Hollow Microspheres Based Fire Fighting Foams

Project Number WP20-1533

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PI's Organization: Materials Modification Inc.

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Materials Modification Inc.

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● The primary technical objective was to develop a fluorine-free surfactant formulation as a “drop-in” replacement for AFFF.
- Identification of specific functionalized HGMs and evaluate their use in AFFF that could potentially replace fluorinated surfactants.
- 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

- **T.S. Sudarshan - Materials Modification Inc.**
- **Kris Rangan- Materials Modification Inc.**

Background

- The project Period: September 2020-2022
- Statement of Need (SON) Number #: SON-WP20-A1

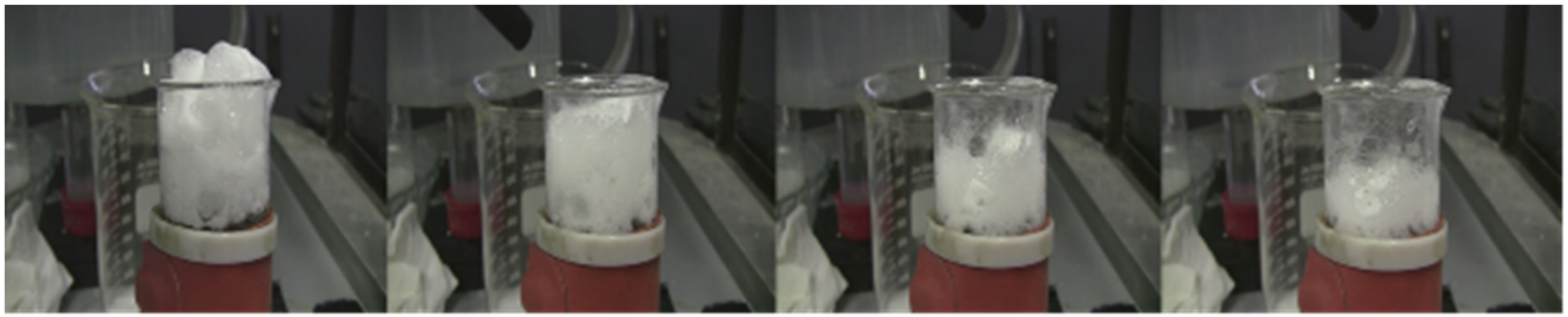
- **The use of firefighting foam containing perfluorooctane sulfonic acid (PFOS) and other per- and polyfluorinated alkylated substances (PFASs) resulted in the contamination of soil, groundwater, drinking water, and surface water, across the US including manufacturing sites and Department of Defense bases.**

- **Continued use of PFAS is not sustainable and PFAS-free materials are needed in firefighting foam formulations.**

- **The primary research objective of this project was to develop a fluorine-free formulation based on hollow glass microspheres (HGMs) and evaluate their chemical stability, physical and fire suppression abilities. The tests included the evaluation of spreading coefficient, and Benchtop fire testing.**

Background

- **Fire-fighting foams are made up of air bubbles dispersed in a continuous aqueous medium. Ostwald ripening, liquid drainage, and air bubble coalescence, cause collapse of the fire-fighting foam bubbles.**
- **It is difficult to make a stable foam, especially with PFAS-free chemicals in the presence of hot fuel vapors.**
- **"Extremely persistent" foams can be made if the air bubbles are made up of solids. The solid air bubbles (particles) should be able float on the gasoline fuel surface.**
- **Hollow Glass Microspheres (HGMs) are potential materials for fire foam application with densities < 0.5 g/cm^3**



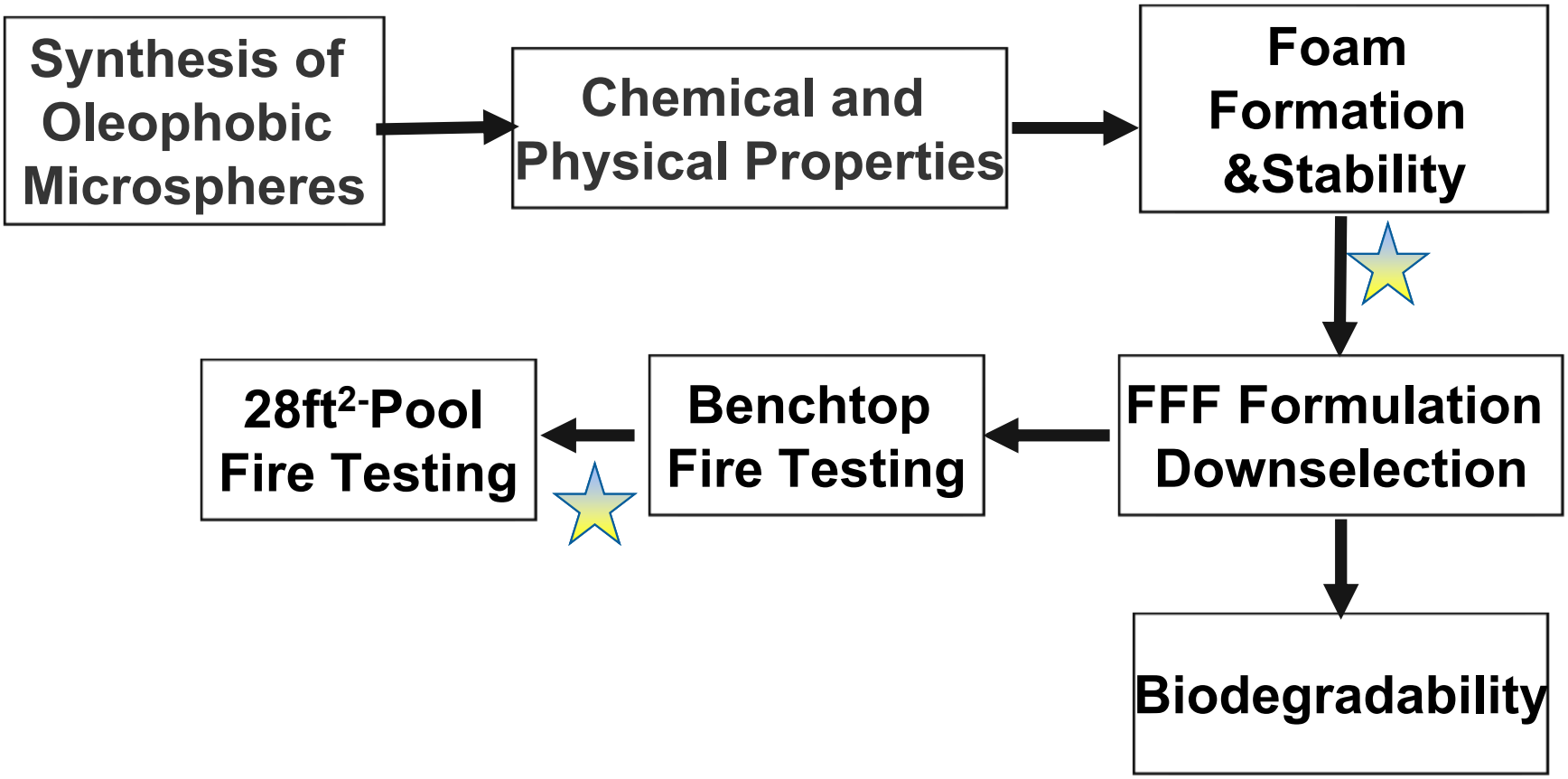
Xanthan Gum

Technical Objectives

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

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



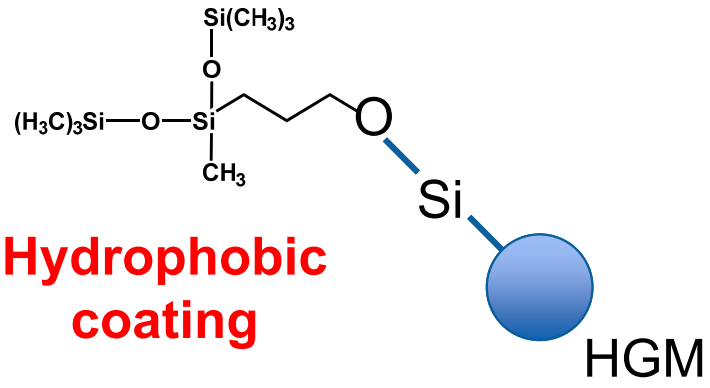
Technical Approach

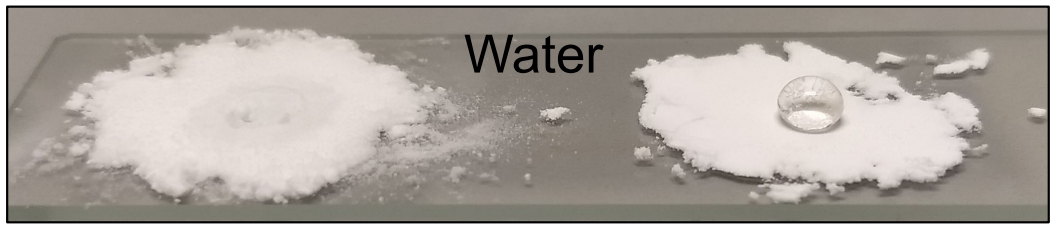
Task	Description Month	1	2	3	4	5	6	7	8	9	10	11	12	13-24
1	Materials Procurement													
2	Preparation of Oleophobic Hollow Glass Microspheres													
3	Preparation of Fire Fighting Foam Formulation with Oleophobic HGM additives													
4	Physical Properties of HGM-based Foam Formulations													
5	Small Scale Fire Fighting Test													
6	28 ft2 Pool Fire Fighting Testing													
7	Biodegradability Testing													
8	Reporting and Planning for Future Testing													
	Contingencies in Project Performance													

Results

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 were researched in order obtain an oleophobic additive for the PFAS-free surfactants.**
- **The oleophobic HGMs could act as a barrier for combustible liquids from supplying fuel vapor and decreasing 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.**

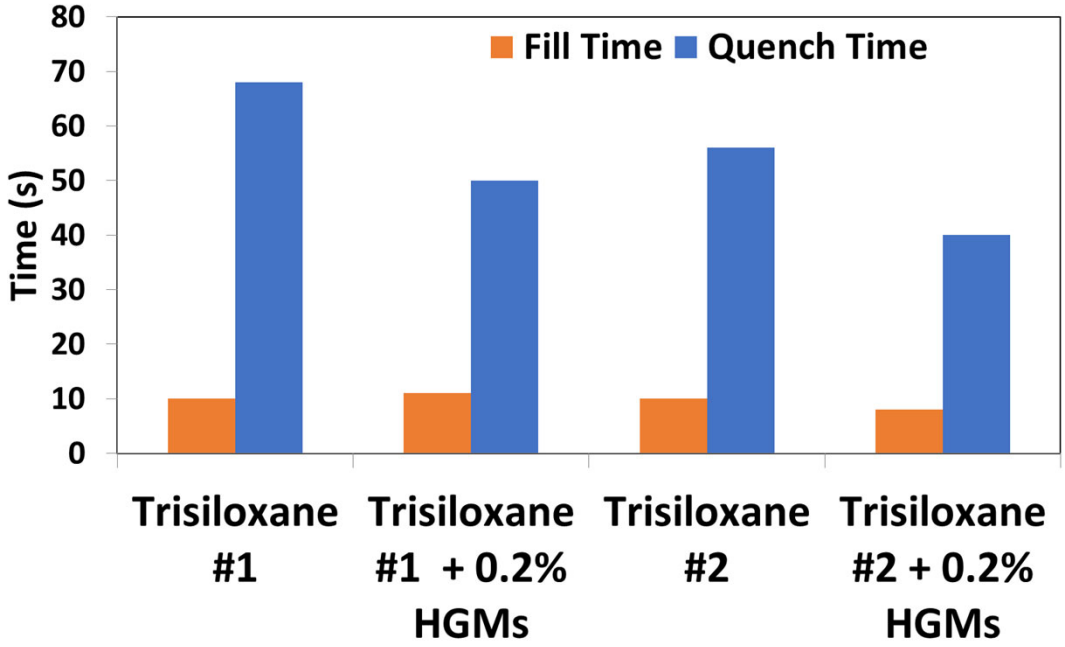




Benchtop Fire Testing Results

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 + 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

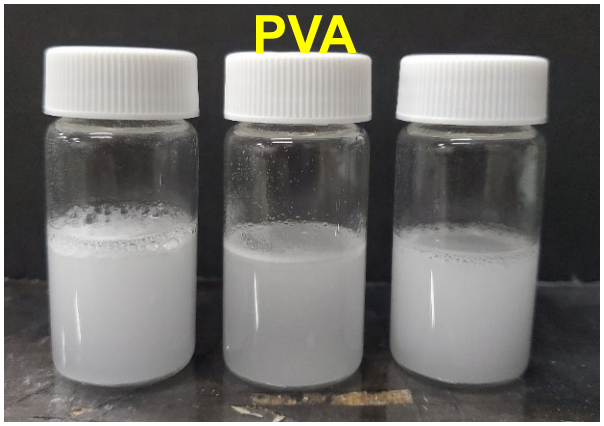
Hydrophobic Hollow Glass Microspheres



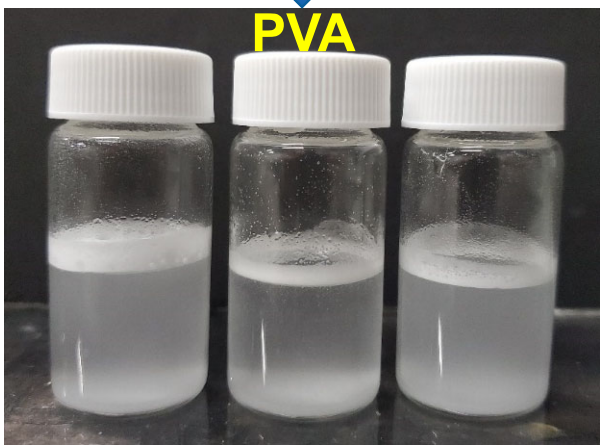
- ***Addition of <u>untreated</u> glass microspheres improved the fire quenching performance of the siloxane foam formulation.***
- ***The PFAS-free formulation with <u>hydrophobic</u> glass microspheres did not quench the pool fire.***

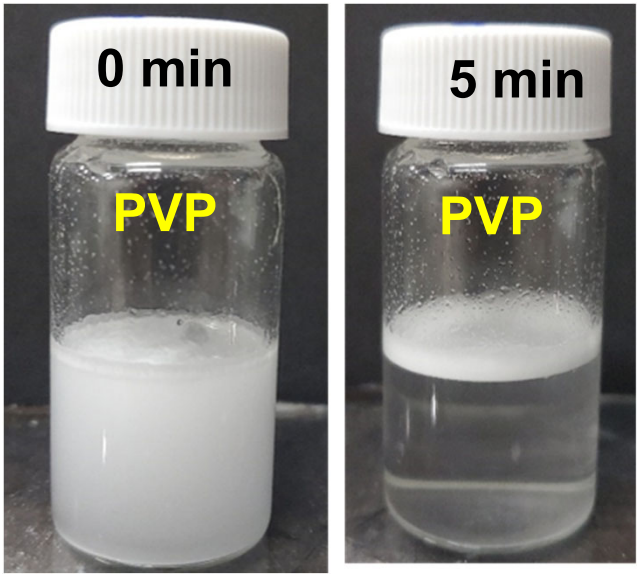
Polymer Coated HGMs

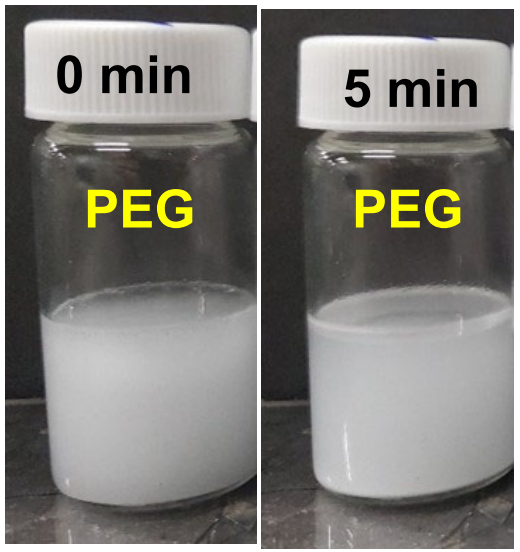
Polymer	Dispersion Stability	Water repellency	FFF formulation in water
PVA	<5 min	Hydrophilic	Poor
PVP	>5 min	Hydrophobic	Poor
PEG	>5 min	Hydrophilic	Good
PVB	Separated quickly	Hydrophobic	No



5 min







PVA = Polyvinyl Alcohol
PVP = Polyvinyl Pyrrolidone
PET = Polyethylene Glycol
PVB = Polyvinyl Butryal

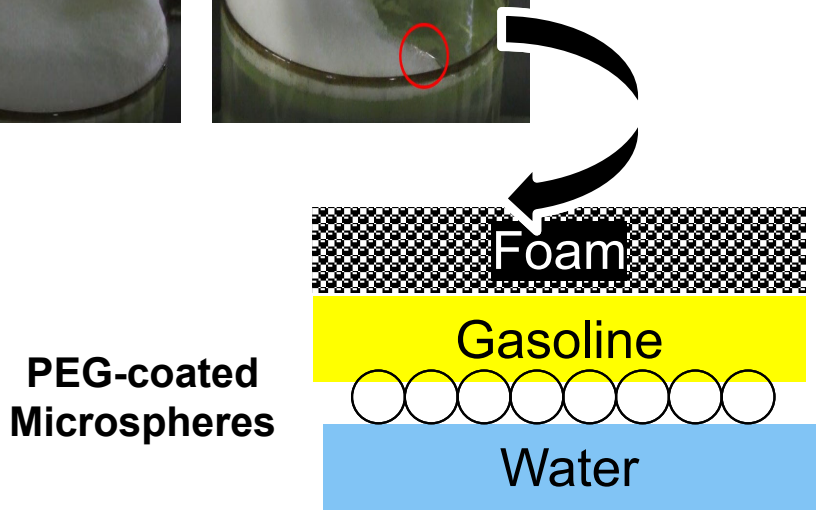
Benchtop Fire Testing

Foam Formulation:

0.5% PEG-coated microspheres, 0.4 % DOWSIL501W, 0.8% Glucopon in water




Quench Time 46 s
Fill time 9 s

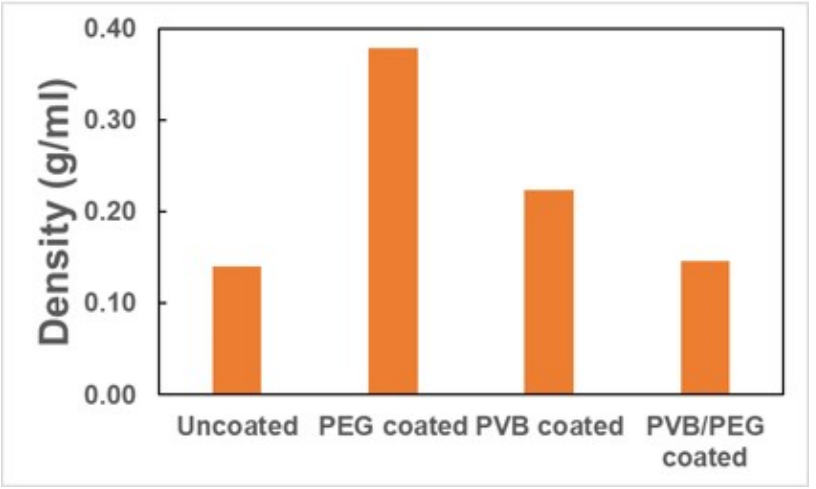


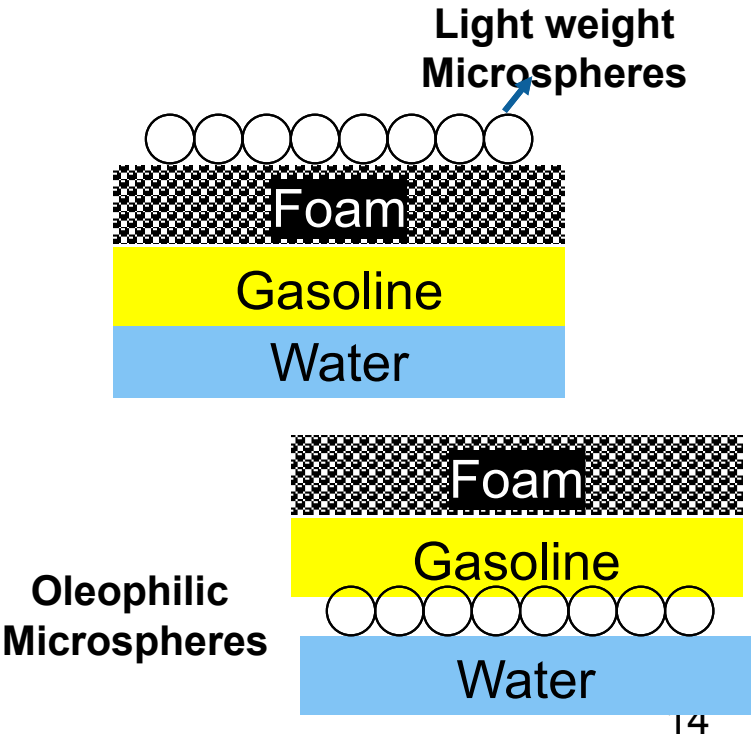
Materials	Density (g/cm^3)
Gasoline	0. 73
As-received HGMs	0.20
Hydrophilic HGMs	0.18
Hydrophobic HGMs	0.20

- **Microparticles found in between gasoline and water layers**

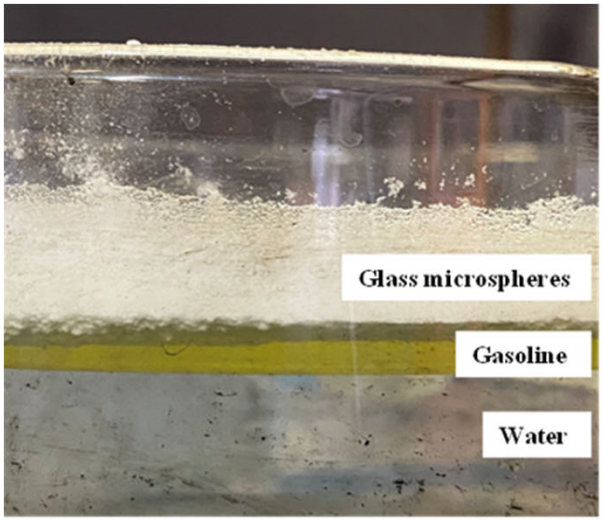
Low density or Oleophilicity? Where Archimedes Principle Fails!

- 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.
- Oleophilic microparticles found in between gasoline and water layers.
- Uncoated and PVB coated microspheres floated on top of gas. PEG coated HGMs went into water and PVB/PEG coated HGMs found to stay on the interface between water and gasoline layers

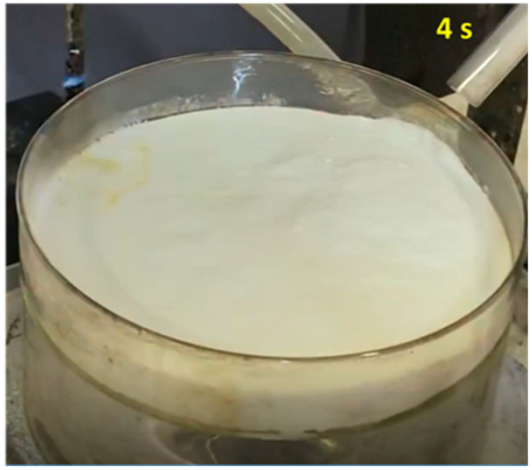




Powder Spraying of Microspheres



- Untreated microparticles found to float on top of gasoline
- Uncoated microsphere powders sprayed on top of gasoline and lit with a lighter. No fire was observed.
- HGMs could be used to improve the burnback time after quenching the fire



Self-quenching of fires by HGMs

Other Approaches

Use microspheres to increase foam stability and overall fire extinguishing performance

Microsphere approach:

- **Foam**
  - **In mixture**
  - **Combined during application**
- **Powder spray**

https://www.americanfiresupply.com/valves/wye-valves

https://www.miraclegro.com/en-us/products/plant-food/miracle-gro-liquafeed-all-purpose-plant-food-advance-starter-kit?bvstate=pg:2/ct:r

Key Points

- **Addition of untreated glass microspheres improved the fire quenching performance of the siloxane foam formulations.**
- **The PFAS-free formulation with hydrophobic glass microspheres did not quench the pool fire.**
- **HGMs could be used to improve the burnback time after quenching the fire**

Next Steps

- Investigate further if hydrophilic or untreated microspheres can quench fire with other surfactants
- Need to determine appropriate device for powder spraying of HGMs.
- Evaluate the use of HGMs to increase burnback time
- Evaluate if HGMs could be additives for commercial PFAS-free firefighting formulations.

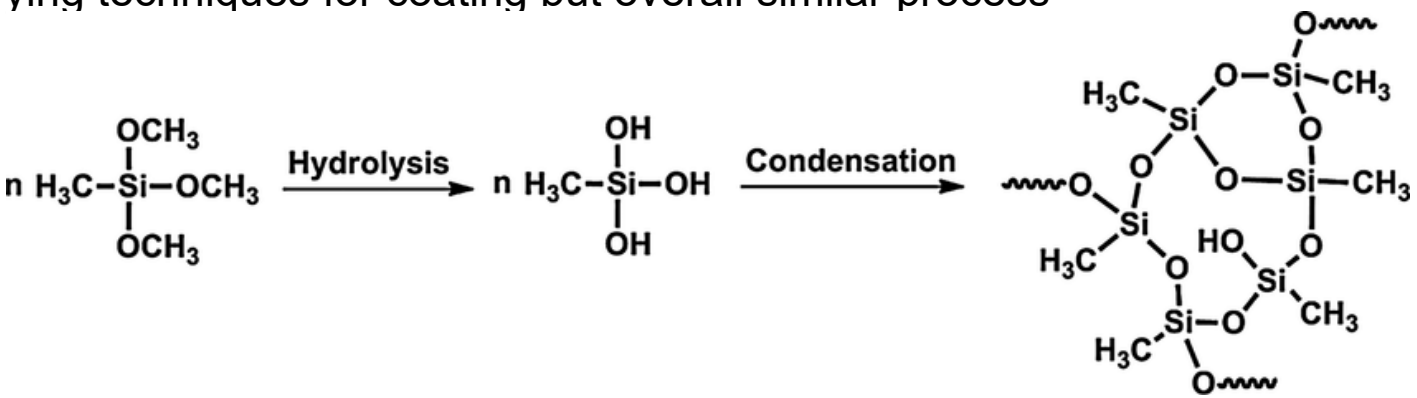
Technology Transfer

- Limited Scope Effort has minimal capability to transfer technology.
- Needs a follow on study to understand the mechanism of interaction to determine the efficacy.

BACKUP SLIDES

Methyltrimethoxysilane (MTMS)

- Could act similar to the oleophobic coating used by Tang and Wu
  - Tridecafluorooctyltriethoxysilane (F8261)
- Used to coat stainless steel mesh, paper, and glass
  - Varying techniques for coating but overall similar process



https://www.researchgate.net/profile/Saeed-Rahemi-Ardekani/publication/333966212/figure/fig2/AS:779907785293826@1562955914414/Hydrolysis-and-condensation-of-methyltrimethoxysilane.ppm

Hydrophilic & Oleophobic Particles

- Hydrolyzed MTMS appeared to result in hydrophobic coating
  - Hydrophobic and hydrophilic?
- If application technique changes, how important is it being hydrophilic?
- Could hydrophilicity contribute to microspheres going into water layer instead of floating on the top layer of gas?

WP20-1533 : Hollow Microspheres Based Fire Fighting Foams

Performers: Materials Modification Inc,

Technology Focus

- *Develop a PFAS-free formulation based on hollow glass microspheres (HGMs)*

Research Objectives

- *Identification of specific functionalized HGMs and evaluate their use in firefighting foams*

Project Progress and Results

- *Addition of untreated glass microspheres improved the fire quenching performance of the siloxane foam formulation.*
- *The PFAS-free formulation with hydrophobic glass microspheres did not quench the pool fire.*

Technology Transition

- Investigation of glass microspheres as additives to commercial PFAS-free formulations to increase their firefighting efficiency
- Glass microsphere powders could be used to improve the burnback time after quenching of fire.