Fluorine-free Foams with Oleophobic Surfactants and Additives for Effective Pool Fire Suppression

WP-2739

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14. ABSTRACT
Develop fluorine free surfactants to reduce fuel permeability through foam and foam degradation by fuel to increase fire suppression. Conduct measurements of aquatic toxicity and biodegradation to assess environmental impact.

15. SUBJECT TERMS
Fluorine free Foams, Oleophobic Surfactants, Additives, Effective Pool Fire Suppression

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Project Team

- R. Ananth (PI), A.W. Snow (Emeritus), K.M. Hinnant, S.L. Giles, J.P. Farley, U.S. Naval Research Laboratory, Washington, DC - Fire Suppression

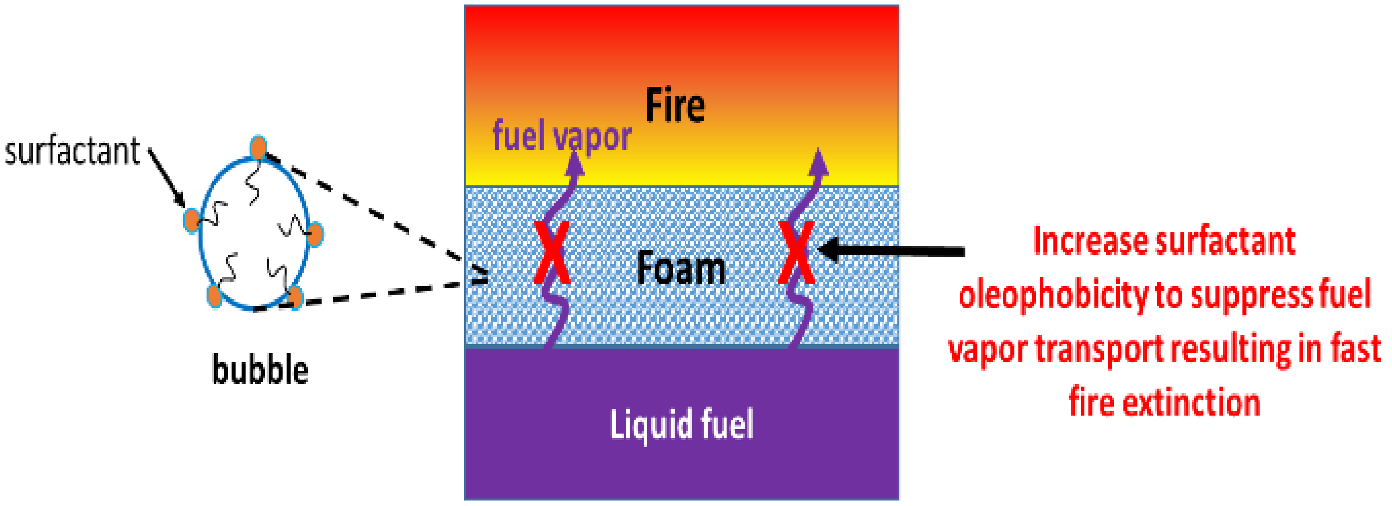
- Professors J. Field and W. Stubblefield, Oregon State University, Corvallis, OR – Environmental Impact Assessment

Background

- Project was initiated in 2017
- SON
    - ♦ Develop fluorine-free surfactant formulation for use in Aqueous Film Forming Foam (AFFF) fire-suppression operations.
    - ♦ Identify and test fluorine-free surfactants for use in AFFF to meet the performance requirements defined in MIL-F-24385F.
    - ♦ New formulations must be compatible with existing equipment.
    - ♦ Include testing to validate persistence and aquatic toxicity.
    - ♦ Include an assessment of human health and environmental impacts of proposed ingredients, formulations, and byproducts.

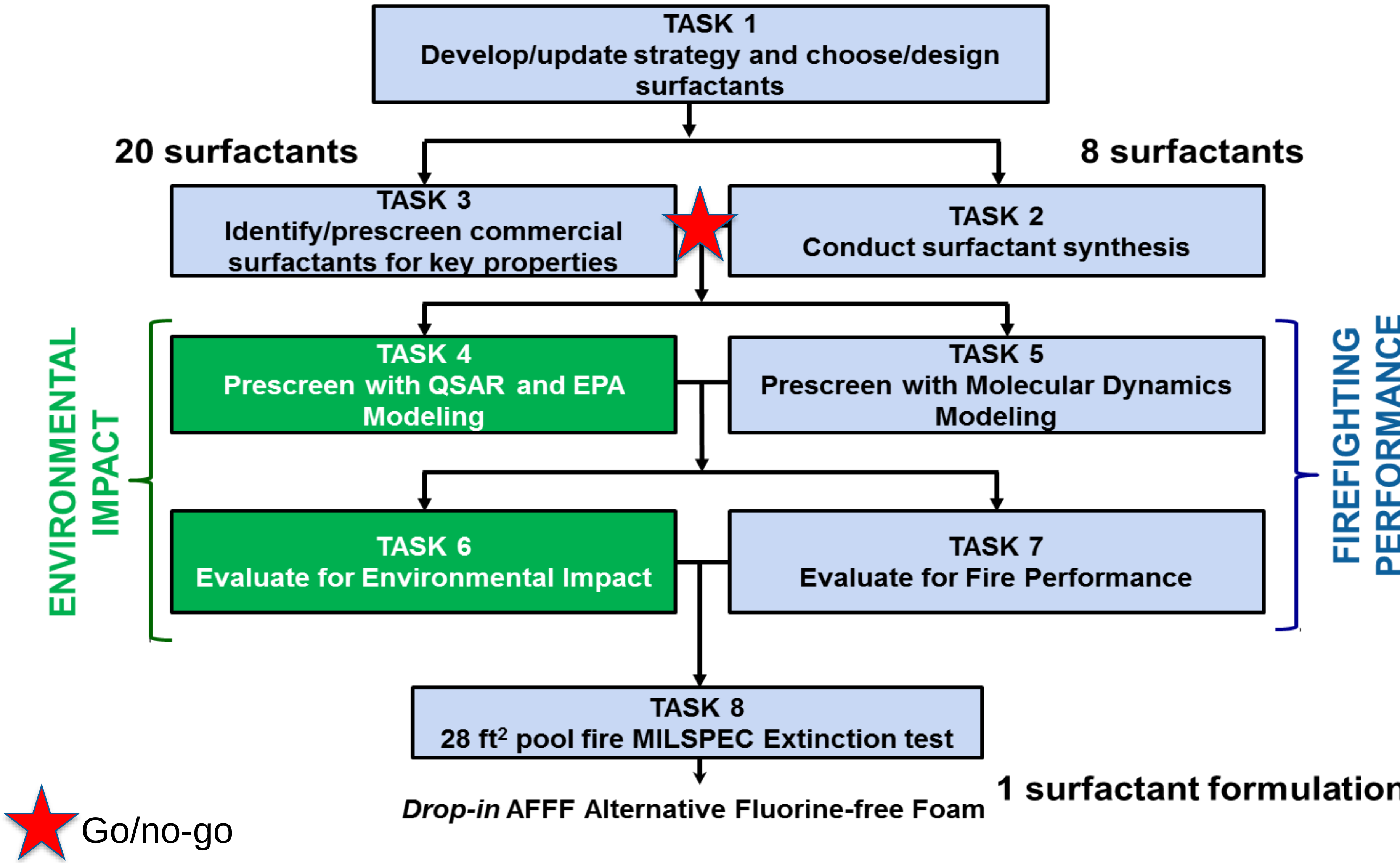
Technical Objectives

- Develop fluorine-free surfactants to reduce fuel permeability through foam and foam degradation by fuel to increase fire suppression.



- Conduct measurements of aquatic toxicity and biodegradation to assess environmental impact.

Technical Approach



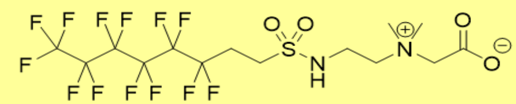
RESULTS

- Designed a simplified AFFF with known composition as a control or Reference AFFF.
- Evaluated bench scale fire extinction of many commercial siloxane and hydrocarbon surfactants against the Reference AFFF. (Go/no-go)
- Identified a commercial siloxane surfactant having remarkable fire suppression properties.
- Discovered surfactant-fuel interactions lower fire suppression.
- Developed strategies and methods to improve fire suppression by varying surfactant chemical structure and fuels.
- Quantified the effects of surfactant's chemical structure on solution and foam properties, and fire extinction.
- Measured aquatic toxicities of siloxane and hydrocarbon surfactants, and developed analytical methods for surfactants.

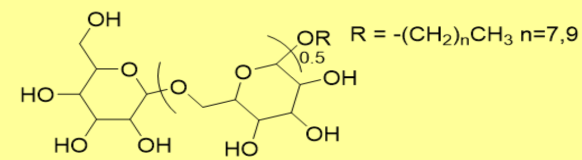
Designed a three-component Reference AFFF unlike proprietary commercial AFFFs

- Commercial AFFFs have proprietary compositions and are complex involving dozen or more components.
- Designed Reference AFFF containing:
  - ♦ fluorocarbon surfactant - Capstone1157
  - ♦ hydrocarbon surfactant – alkylpolyglycoside or glucopon
  - ♦ Solvent – Butyl Carbitol
- Foams generated from RefAFFF passed MilSpec extinction and burnback tests at 28 ft^2 pool scale.

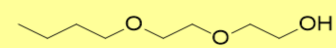
Known structures



Capstone® 1157, Forafac® 1157



Glucopon® 215 UP



Butyl Carbitol®, DGBE

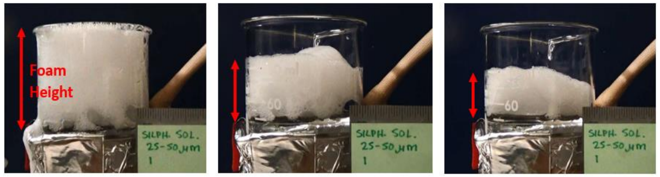
MilSpec 28 ft^2 Pool Fire Extinction and Burnback

Formulation	Extinction, s - heptane	Extinction, s-gasoline	Burnback, s-heptane	Burnback, s - gasoline
Commercial AFFF	22	28	697	433
Reference AFFF	30	26	981	562

Go/No-go Decision
Evaluation of Multipurpose, Commercial, Surfactants for Firefighting Foams

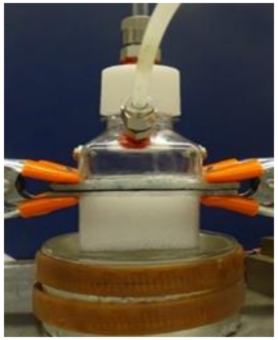
- Substituted commercial siloxane and hydrocarbon surfactants for the fluorocarbon surfactant in RefAFFF and generated foams.
- Commercial surfactants were carefully chosen to have somewhat related chemical structures to establish trends in structure versus fire extinction time.
- Measured foam degradation, fuel permeation through foam, and heptane-fire extinction time at bench scale.

Foam Degradation

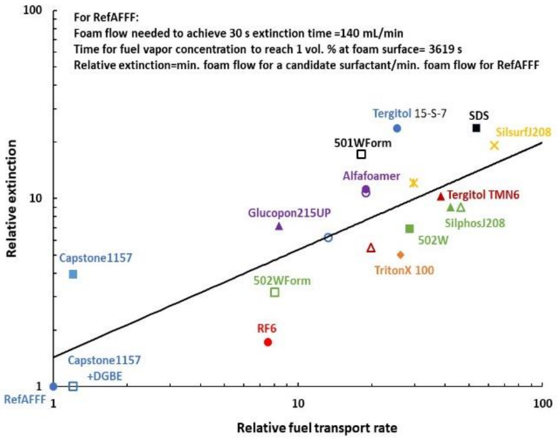


Time: 0 min   3 min   4 min

Fuel Vapor Transport



Correlation with extinction time

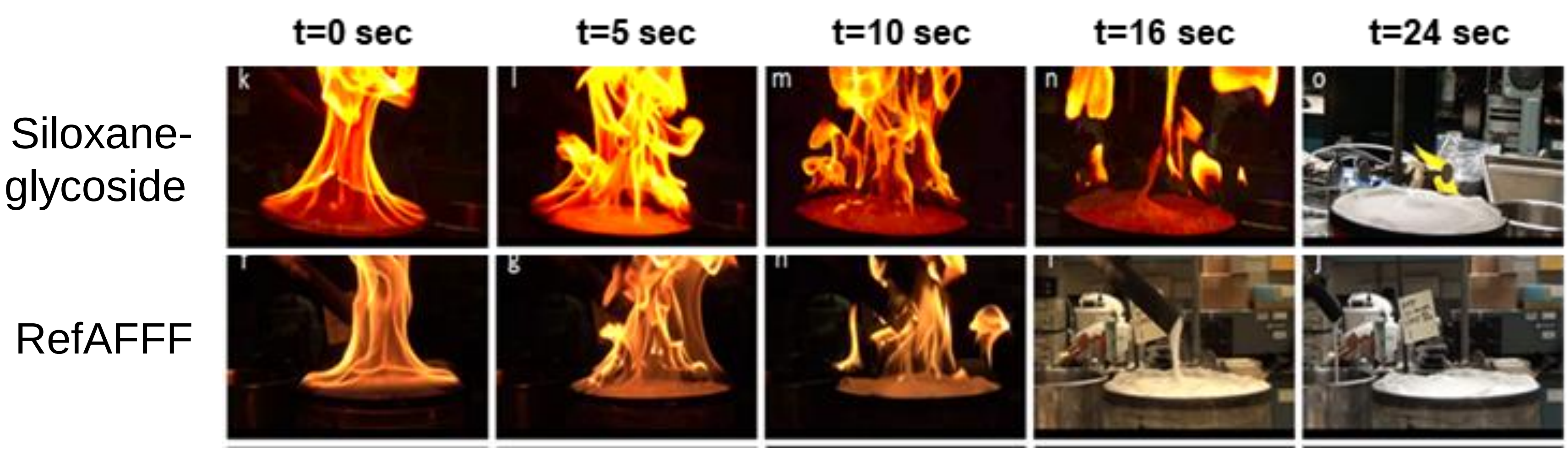


- **Go/No-go Decision:** *Established correlation among foam degradation, fuel vapor transport, and fire extinction by bench scale testing.*

Discovery of Commercial Nonionic Siloxane (Dowsil 502W)-glycoside for Firefighting

- Dowsil 502W is a siloxane surfactant used in making polyurethane foams.
- Substituted 502W for the fluorocarbon in RefAFFF to make siloxane-glycoside formulation and generate foams;
  - ♦ 3 % concentrate viscosity 7.4 cP is within MilSpec <20 cP.
  - ♦ 3% concentrate maintained performance after MilSpec aging at 60 ^{o}C.
  - ♦ U.S. Patent application filed.
- Bench and large scale testing showed it to be very effective on heptane.

19-cm diameter bench scale Heptane pool at 1000 mL/min foam

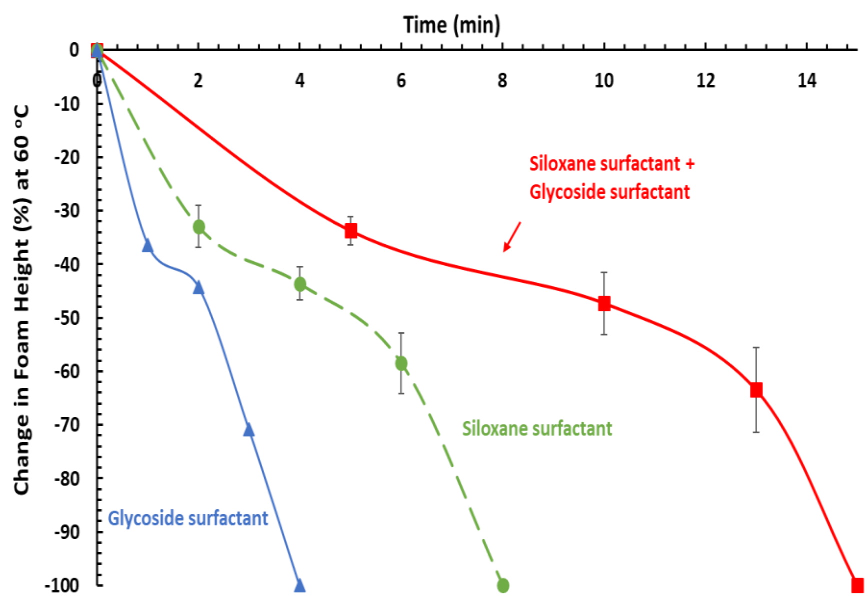


Synergistic Interactions Between Nonionic Siloxane-glycoside Surfactants

- Siloxane-glycoside mixtures have higher foam stability and much faster fire extinction time than the individual surfactants.
- Molecular Dynamics simulations showed increased packing density at heptane-water interface for the mixtures

Foam degradation on a hot heptane pool

Time: 0 min 3 min 4 min



Gasoline Problem

28 ft^2 MilSpec fire test at 2 gpm for heptane and gasoline

t=0 sec | t=15 sec | t=30 sec | t=51 sec

NRL's nonionic Siloxane/ Glycoside on heptane

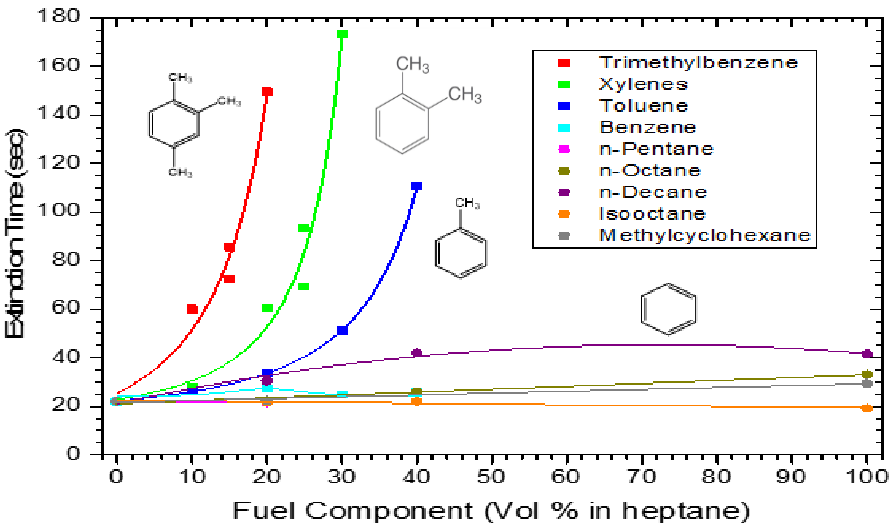
AFFF on heptane

NRL's Siloxane/ Glycoside on gasoline

No extinction of gasoline pool fire with nonionic siloxane-glycoside surfactants even after 75 s

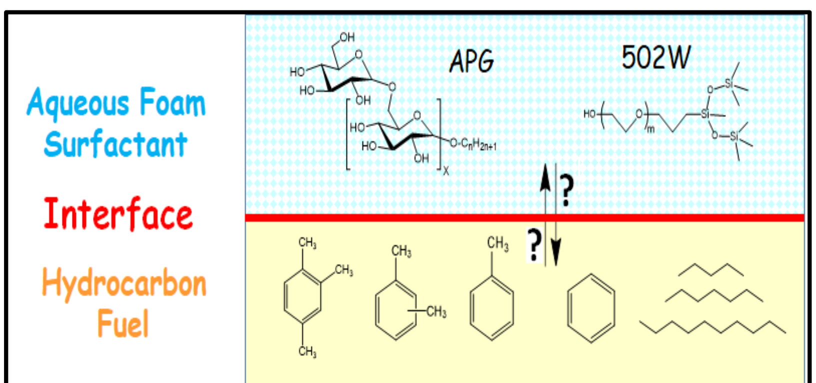
Fire Extinction for individual components in gasoline

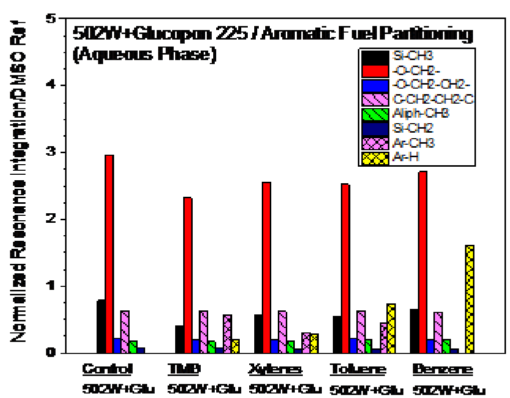
longer extinction for aromatic fuel fires than aliphatic fuel fires

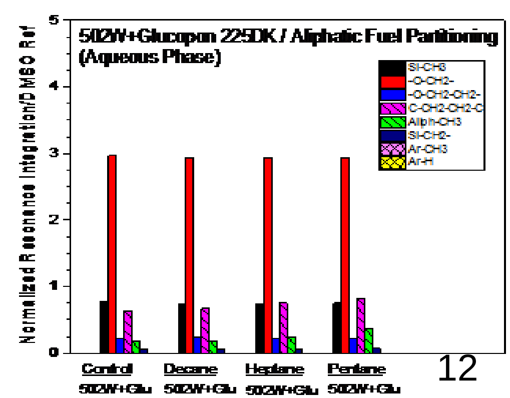


Suppressing surfactant extraction by aromatic fuels in gasoline is key

Nonionic siloxane surfactant is extracted by aromatic fuels, but not by aliphatic fuels



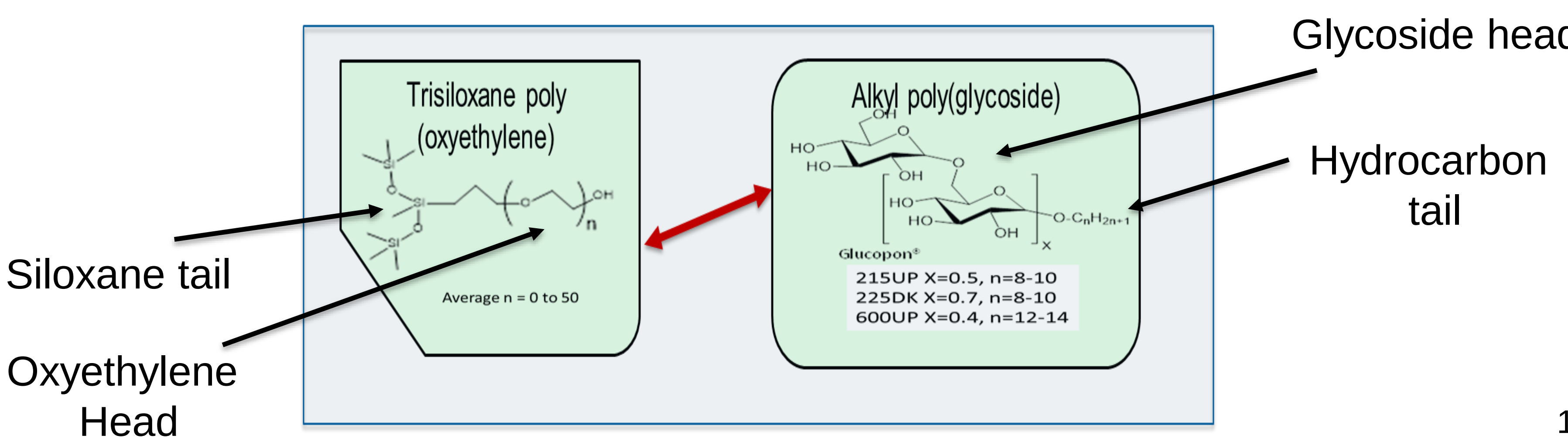




Strategy for Improving Fire Extinction:

Suppress extraction by fuel and increase synergism

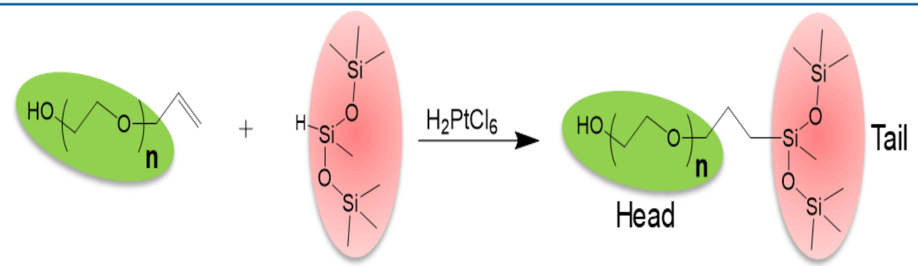
- Vary siloxane head size by synthesizing polydispersed homologues of siloxanes.
- Vary glycoside head and tail sizes
  - ♦ Commercially available monodispersed glycosides.
  - ♦ Fractionation of polydispersed BASF's Glucopon 225DK.
- The results show no further improvement in extinction but reveal new principles for designing novel siloxanes.



Synthesis of Nonionic Polydispersed Siloxanes with Different Head Sizes

- Hydrosilylation reaction, single step, 20 g scale.
- Characterization by NMR and LC/MS.

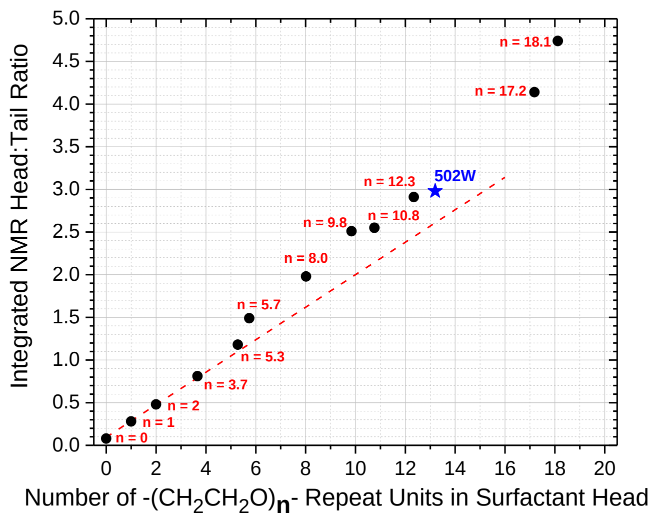
Polyoxyethylene-Trisiloxane Surfactant Synthesis



Monitored conversion by ^{1}H NMR

Polydispersed head lengths, n

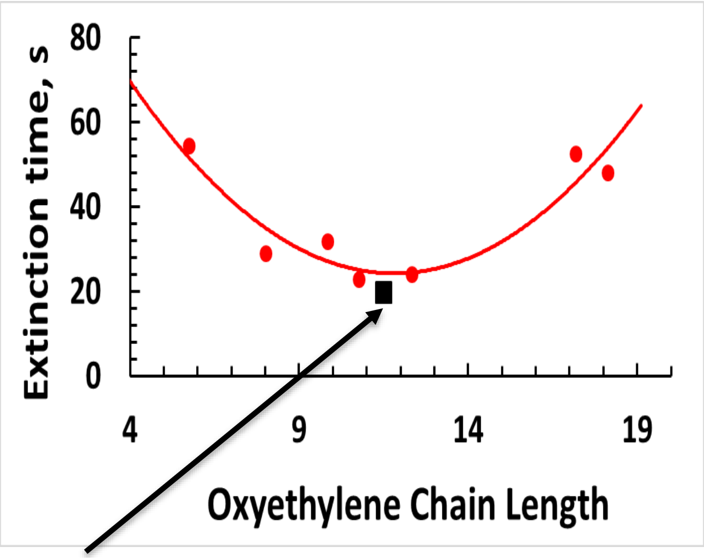
Synthesized siloxanes with average n from 0 to18.



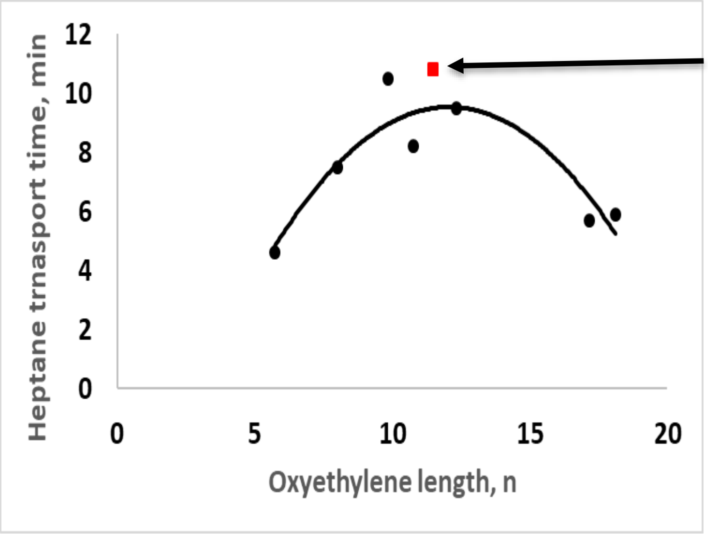
- Characterized solution properties
- Generated foams
- Characterized foam properties
- Measured
  - Foam degradation
  - Fuel transport
  - Fire extinction

Effects of Oxyethylene Head Size on Heptane-Fire Extinction With the Siloxane Tail Fixed.

- Optimum in extinction and heptane-transport times with increased head size.
- As the head size is increased, surfactant hydrophilic-oleophilic balance shifts to more hydrophilic affecting amphiphilicity.
- Head and tail should be varied simultaneously.



Dowsil 502W

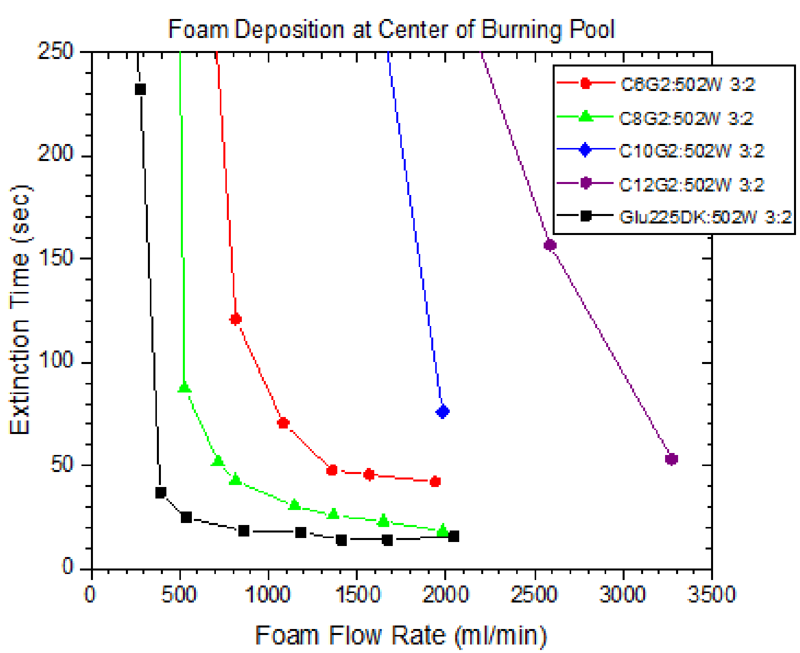


Dowsil 502W

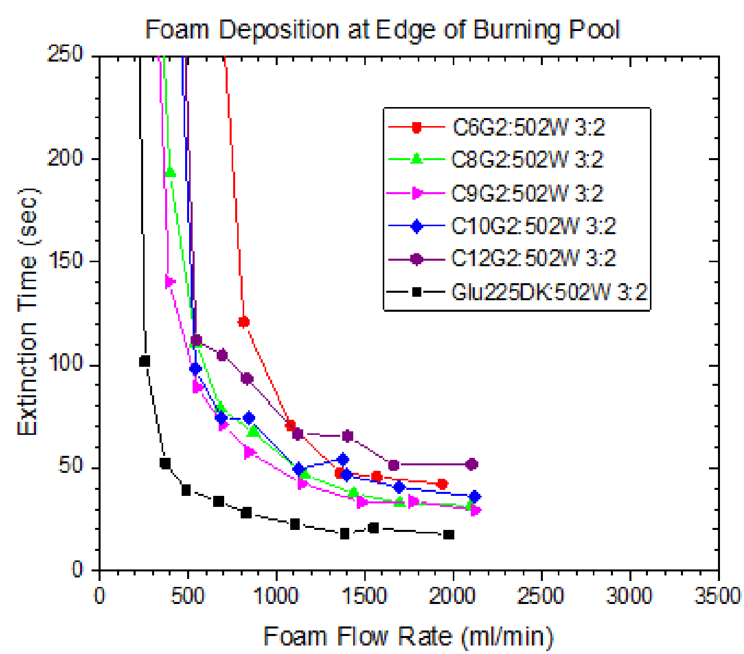
Effects of Commercial, Monodispersed, Glycosides with Different Head and Tail Sizes

- Significant chemical structure effects on heptane fire extinction.
- Surfactant amphiphilicity should be maintained when varying structure.
- No clear trends with structure variation on foam degradation and heptane transport through foam.

Vary tail size with head size fixed

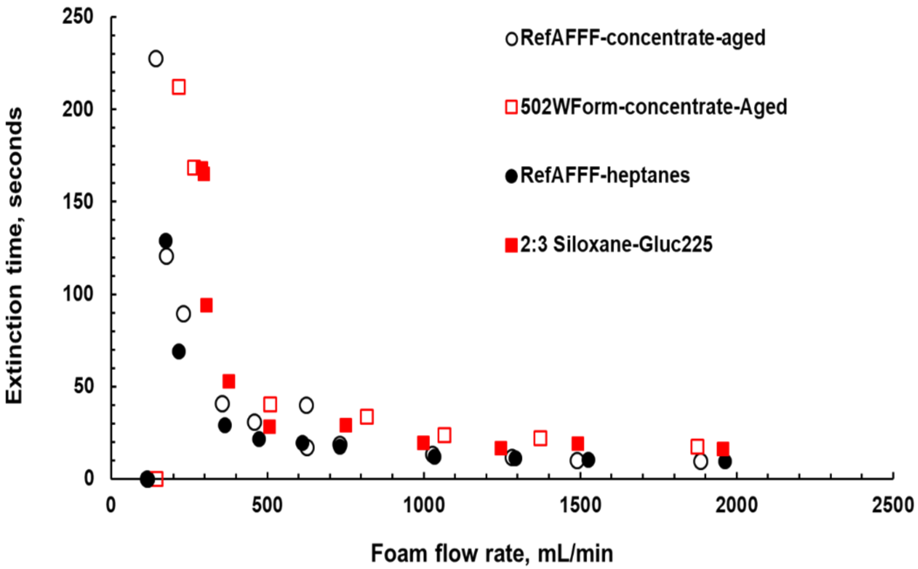


Vary head size with tail size fixed



Shelf-life and Hydrolytic Stability of Siloxane-glycoside Surfactants

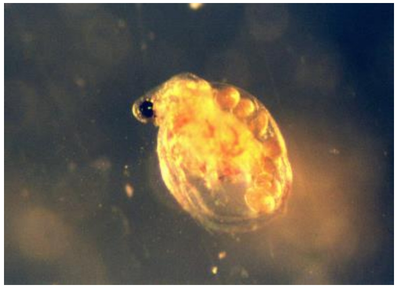
- Siloxane tail slowly gets hydrolyzed by water over time.
- Accelerated aging test on Siloxane-Glycoside formulation:
  - ♦ Held 3% concentrate and premix at 60 ºC for 10 days in an oven.
  - ♦ Performed bench scale tests before and after the aging.
- No effect of aging on fire extinction for the 3% concentrate as shown below, but the premix lost its fire suppression property.



- **Increased micelle formation in 3% concentrate vs premix.**
- **Siloxane tails are hidden inside micelles protecting themselves from hydrolysis.**

Ecological concerns: Tiered strategy

Water Flea
(*Ceriodaphnia dubia*)



- *Tier 1:* QSAR modeling, development of analytical methods for exposure concentration confirmation, and range-finding toxicity tests conducted.
- *Tier 2:* Acute toxicity tests (survival) conducted in accordance with OECD and EPA standard test guidelines.
  - National foam, Capstone 1157, Navy reference AFFF, butyl carbitol, Glucopon 215 UP, Dow Corning 5575, Silwet L-77, and Dow 502W.
- *Tier 3:* Chronic toxicity tests conducted with invertebrate, fish, and algae in accordance with OECD and EPA guidelines.
- *Tier 4*: Evaluation of the fluorine-free foam mixtures (assessment approach).

Tier 1: QSAR Modeling of Fluorine-free Foam

- Candidate siloxane surfactants evaluated using QSAR model (ECOSAR). Estimates of acute and chronic toxicity for freshwater and marine fish, invertebrates and algae obtained:
  - ♦ Little useful information gathered due to a lack of information on existing chemicals and poor QSAR agreement.

Tier 2/3: Aquatic Toxicities of Fluorine-free Foam Components

- A series of acute and chronic tests were conducted following standard EPA, or OECD methods.
- Test materials selected as “candidate components” of final fluorine-free foam.

Compound	*Ceriodaphnia dubia*		*Pimephales promelas*	
	LC_{50} (95% CI) (mg/L)	EC_{20} (95% CI) (mg/L)	LC_{50} (95% CI) (mg/L)	EC_{20} (95% CI) (mg/L)
DOWSIL™ 502W Additive	24 (21 – 28)	6.3 (4.7 – 8.6)	5.1 (4.8 – 5.4)	2.0 (0.8 – 4.8)
Diethylene Glycol Butyl Ether (Butyl Carbitol)	2689 (2455 – 2946)	857 (N/A) [A]	2321 (2243 – 2402)	693 (621 – 772)
Glucopon® 225 DK	74 (67 – 83) Nominal	34 (29 – 41) Nominal	139 (131 – 147) Nominal	77 (64 – 91) Nominal

Tier 4: Aquatic Toxicities of Fluorine-free Foam Mixtures

- Fluorine-free foam formulations are mixtures of cationic/anionic surfactants, hydrocarbon solvents, and water. Assessments based on evaluation of the individual components and assumptions regarding potential interactive effects. Valid approach?
- Toxic unit (TU) approach employed to determine if the mixture was
  - less than-additive (less toxic),
  - additive (equally toxic), or
  - more-than-additive (more toxic).
- Nominal TUs defined as:
  - 1 acute TU = LC50 (median-lethal concentration) of each individual component for acute testing per species and
  - 1 chronic TU = EC_{20} (20% sublethal effect concentration) of each individual component from chronic testing per species

Aquatic Toxicities of Surfactant Mixtures

- Potential end-use fluorine-free foam formulation (Hinnant et al. 2018) used to evaluate mixture approach.

<table>
<tr><th rowspan="2">Compound</th><th rowspan="2">Mix Conc.</th><th colspan="2">Acute TU in mixture</th><th colspan="2">LC50 (TU)</th><th colspan="2">Chronic TU in mixture</th><th colspan="2">EC20 (TU)</th></tr>
<tr><th>C. dubia</th><th>P. promelas</th><th>C. dubia</th><th>P. promelas</th><th>C. dubia</th><th>P. promelas</th><th>C. dubia</th><th>P. promelas</th></tr>
<tr><td>DOWSIL™ 502W Additive</td><td>2000 mg/L</td><td>83.3</td><td>392.2</td><td rowspan="4">0.67 (0.59-0.77) >Additive</td><td rowspan="4">1.02 (0.91-1.14) Additive</td><td>317.5</td><td>1000.0</td><td rowspan="4">0.97 (0.84-1.12) Additive</td><td rowspan="4">1.29 (1.09-1.54) <Additive</td></tr>
<tr><td>Diethylene Glycol Butyl Ether (Butyl Carbitol)</td><td>3000 mg/L</td><td>1.1</td><td>0.8</td><td>3.5</td><td>4.3</td></tr>
<tr><td>Glucopon® 225 DK</td><td>5000 mg/L</td><td>67.6</td><td>36.0</td><td>147.1</td><td>64.9</td></tr>
<tr><td>Water</td><td></td><td>SUM (TU) 152</td><td>SUM (TU) 429</td><td>SUM (TU) 468</td><td>SUM (TU) 1069</td></tr>
</table>

General Principles Learned

- Candidate end-use fluorine-free foam mixture did not contain equivalent amounts of each single component, toxic contribution of the individual components was a function of its relative toxicity and content in the mixture.
    - Dominated by contribution from DOWSIL 502W
- Acute studies demonstrated that the mixture tested had additive or more-than-additive effects. Chronic tests resulted in additive or less-than-additive effects.
- Comparing species, *P*. *promelas* and *C*. *dubia* were more sensitive to chronic exposures versus acute exposures, while the algae, *R*. *subcapitata* was the least sensitive.
- Assumption of Concentration Addition (CA) model approach seems appropriate until additional data available.

Next Steps

- Further research on novel siloxane surfactants and suitable additives is needed to develop a *drop-in* replacement for AFFF for *on-shore and off-shore applications using existing hardware*
  - To be effective on different fuels: Jet A, Heptane, and Gasoline
  - Long shelf-life
  - PKP compatibility
  - Other requirements in MIL-F-24385F

Potential Technology Transfer

- Commercialization of novel siloxane surfactant and foam technologies for fire suppression:
  - R&D collaboration with Dow Silicones Co.
- NAVSEA and other DOD organizations
- Presentations and Publications
  - 1 Invited talk
  - 7 presentations
  - 7 journal articles
  - 1 NRL memorandum report
  - 1 full U.S. patent application filed

Key Points

- Novel siloxane surfactants are shown as a key part of a suitable fluorine-free *drop-in* replacement formulation for AFFF.
- Bench scale measurements are key
  - ♦ Screening tools prior to large scale fire testing.
  - ♦ Establishing key fire suppression concepts and principles for developing novel surfactants.

BACKUP SLIDES

Publications

[1] Ananth, R., Giles, S.L., Hinnant, K.M., S.L. Giles, A.W. Snow, Farley, J.P., Stubblefield, W., Field, J. 2020 Fluorine-free foams with oleophobic surfactants and additives for effective pool fire suppression, 2020 SERDP/ESTCP Symposium, Web presentation, November 30-December 4, 2020

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[3] Hinnant, K.M., Giles, S.L., Smith, E.P., Snow, A.W., Ananth, R. 2019 Characterizing the roles of fluorocarbon and hydrocarbon surfactants in firefighting foam formulations, Fire Technology Journal https://doi.org/10.1007/s10694-019-00932-7, November 19, 2019

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[6] Hinnant, K.M., Giles, S.L., Snow, A.W., Farley, J.P. Fleming, J.W., Ananth, R. 2019 An analytically defined ire suppressing foam formulation for evaluation of fluorosurfactant replacement, Invited Talk, American oil chemists society annual meeting and expo, St. Louis, Missouri, May 5-8, 2019

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[9] Hinnant, K.M., Giles, S.L., Snow, A.W., Farley, J.P., Fleming, J.W., Ananth, R. 2018 An analytically defined fire suppressing foam formulation for evaluation of fluorosurfactant replacement, Journal of Surfactants and Detergents, https://doi.org/10.1002/jsde.12166, July 2018

[10] Kennedy, M.J., Conroy, M.W., Fleming, J.W., Ananth, R. 2018 Velocimetry of Interstitial Flow in Freely Draining Foam, Colloids and Surfaces A, 540, 158-166.

[11] Hinnant, K.M., Snow, A.W., Giles, S.L., Ananth, R. 2018 Evaluating Foam Degradation and Fuel Transport through Novel Surfactant Firefighting Foams for the Purpose of AFFF , Replacement. Proceedings of the Eastern States Section of the Combustion Institute Meeting, paper# 36FI_0047, State College, PA, March 4-7.

Publications

[12] Ananth, R., Giles, S.L., Hinnant, K.M., Zhuang, X., Snow, A.W., Fleming, J.W., Farley, J.F. 2018 Liquid-pool Fire Extinction Characteristics of Aqueous Foams Generated from Fluorine-free Surfactants. Proceedings of the Eastern States Section of the Combustion Institute Meeting, paper# 36FI_0107, State College, PA, March 4-7.

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WP-2739: Fluorine-free Foams with Oleophobic Surfactants and Additives for Effective Pool Fire Suppression

Performers: NRL, Washington DC and OSU, Corvallis, OR

Technology Focus

- *Environmentally-friendly firefighting foams*

Research Objectives

- *Develop/synthesize fluorine-free surfactants that generate foams with MilSpec-fire performance and low OECD/ASTM toxicity/bio-persistence*

Project Progress and Results

- *Developed a siloxane formulation and demonstrated 60 % effectiveness of AFFF using bench scale and MilSpec 28 ft^2 fire test for heptane fuel.*
- *Discovered synergism between siloxane-polyether and alkylpoly-glycoside surfactants that dramatically improves heptane fire extinction.*
- *Discovered that fire extinction is prolonged for gasoline relative to heptane because of surfactant extraction by the aromatic components..*
- *Synthesized 12 new siloxane-polyether surfactants to vary polyether head length, and varied head and tail structures of alkylpolyglycosides.*
  - *Increased polyether length showed a minimum in extinction time.*
  - *Maintaining surfactant's amphiphilicity is important for fire extinction.*
- *Developed molecular dynamics models and predicted a maximum in lamella stability (Gibbs elastic modulus) with increased head size.*
- *Developed analytical characterization methods for surfactants and evaluating toxicity of the individual siloxane surfactants and mixtures.*

Technology Transition

- *NDA with Dow Silicones Inc. to synthesize and develop new silicone surfactants and foams effective for heptane/gasoline fires with NRL*