Fenton, W. N.; Owen, M. J., Synthesis and characterization of zwitterionic silicone sulfobetaine surfactants. *Langmuir* 1990, *6* (2), 385-391.
14. Gentle, T. E.; Snow, S. A., Adsorption Of Small Silicone Polyether Surfactants At The

Air/Water Interface. *Langmuir* 1995, *11* (8), 2905-2910.

15. 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.
16. 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
17. D. Blunk, R.H. Hetzer, A. Sager-Wiedmann, K. Wirz, Siloxane-containing fire extinguishing foam, US Patent Application # US 2014/0306141 (2014)
18. 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
19. Environment Friendly Fluorine-free Firefighting Foam, CetainTech, Inc., US Air Force SBIR Contract Number: FA805119PA005 (2019)
20. *P. Walstra*, Principles of Foam Formation and Stability, Foams: Physics, Chemistry and Structure, Edited by A. J. Wilson, BSc, DPhil, MIBiol pp. 1-16 (1989)
21. Chen Wei-hong,LIU Ran,Guo Zi-dong,Liu, Heng-qi, Luo Wen-dong(Chinese People's Armed Police Academy,langfang Hebei,065000); Effect of the Hollow Microsperes on the Foamability and Stability of Fire Fighting Foam[J];Fire Safety Science;2007-03
22. B. Tang and Z. Wu, Oleophobic Modification of Hollow Glass Microspheres and Its Effect on the Foaming Capacity and Stability of Foam Extinguishing Agent, Journal of Chemistry, **2015**, Article ID 923894, https://www.hindawi.com/journals/jchem/2015/923894/
23. C. Weihong, L. Ran, and G. Zidong, “Effects of the hollow glass microsphere on the foaming ability and stability of fire fighting foam,” Fire Science, vol. 16, no. 3, pp. 133–136, 2007. View at Google Scholar
24. W.-H. Chen, W.-F. Du, and X.-N. Xu, “Experimental study on snti-solubility and snti-burning property of hollow microsphere three-phase foam,” Fire Safety Science, vol. 17, no. 1, pp. 15–19, 2008. View at Google Scholar
25. W.-H. Chen, W.-F. Du, and W. He, “Effect of fluorocarbon surfactants on anti-solubility and anti-burning property of hollow microsphere three-phase foam,” Fire Safety Science, vol. 18, no. 3, pp. 182–186, 2009.
26. R. Sadler, M. Sharpe and K. Shivakumar, A comparison of mechanical and fire properties of eco-core with a competitive commercial material, SAMPE 2007 (http://www.urweb.tv/material/fireResistant CoreMaterials/Sampe_2007_Paper.pdf)
27. Franklin Veatch, Lyndhurst, Harvey E. Alford, Amherst, and Richard D. Croft, Wapakoneta, Ohio, assignors to . The Standard Oil Comp, Method Of Producing Hollow Glass Spheres US Patents No. 2,978,339 (1961)
28. X-C. Bian, J-H. Tang, Z-M. Li, Flame retardancy of Hollow Glass Microsphere/Rigid Polyurethane Foams in the Presence of Expandable Graphite, J. App. Polymer Sci., 109, 1935-1943 (2008)
29. Ananth, R.; Snow, A. W.; Hinnant, K. M.; Giles, S. L.; Farley, J. P., Synergisms between Siloxane-polyoxyethylene and Alkyl Polyglycoside Surfactants in Foam Stability and Pool Fire Extinction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2019.
30. Tang, B.; Wu, Z., Oleophobic Modification of Hollow Glass Microspheres and Its Effect on the Foaming Capacity and Stability of Foam Extinguishing Agent. Journal of Chemistry 2015, 2015, 923894.

31. Jiang, L.; Tang, Z.; Park-Lee, K. J.; Hess, D. W.; Breedveld, V., Fabrication of non-fluorinated hydrophilic-oleophobic stainless steel mesh for oil-water separation. Separation and Purification Technology 2017, 184, 394-403.
32. Widati, A. A.; Nuryono, N.; Kartini, I., Water-repellent glass coated with SiO2–TiO2–methyltrimethoxysilane through sol–gel coating. AIMS Materials Science 2019, 6, 10-24.
33. Mitrinova, Z.; Tcholakova, S.; Golemanov, K.; Denkov, N.; Vethamuthu, M.; Ananthapadmanabhan, K. P., Surface and foam properties of SLES+CAPB+fatty acid mixtures: Effect of pH for C12–C16 acids. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2013, 438, 186-198.