Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foam (F^3)

Weapons Systems and Platforms WP18-1519

Matthew C Davis Ph. D.
Naval Air Warfare Center China Lake

20 May 2019

NAWCWD
Naval Air Warfare Center Weapons Division
China Lake & Point Mugu, CA

SERDP
DOD ▪ EPA ▪ DOE

Project Team

M. Joseph Roberts Ph. D.,
Chemistry Department NAWC China Lake

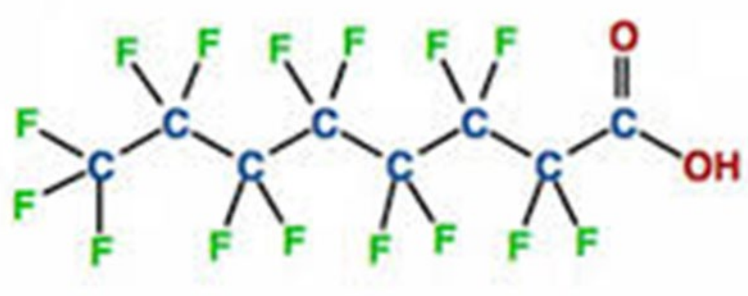
Erik D. Tolmachoff Ph. D. and Eric S. Sievert,
Fire Sciences Branch NAWC China Lake

Ramagopal Ananth Ph. D. and Arthur W. Snow Ph. D.,
Chemistry Department Naval Research Laboratory

Background

Project WP18-1519 was a SERDP Exploratory Development (SEED) project executed from March 2018 to March 2019

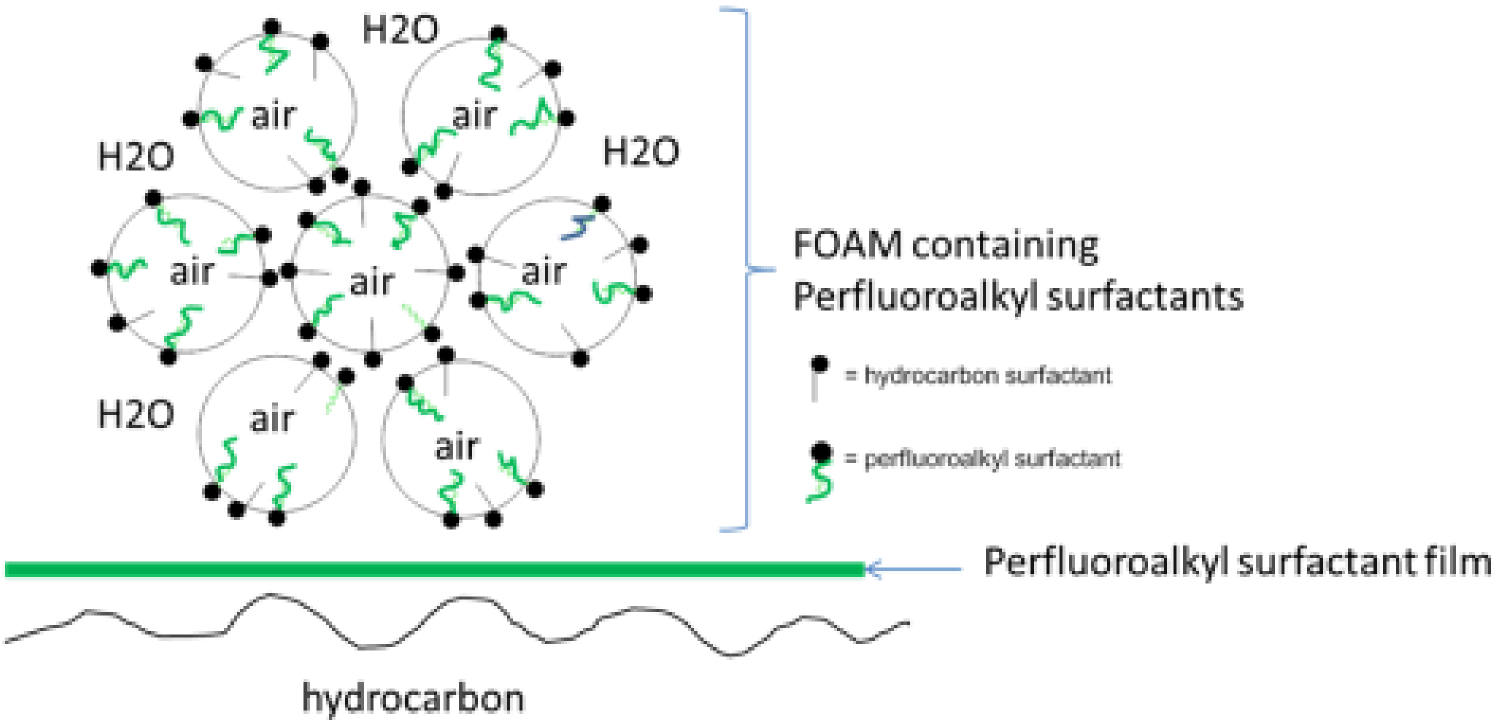
The project responded to the FY18 Statement of Need: *Innovative Approaches to Fluorine-Free Aqueous Film Forming Foam*



PFOA - perfluorooctanoic acid

Background

AFFF mechanism



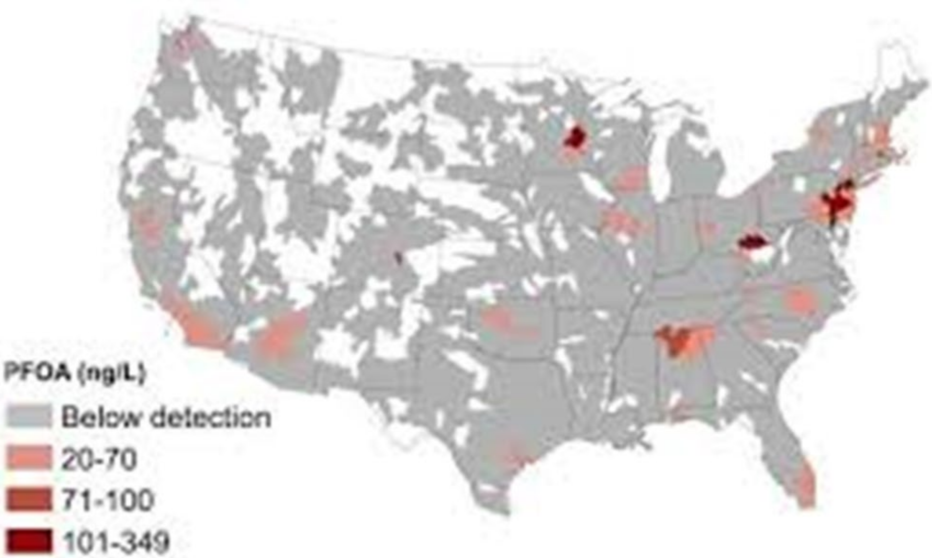
spreading coefficient of Phos-Chek (AFFF) on cyclohexane (+6.51 mN/m)

Background

Fluorinated surfactants do not breakdown in the ecosystem

NEED TO FIND ALTERNATIVES QUICKLY

Groundwater contamination by PFOA



Governments endorse global PFOA ban, with some exemptions

Restrictions placed on firefighting foam with PFOA, PFOS, or both

by Cheryl Hogue

MAY 11, 2019 | APPEARED IN VOLUME 97, ISSUE 19

09719-leadcon-foamscxd.jpg

Credit: Shutterstock

Under an international treaty, countries are prohibiting the use of firefighting foams containing PFOA or PFOS in training exercises like this one.

A widely used industrial fluorochemical that is linked to cancer and pollutes drinking water around the world is on its way to a global phaseout.

More than 180 countries, including China, agreed on May 3 to ban the production and use of perfluorooctanoic acid (PFOA), its salts, and PFOA-related compounds under the international Stockholm Convention on Persistent Organic Pollutants (POPs). The International Agency for Research on Cancer considers PFOA possibly carcinogenic to humans. Exposure to it is also linked to hormonal disruption.

At a meeting of Stockholm convention treaty partners in Geneva, governments carved out exemptions that allow some applications of PFOA to continue, including use in firefighting foams—a practice that has contaminated groundwater in many areas around the globe. Tons

MOST P(
ENVIRO

New electroc
PFOS and Pl

Chemistry ma
plastic trash p

Plastics recyc
worms is furt

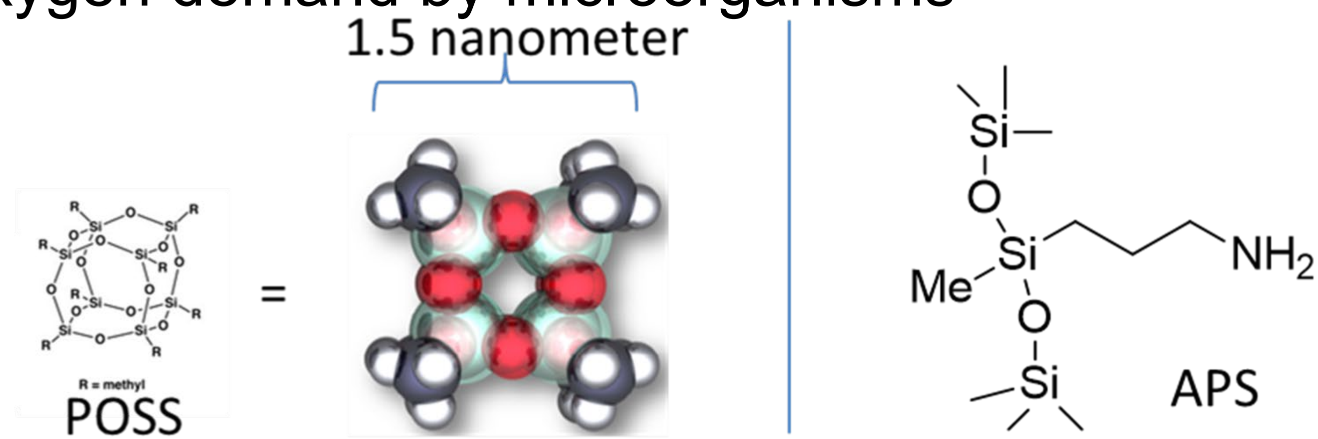
Video: How e
forecasts

Using CO2 a
slash greenh

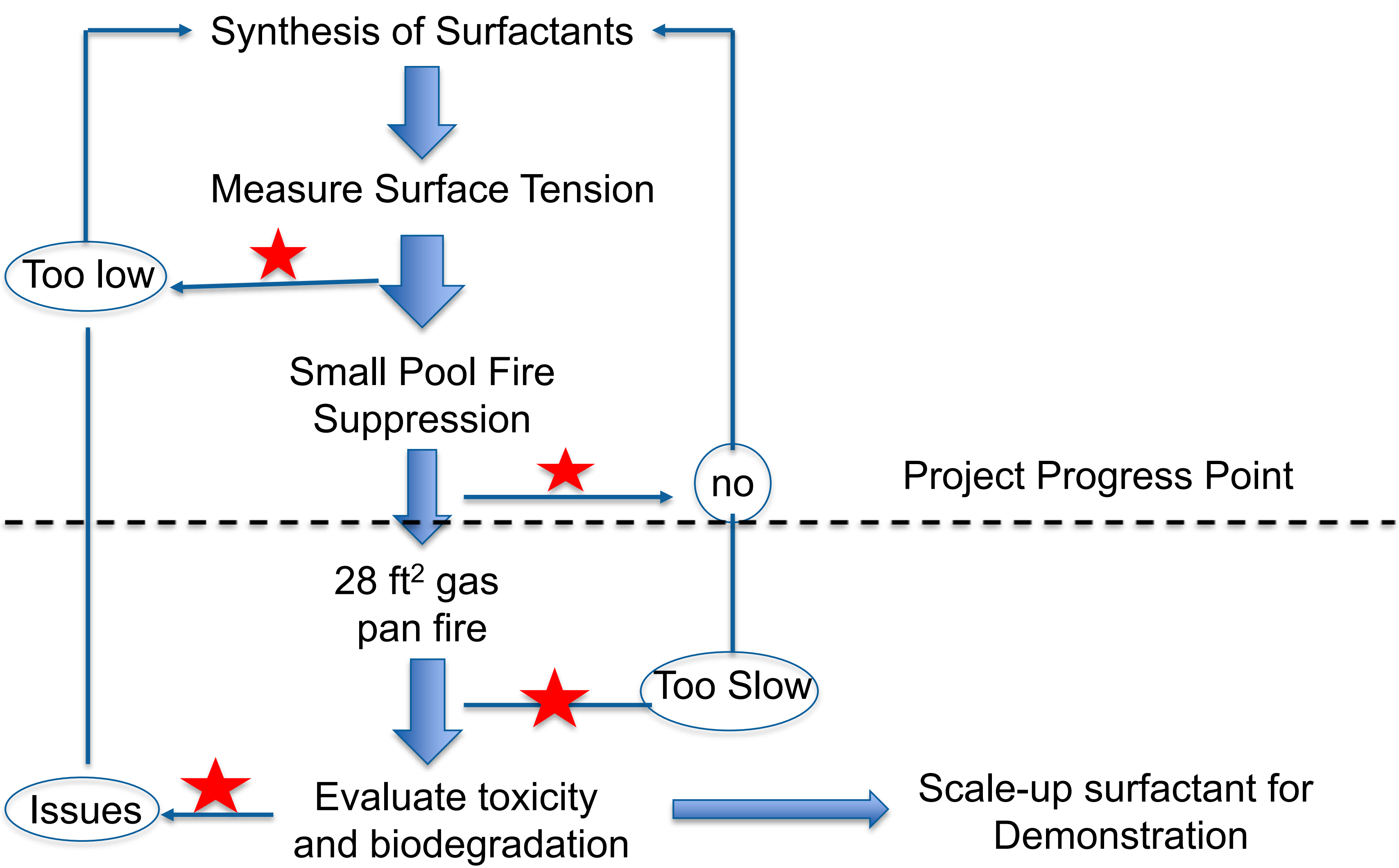
US EPA stru
for pesticide

Technical Objectives

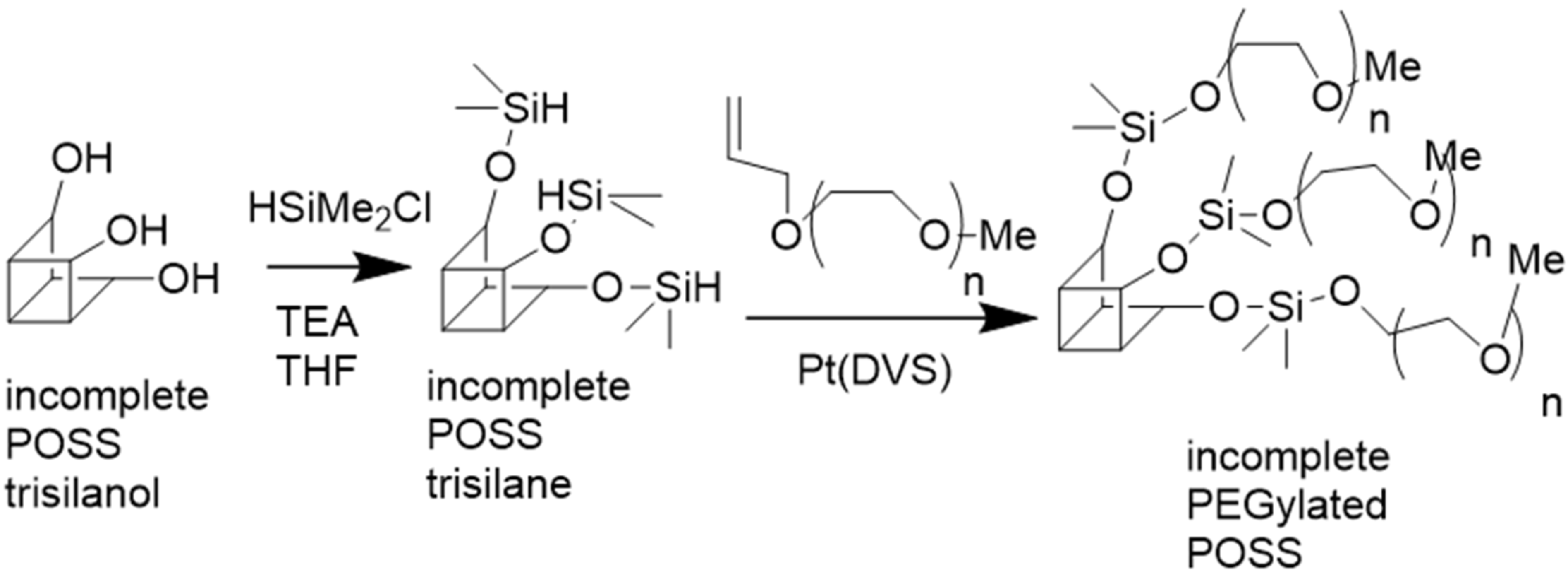
- Synthesize surfactants from POSS and aminoalkylsiloxanes as drop-in replacements for perfluorosurfactants in AFFF
- Foams with new fluorine-free surfactants will be formulated to extinguish gasoline pool fire in 45 seconds or less
- POSS and aminoalkylsiloxane surfactants will be tested for biodegradation by measuring chemical and biological oxygen demand by microorganisms



Technical Approach

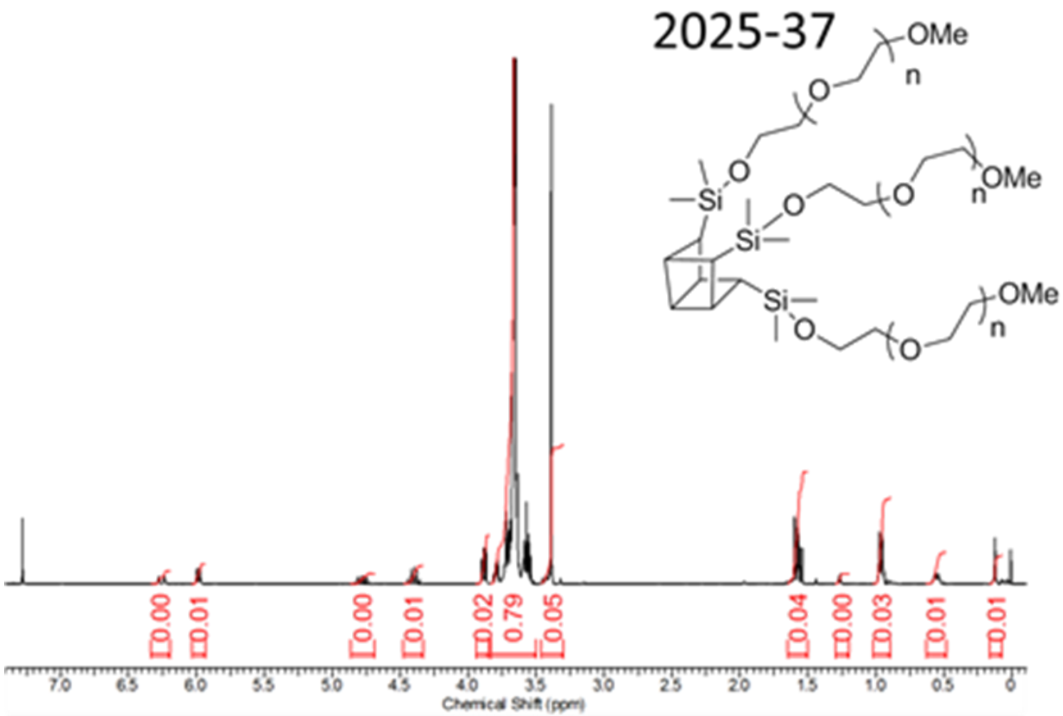


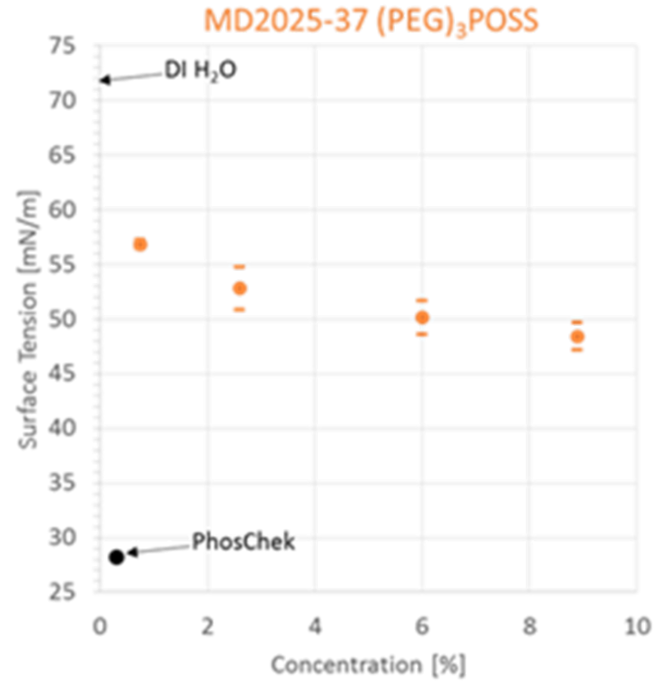
Results



OH
OH
OH
incomplete
POSS
trisilanol
HSiMe2Cl
TEA
THF
SiH
O
HSi
O
O
SiH
incomplete
POSS
trisilane
O
O
Me
n
Pt(DVS)
Si
O
O
Me
n
Me
Si
O
O
n
Me
O
O
Si
O
O
n
incomplete
PEGylated
POSS

Results



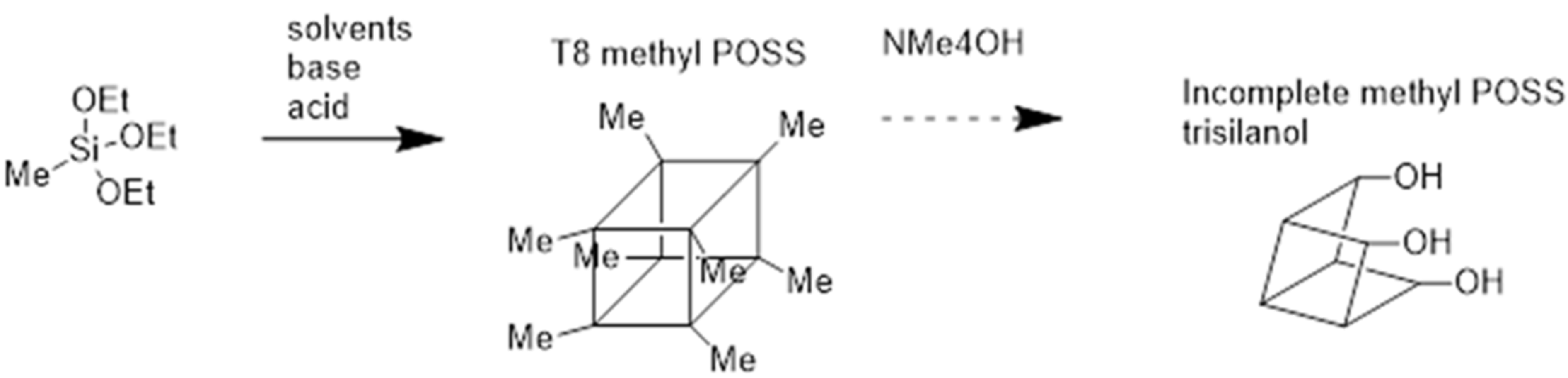


Surface tension only 48 mN/m at 9 wt% loading

dilute Phos-Chek = 27 mN/m

Results

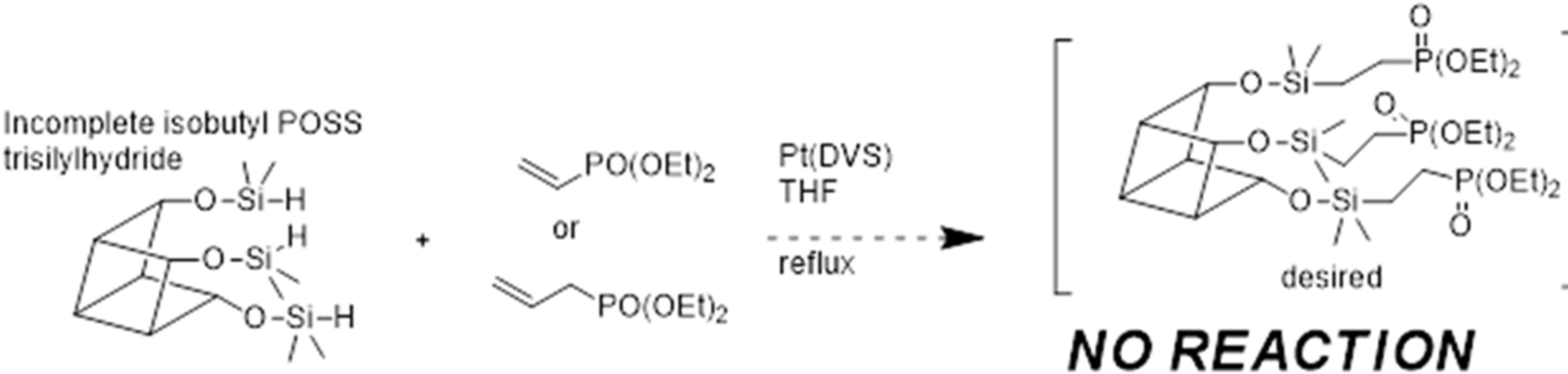
Synthesize Less Hydrophobic POSS cage?



Synthetic Difficulties in Preparing Alternate POSS Cage

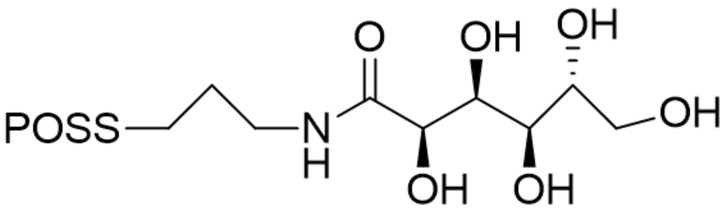
Results

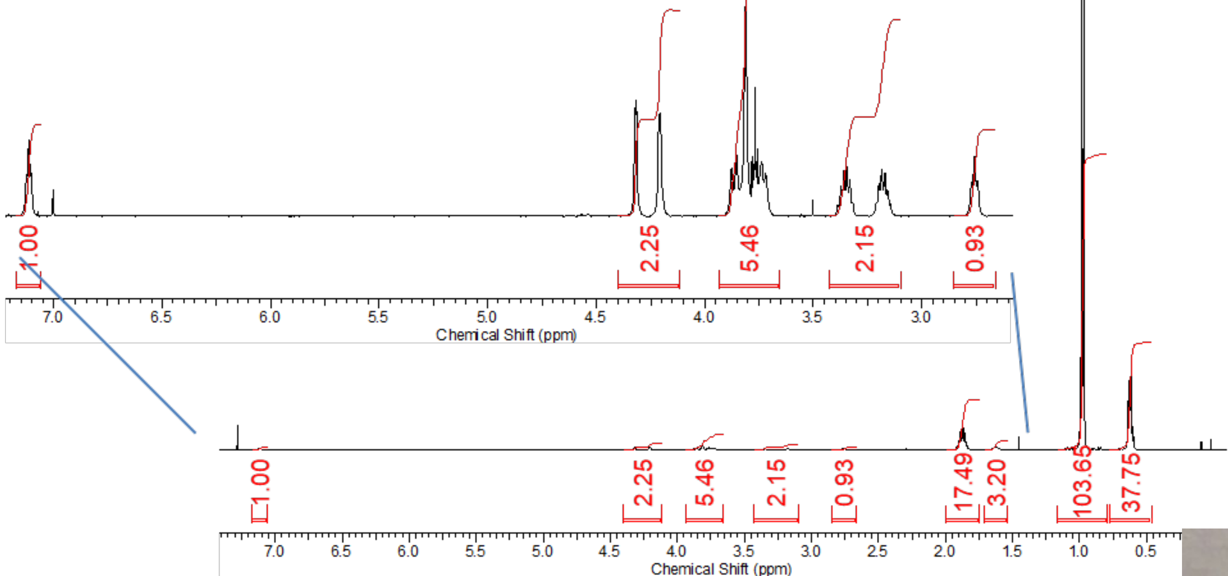
Incorporate Phosphate Into POSS For water Solubility?



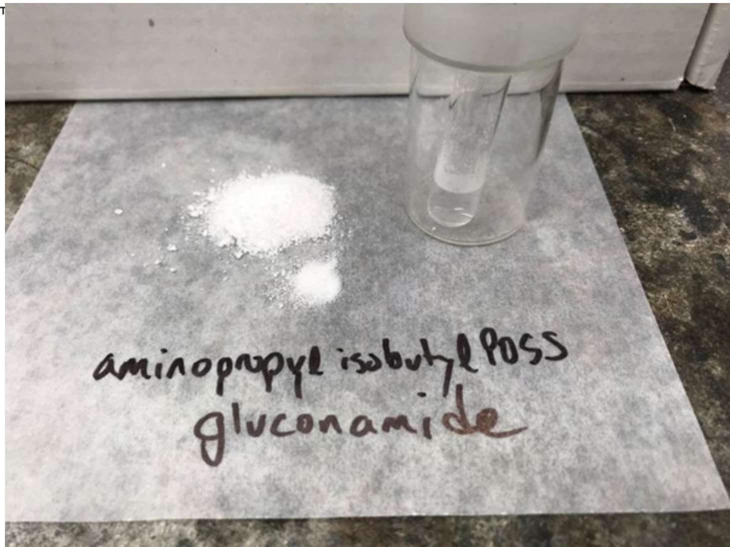
Could not couple alkenylphosphonate to POSS

Results

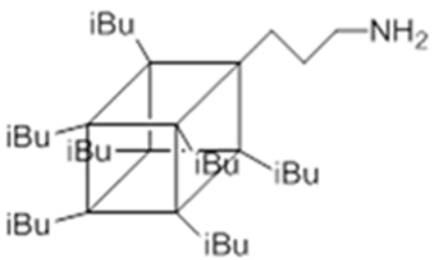




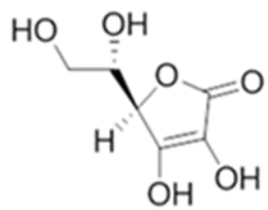
POSS Sugar derivative insoluble in water



Results

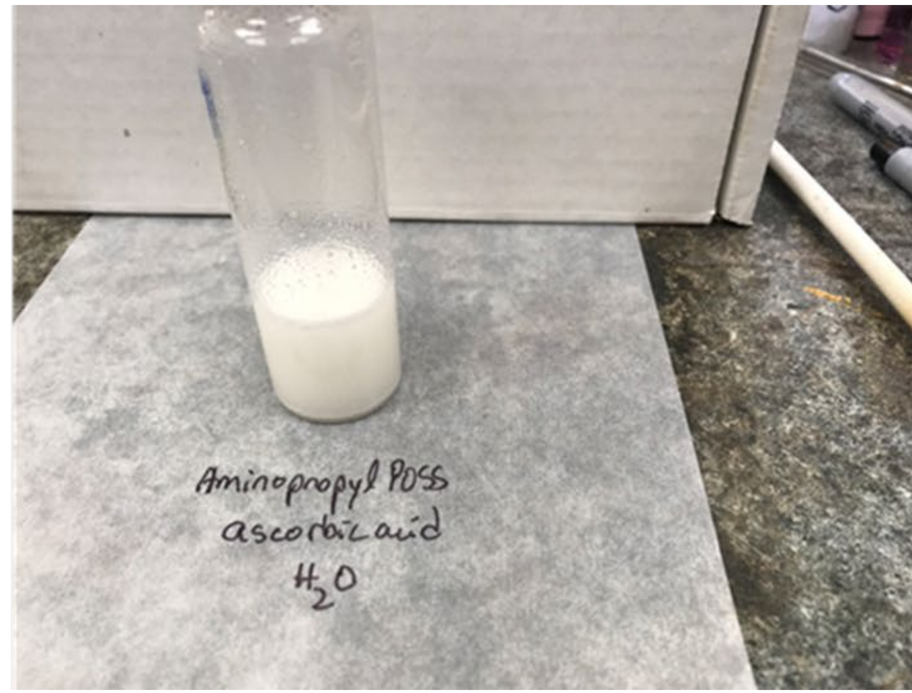


+



L-ascorbic acid (Vitamin C)

'AA'

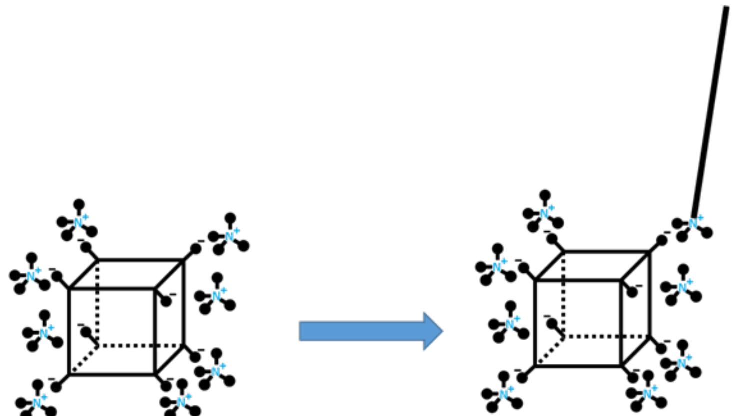


aminoPOSS ascorbate salt not water soluble

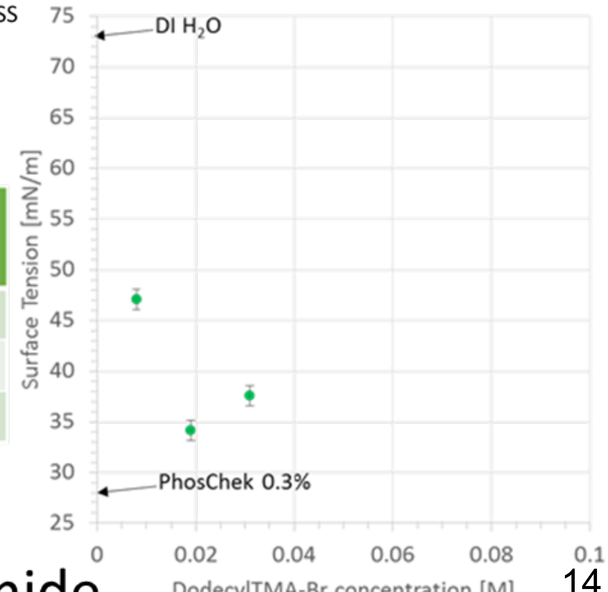
Results

OctaTMAPOSS (OTMA) Metathesis with Fattyammonium salts

Foam aged 10 minutes above 0.0019M **C_{12}TMABr + OctaTMAPOSS** mixture



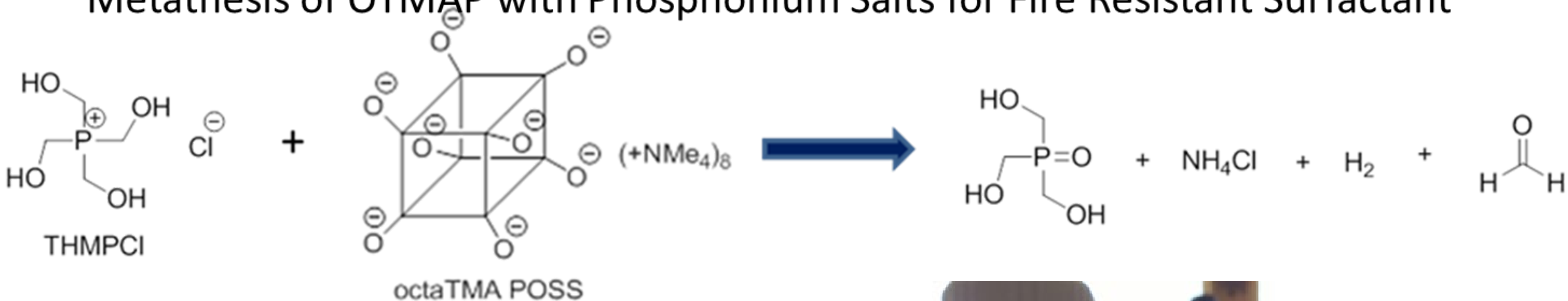
OctaTMA-POSS concentration, M	DodecylTMA-Br concentration, M	Surface Tension [mN/m]	Standard Deviation [mN/m]	Temperature [°C]
0.004	0.008	47.03	1.01	24.8
0.001	0.014	34.10	1.62	24.8
0.031	0.031	37.53	1.19	24.4

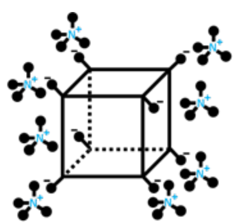


Best case with Dodecyltrimethylammonium bromide

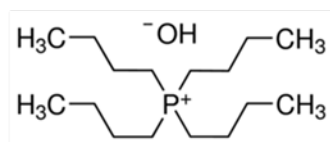
Results

Metathesis of OTMAP with Phosphonium Salts for Fire Resistant Surfactant

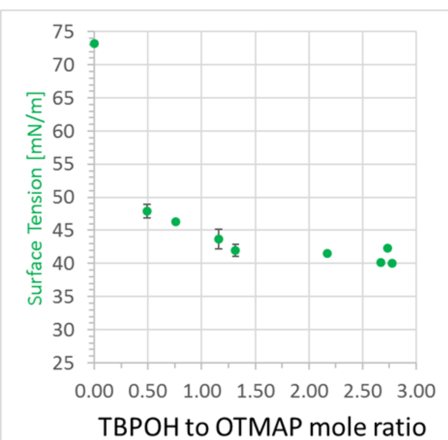


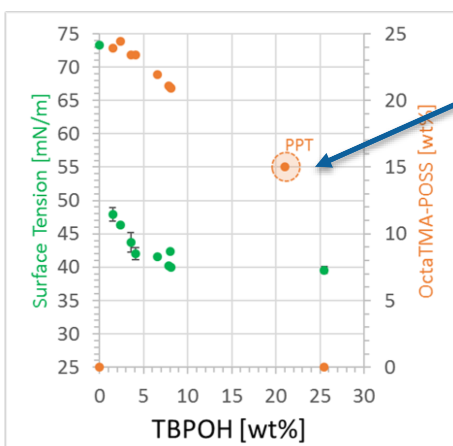


OctaTMA-POSS
OTMAP

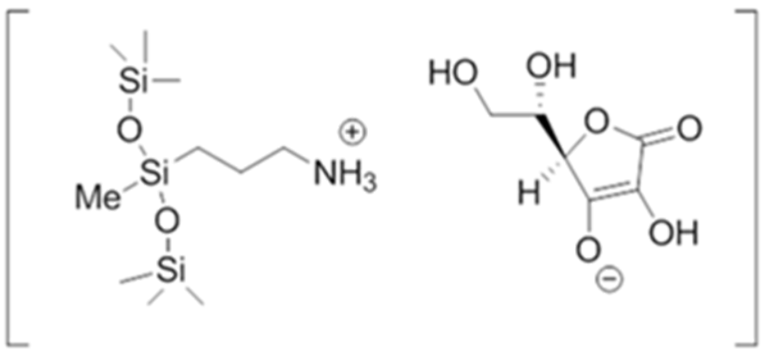


tetrabutylphosphonium hydroxide
TBPOH

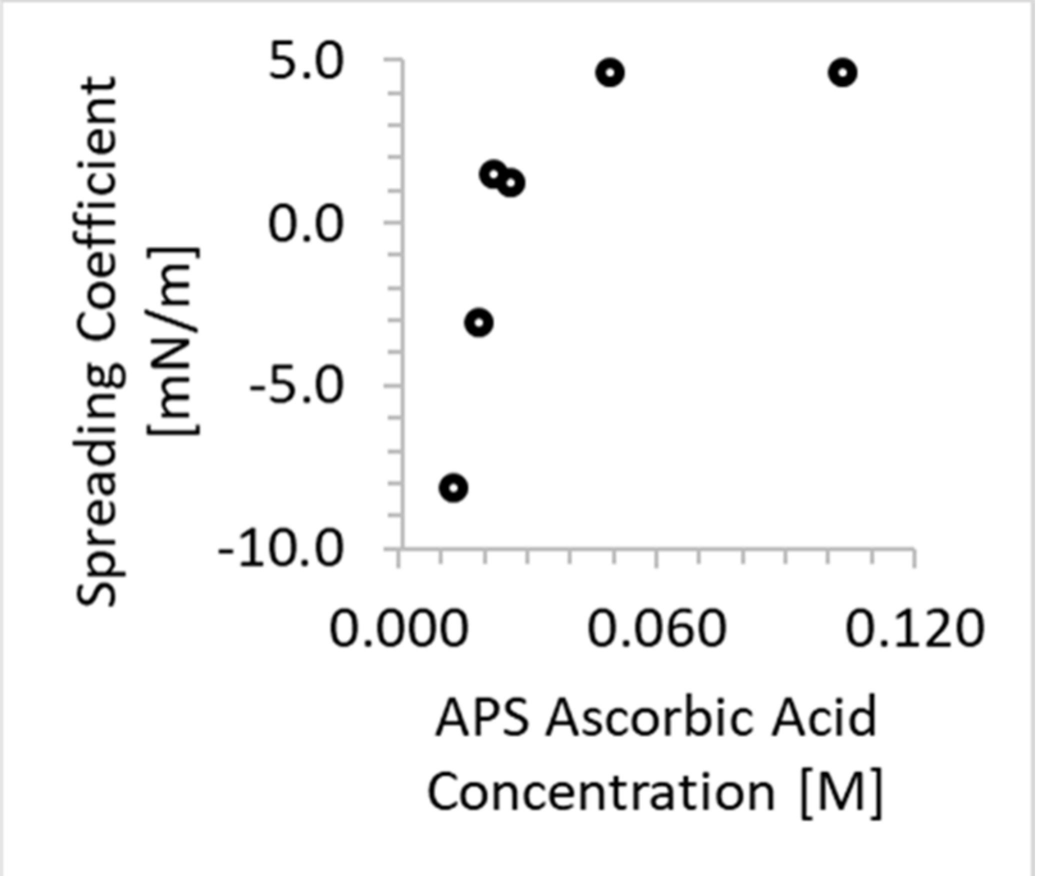




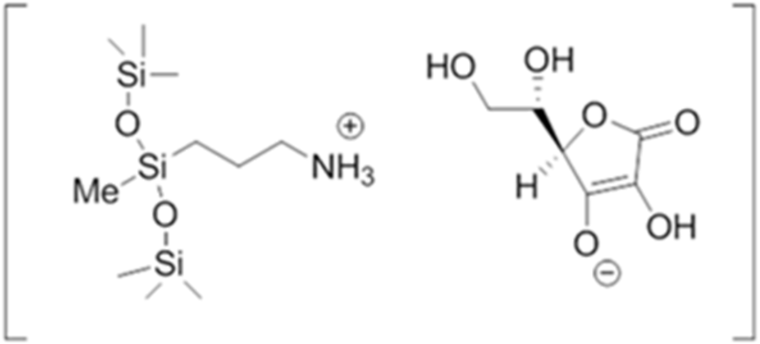
Results



'APS/AA surfactant'

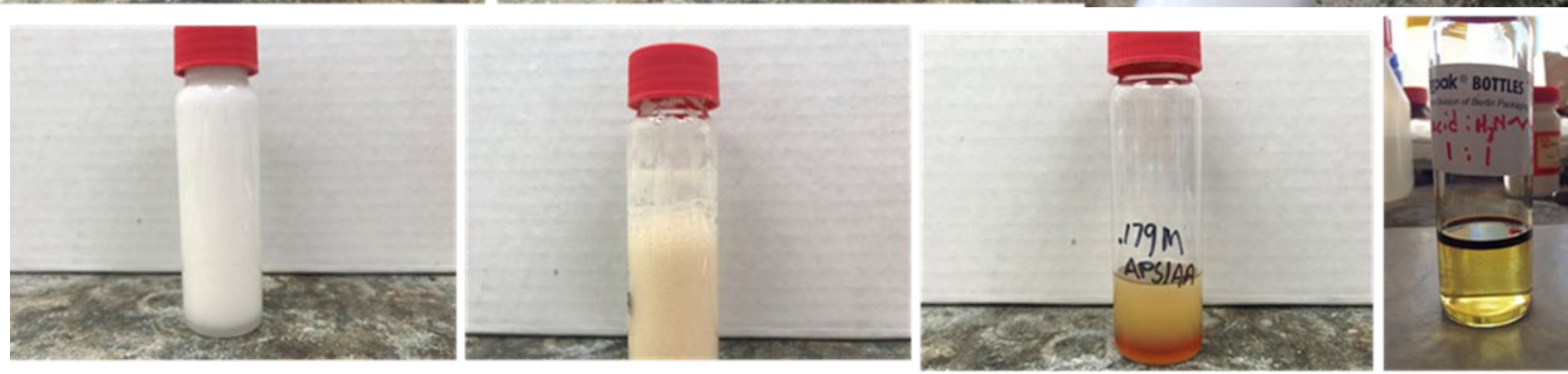


spreading coefficient of +4.6 mN/m on cyclohexane and +0.74 mN/m on heptane



Results

'APS/AA surfactant'



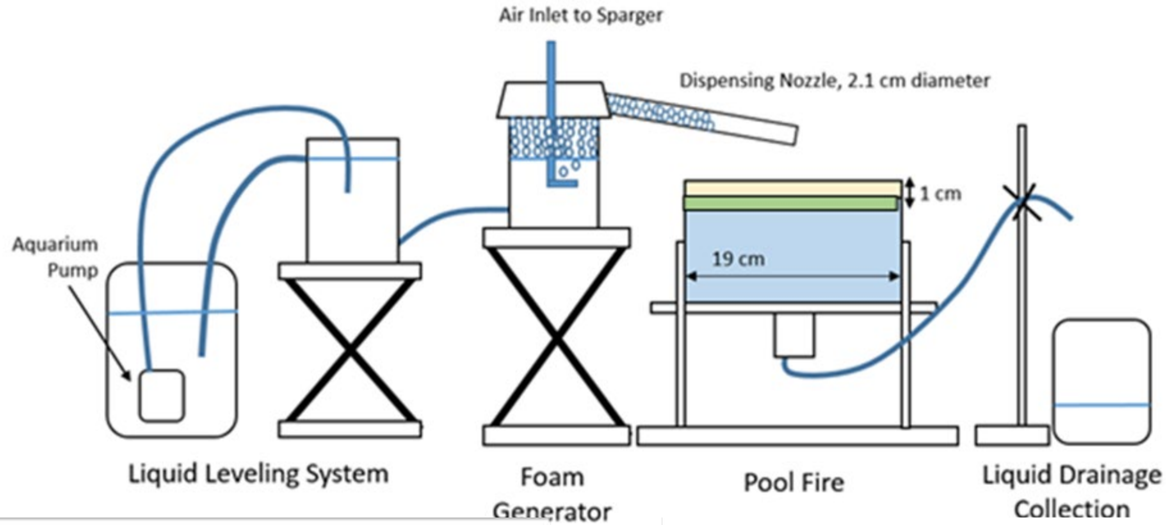
Freshly prepared and shaken

After 5 days (120 hours) and shaken

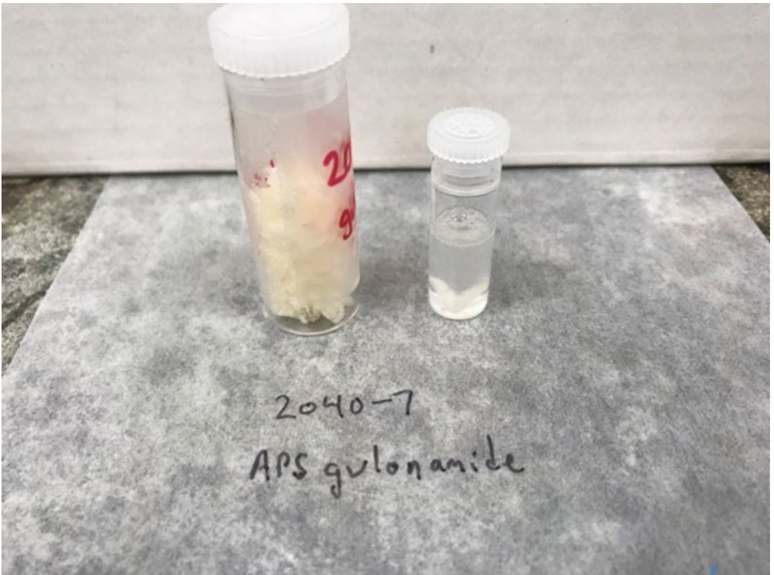
After 7 days atmospheric conditions

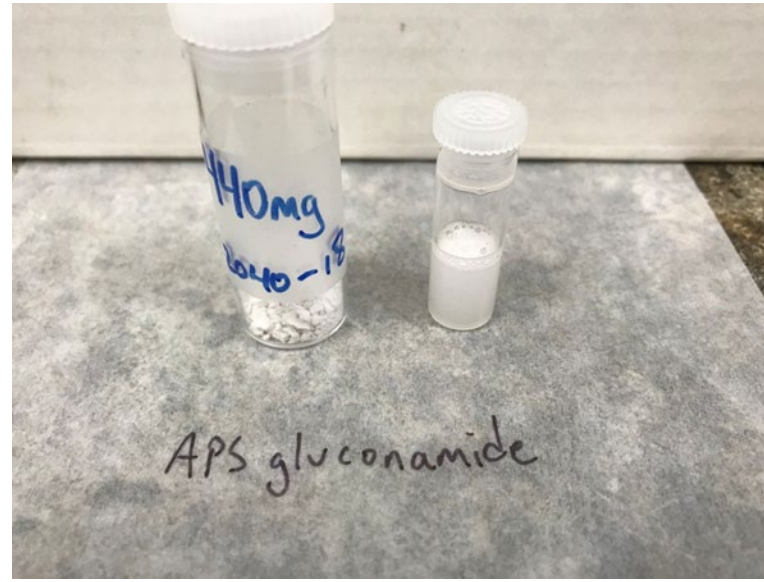
Results

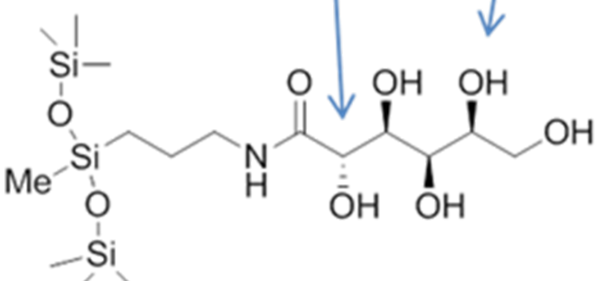
Testing APS-AA versus heptane pool fires at NRL



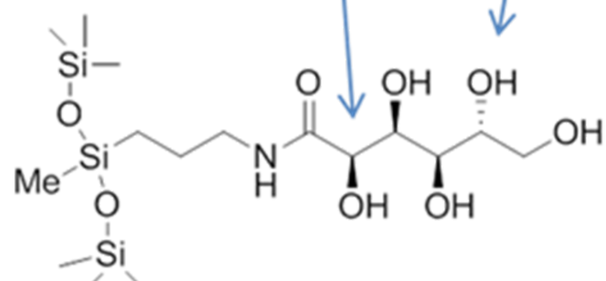
Results







2040-7
gulonamide



2040-18
gluconamide

WATER SOLUBLE: NO YES

US 3677347 (1972)

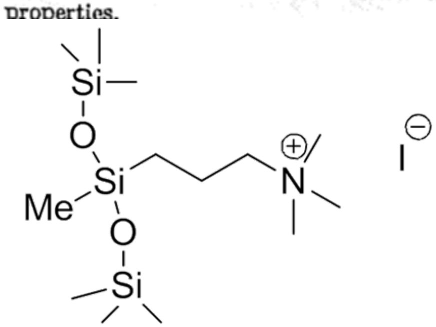
"Method of extinguishing fires...."

Results

TABLE 1

Example number	Surfactant number	Surfactant structure	A. Time for foam break-down on gasoline (minutes)	B. Time that film lasts on gasoline (minutes)	D. Elastic properties (days)
1	1	$[(Me_3SiO)_2MeSi(CH_2)_3\overset{+}{N}Me_3]I^-$	7	4 hours	Yes (8).
2	2	$[(Me_3SiO)_2MeSi(CH_2)_3\overset{+}{N}Me_3]Cl^-$	About 1	>4 hours	No (7).
3	3	$[(Me_3SiO)_2MeSi(CH_2)_3\overset{+}{N}Me_3]Br^-$	25	About 18 hours	Do.
4	4	$[(Me_3SiO)_2MeSi(CH_2)_3(Me)\overset{+}{N}(CH_2CH_2)_2O]Br^-$	14	37	No (1).
5*	5	$[(Me_3SiO)_2MeSi(CH_2)_3(Me)\overset{+}{N}HC_6H_{11}]I^-$	About 1	0	No (5).
6	6	$[(Me_3SiO)_2MeSi(CH_2)_3\overset{+}{N}Et_3]I^-$	24	3	Yes (11).
7	7	$[(Me_3SiO)_2MeSi(CH_2)_3\overset{+}{N}Et_3]I^-$	16	3	Yes (13).
8	8	$[(Me_3SiO)_2MeSi(CH_2)_3(Me)\overset{+}{N}C_5H_{10}]I^-$	5	About 4 hours [1]	
9	9	$[(Me_3SiO)_2MeSi(CH_2)_3(Et)\overset{+}{N}C_5H_{10}]I^-$	16	2	Yes (1). Small amount.
10	10	$[(Me_3SiO)_2MeSiOCHMeCH_2\overset{+}{N}Me_3]I^-$	15	>15	No (7).
11**	11	$[(Me_3SiO)_2MeSiO(CH_2)_2O(CH_2)_3(Me)\overset{+}{N}(CH_2CH_2)_2O]I^-$	1	0	Yes (1).
12	12	$[(Me_3SiO)_2MeSi(CH_2)_2CHMe(Me)\overset{+}{N}(CH_2CH_2)_2O]I^-$	7	0.5	No (1).
13	13	$[(Me_3SiO)_2MeSi(CH_2)_3OCHMeCH_2(Me)\overset{+}{N}(CH_2CH_2)_2O]I^-$	>48	>3 hours [1]	Yes (5).
14	14	$[(Me_3SiO)_2MeSi(CH_2)_3(Me)\overset{+}{N}]I^-$	10	3	No.

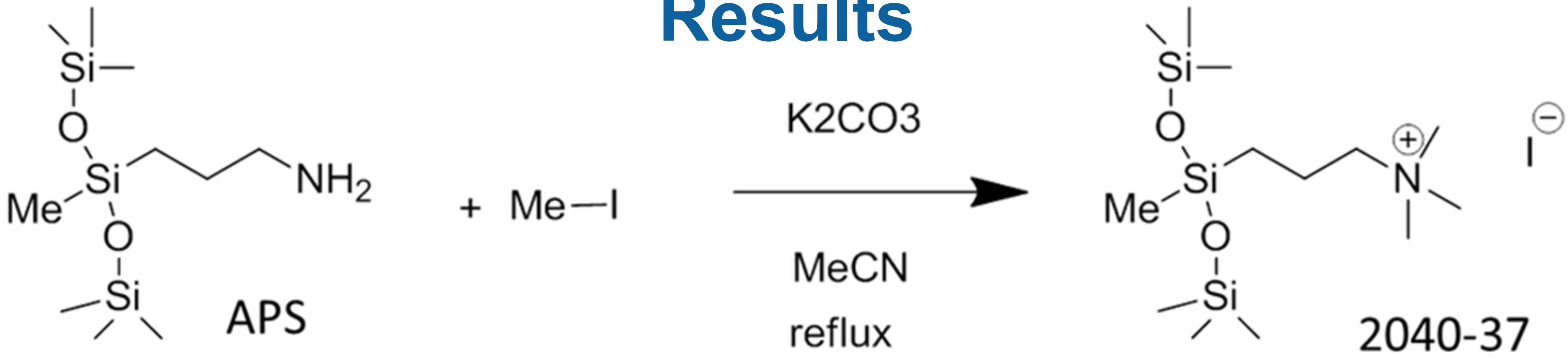
[1] Excellent resealing properties.

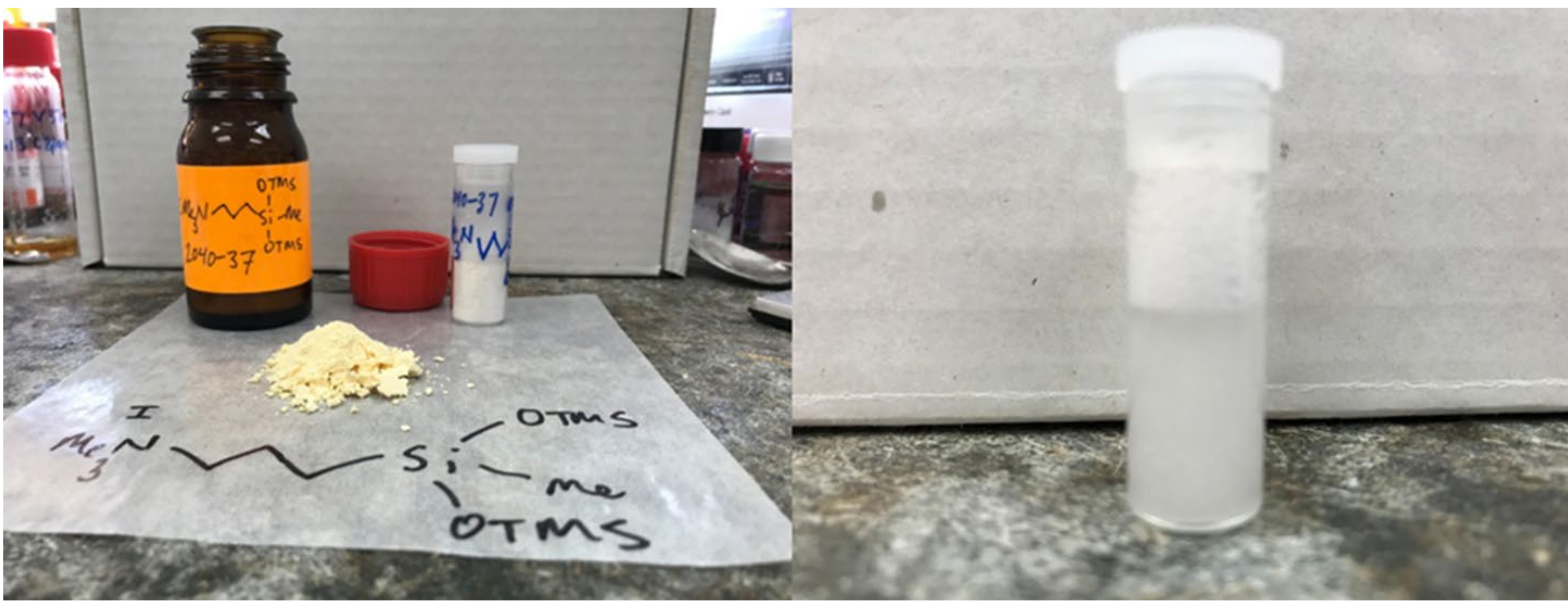


7 minute foam duration on gasoline

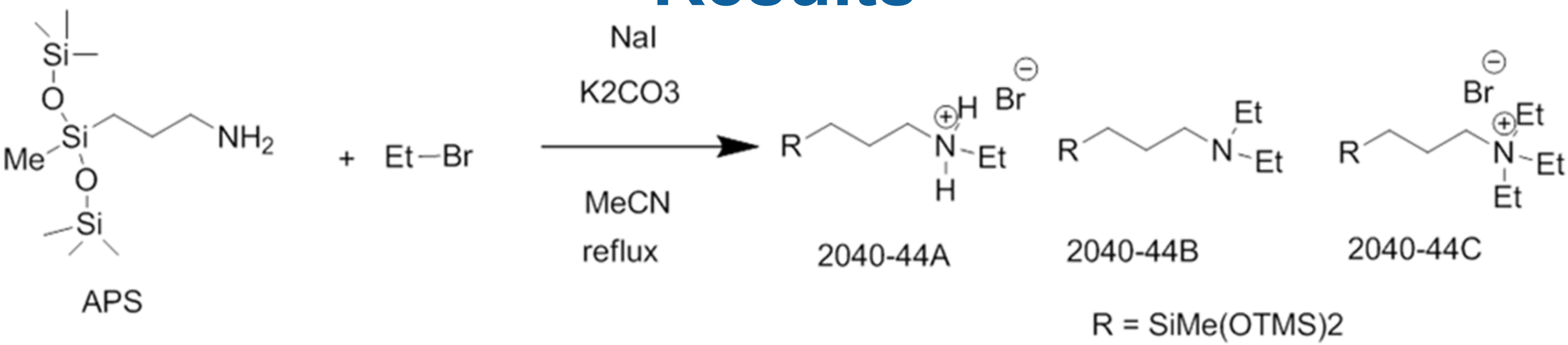
4 hour film duration on gasoline

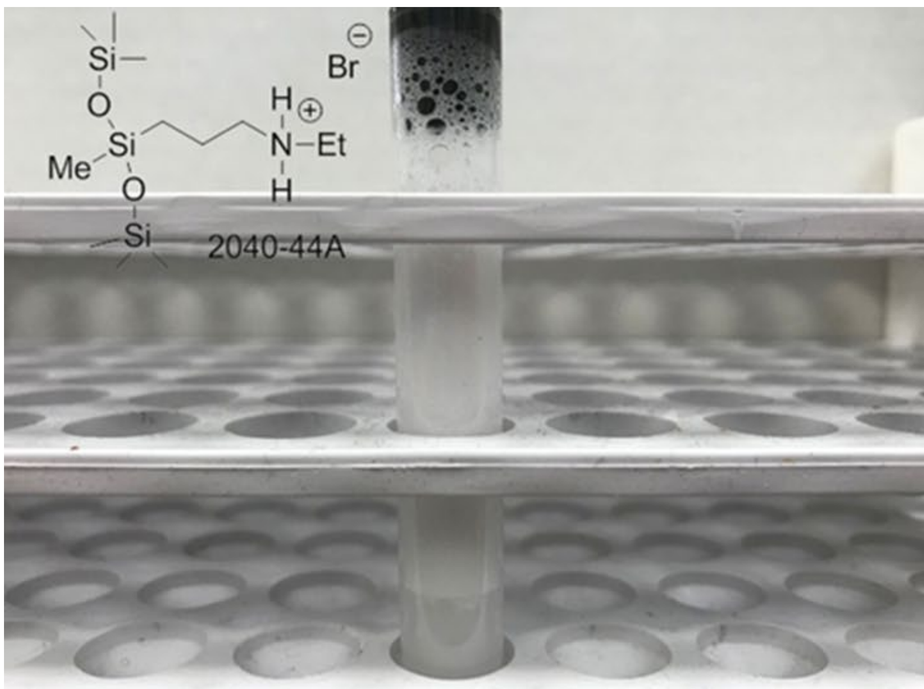
Results

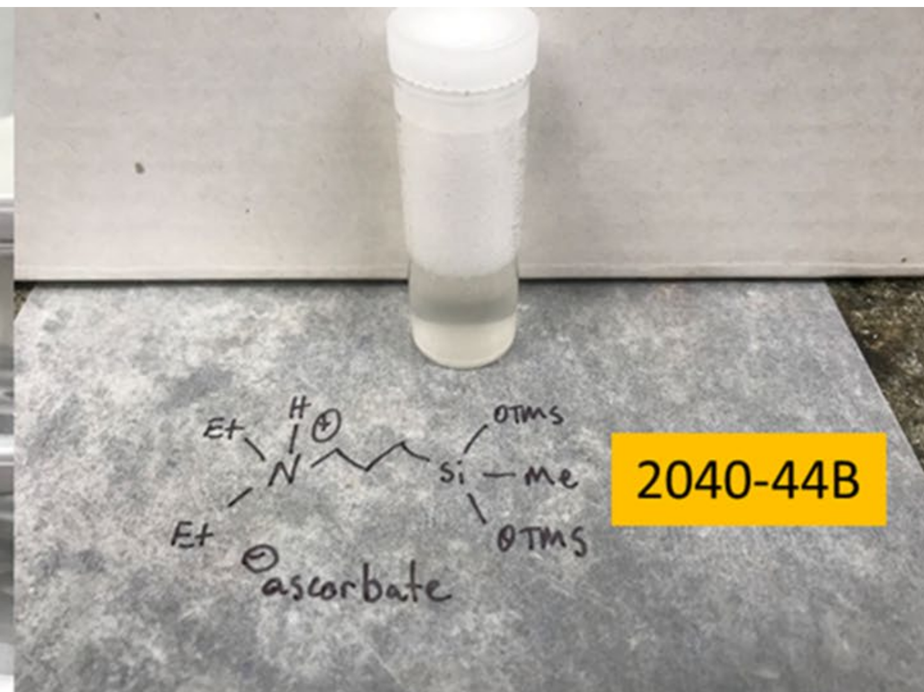

Si
O
Si
Me
O
Si
NH_2
APS
+ Me—I
K2CO3
MeCN
reflux
Si
O
Si
Me
O
Si
N
I
2040-37


OTMS
2040-37
OTMS
I
Si
OTMS
OTMS

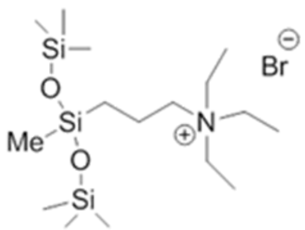
Results


APS
+ Et—Br
NaI
K2CO3
MeCN
reflux
2040-44A
2040-44B
2040-44C
R = SiMe(OTMS)2

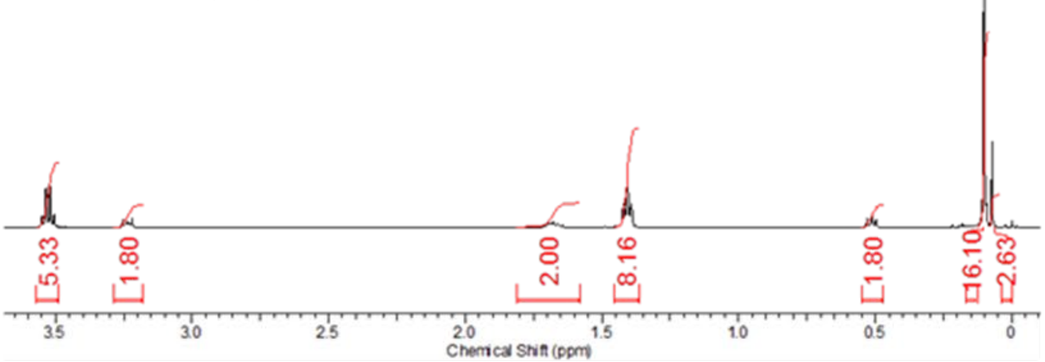

2040-44A

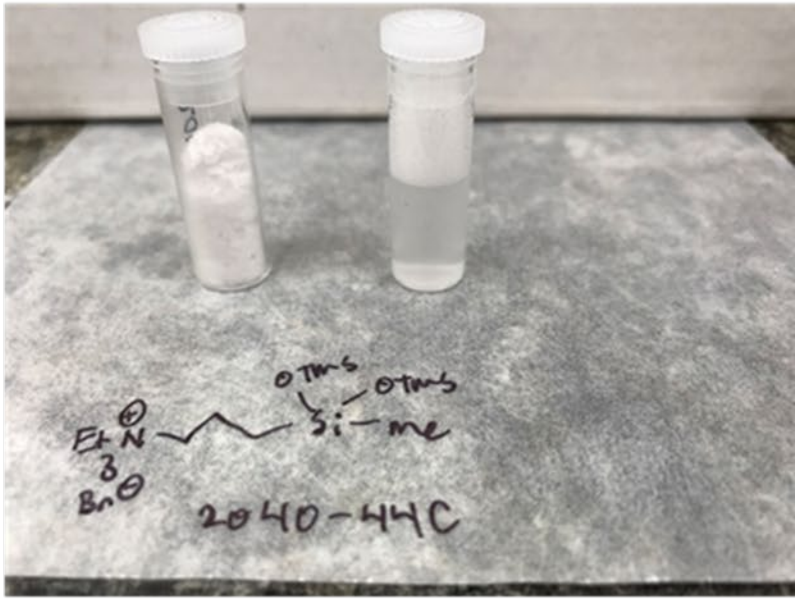

ascorbate
2040-44B

Results



2040-44C





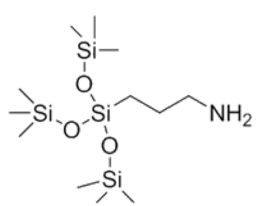
Results

Schmaucks et al Langmuir 1992, 8, 1724-1730

Table IV. Interfacial Activity of Alkyl-*N,N*-dimethyl(3-siloxanylpropyl)ammonium Halides

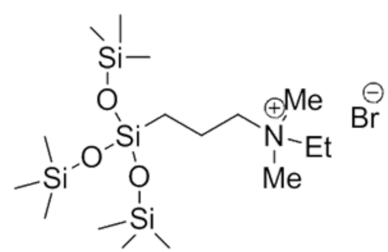
compound	cmc, mol/dm³	max surface tension depression, mN/m	interfacial tension $c >$ cmc, mN/m	contact angle $c >$ cmc, deg	foamability $c = 5$ g/dm³ Bartsch tube, [cm]	surface area per molecule, Å²
Disiloxanes $Me_3SiOSiMe_2(CH_2)_3N^+Me_2R\ Br^-$						
3b, R = C_2H_5	6.9×10^{-2}	26.5	4.5	48.9	0	34.2
3c, R = C_3H_7	2.6×10^{-2}	23.5	1.8	55.4	0.3	43.1
3d, R = C_4H_9	5.7×10^{-2}	24.6	2.7	33.4	0	47.4
Straight Chain Trisiloxanes $Me_3SiOSiMe_2OSiMe_2(CH_2)_3N^+Me_2R\ Br^-$						
4b, R = C_2H_5	2.3×10^{-2}	20.4	1.1	spr[a]	2.0	44.2
4c, R = C_3H_7	9.7×10^{-3}	19.0	1.0	spr	13.0	43.1
4d, R = C_4H_9	1.0×10^{-2}	20.0	~0	spr	14.0	45.1
Branched Trisiloxanes $(Me_3SiO)_2SiMe(CH_2)_3N^+Me_2R\ X^-$						
5a, R = CH_3 Br	1.4×10^{-2}	22.5				64.6
5b, R = C_2H_5	2.2×10^{-2}	20.6	~0	spr	0	58.9
5c, R = C_3H_7	2.0×10^{-2}	20.2	1	spr	0	64.6
5d, R = *n*-C_4H_9 Br	9.6×10^{-3}	18.5	~0	spr	12.0	62.8
5e, R = *i*-C_4H_9	1.3×10^{-2}	21.6				61.2
5f, R = allyl	2.4×10^{-2}	19.5	~0	spr	0	63.2
5g, R = CH_3 I	2.2×10^{-3}	30.7				59.0
5h, R = allyl	2.1×10^{-2}	24.0	~0	spr	0	60.5
Branched Tetrasiloxanes $(Me_3SiO)_3Si(CH_2)_3N^+Me_2R\ Br^-$						
6a, R = CH_3	4.5×10^{-3}	22.4				69.9
6b, R = C_2H_5	2.4×10^{-3}	17.9	1	spr	15.0[b]	69.4
6c, R = C_3H_7	2.8×10^{-3}	18.8	~0	spr	17.5[b]	77.9
6d, R = *n*-C_4H_9	2.6×10^{-3}	19.3	~0	spr	12.0[b]	76.6
6f, R = allyl	2.9×10^{-3}	18.4	~0	40.0	19.0[b]	74.5

[a] spr is spreading of a drop of water on paraffin surface. [b] Foamability by the method of Ross–Miles (%) at a concentration of 3 g/dm³:



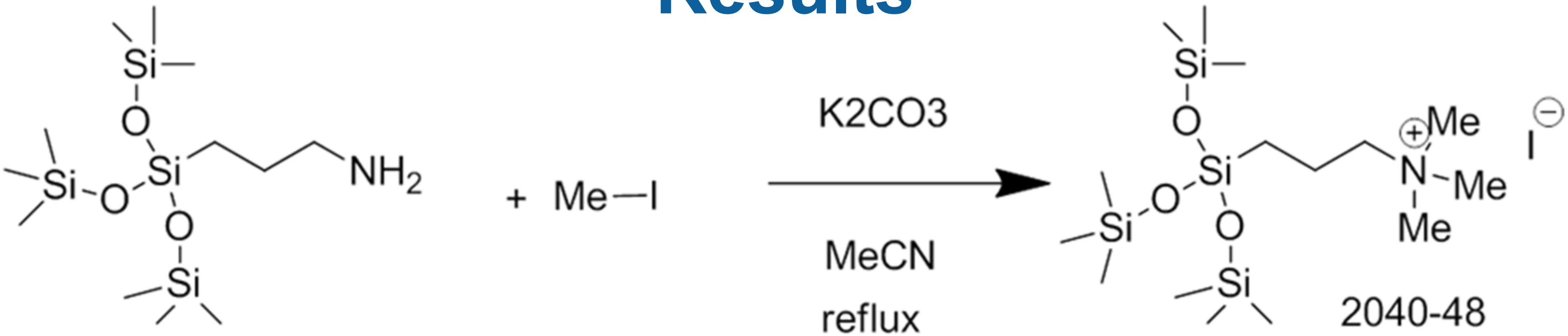
3-aminopropyltris(trimethylsiloxy)silane

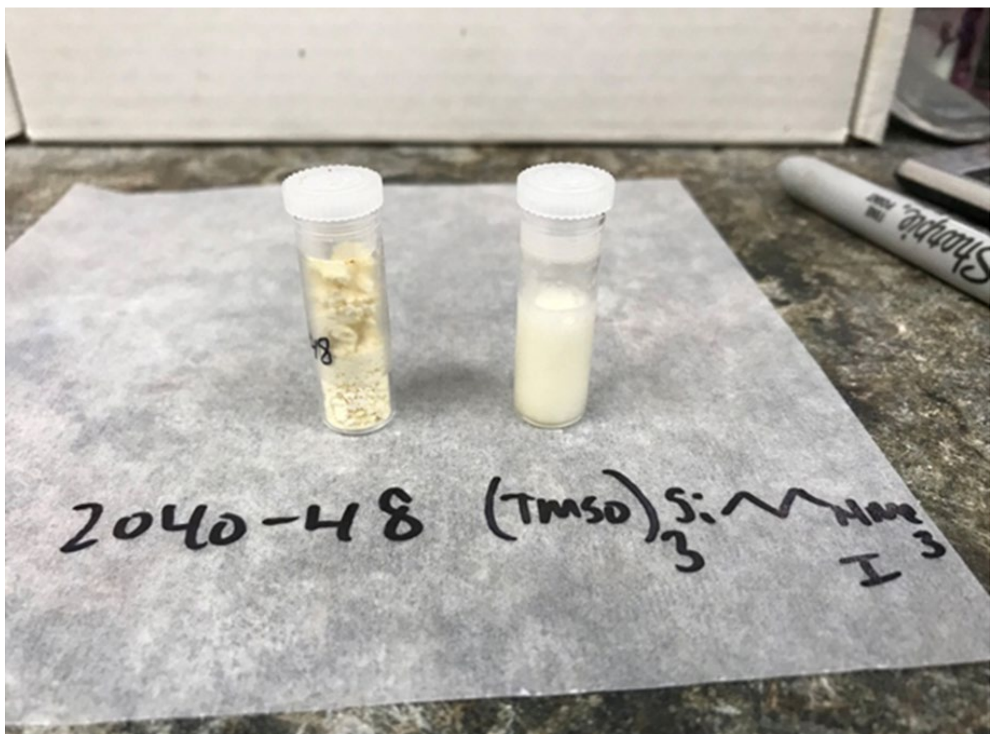
APS4



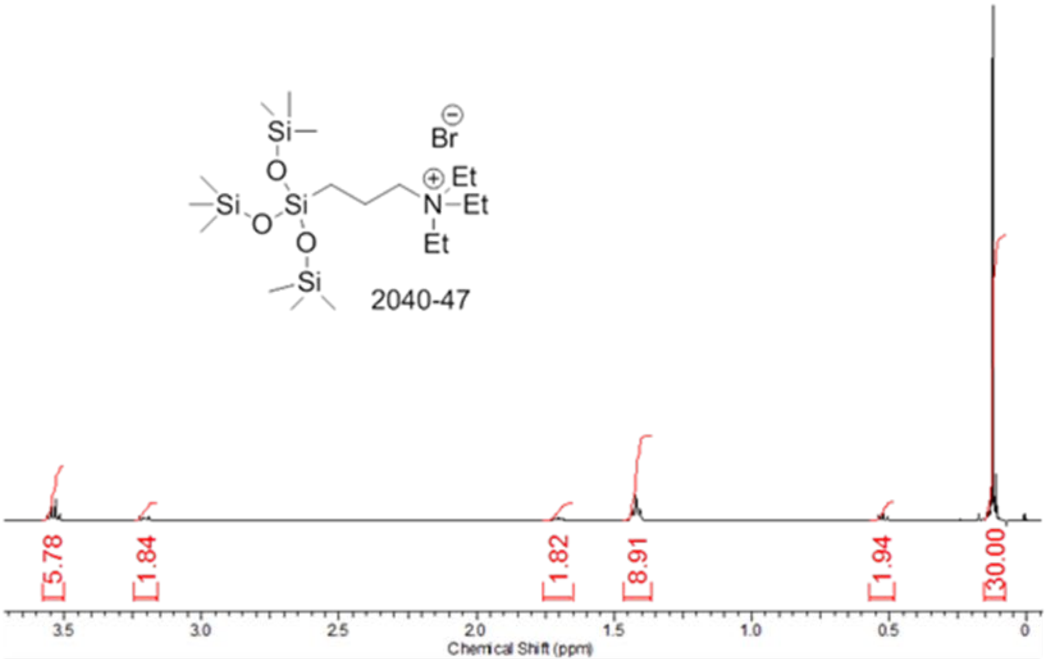
17.9 mN/m in air

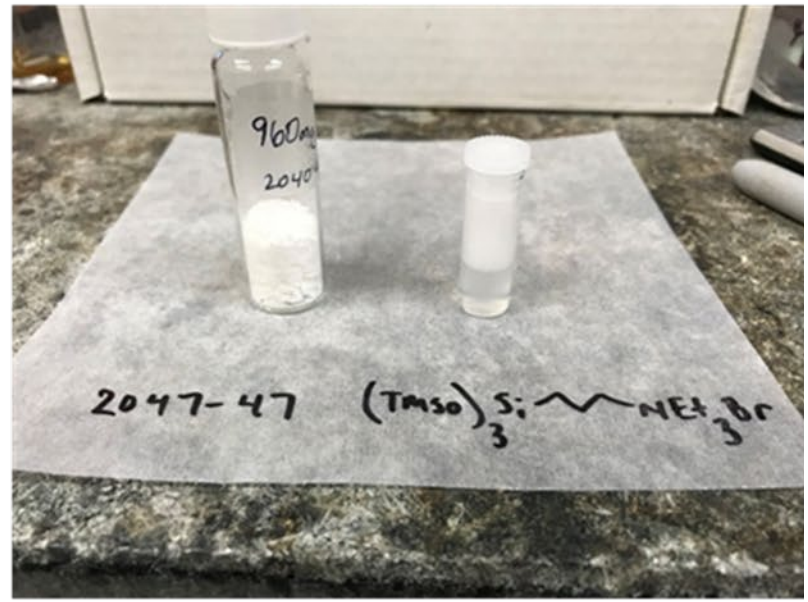
Results





Results





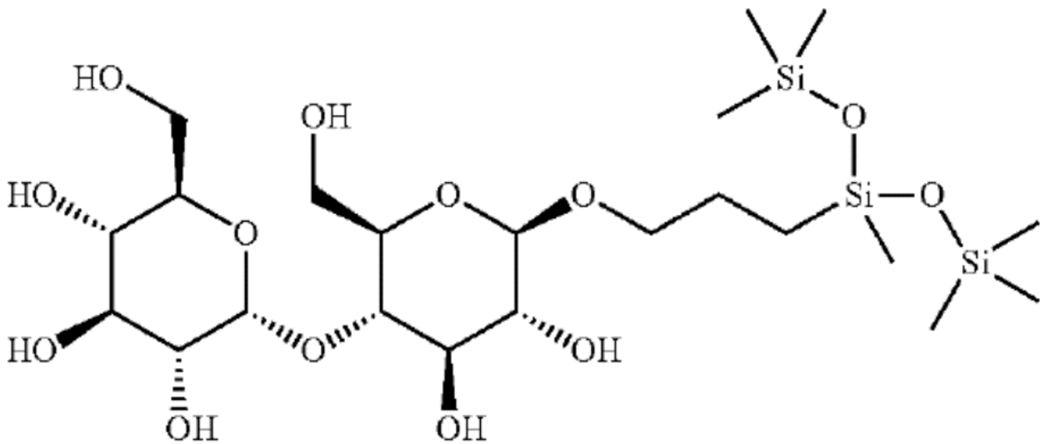
Counter Ion Could be important to surface tension

Sugar Siloxane by Blunk for Fire fighting

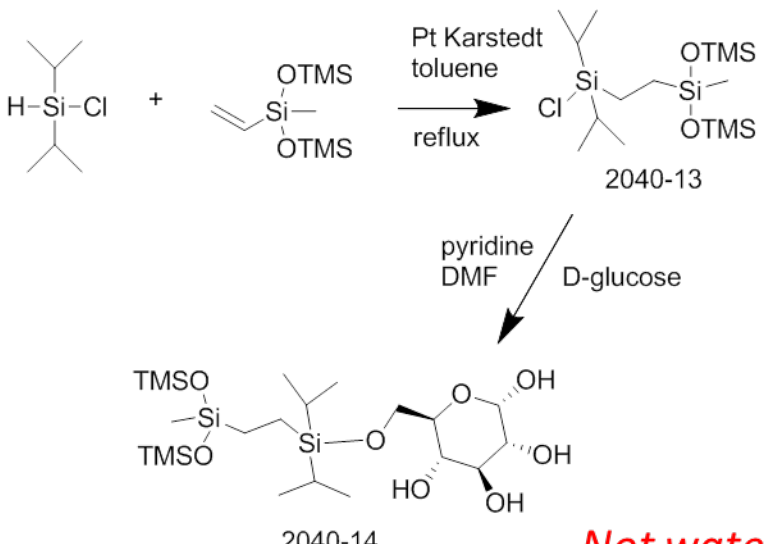
Results

Diesel Fire

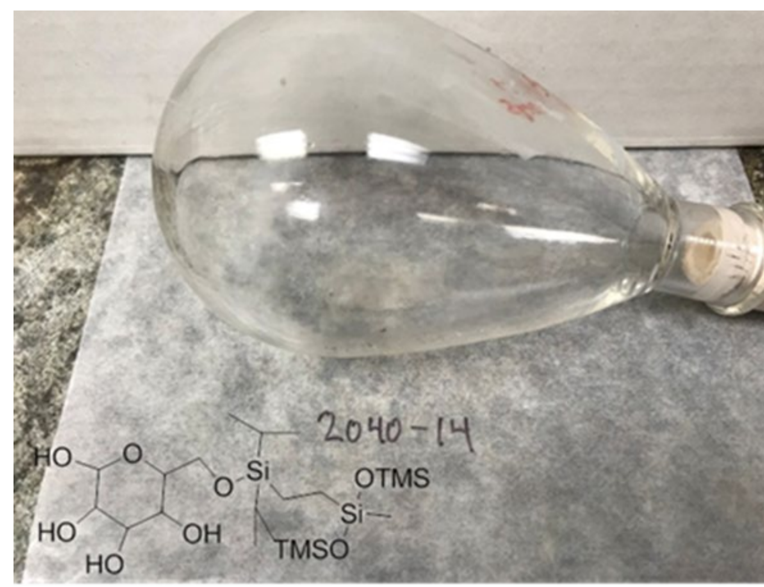
AFFF 78 seconds



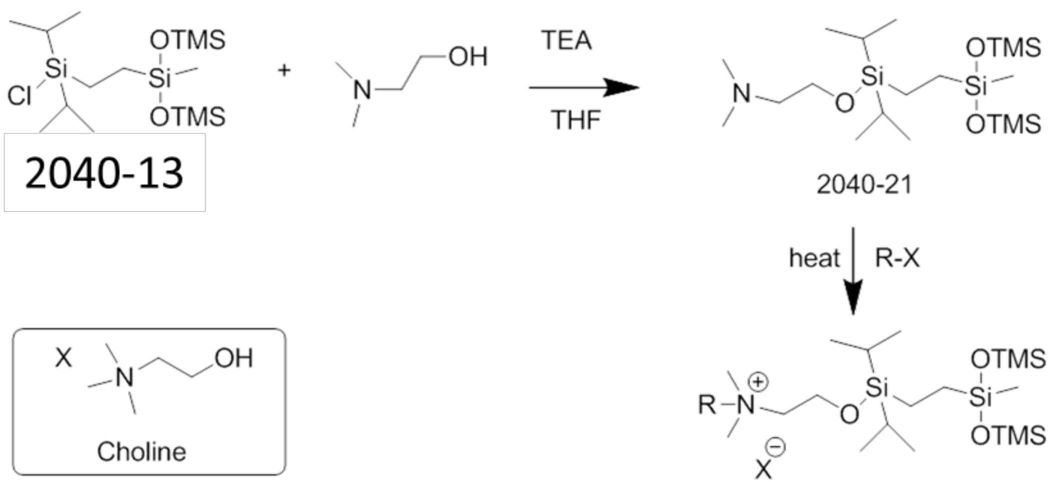
95 seconds



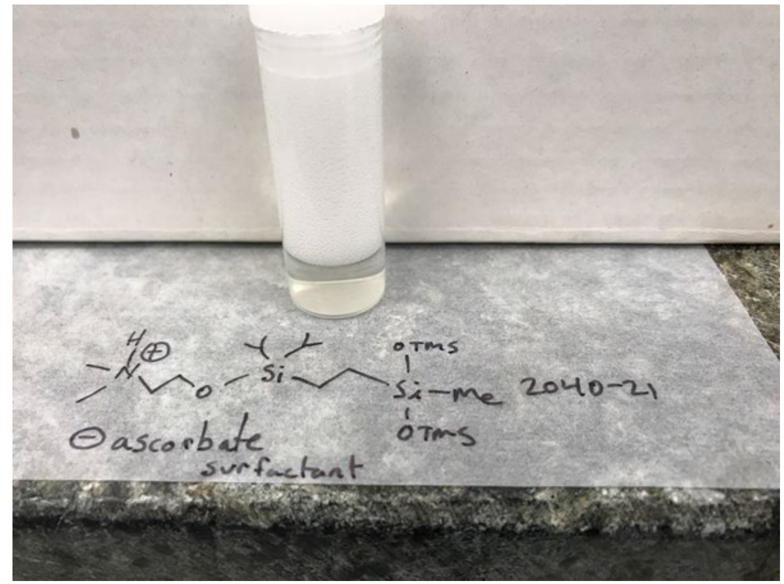
Not water soluble



Results



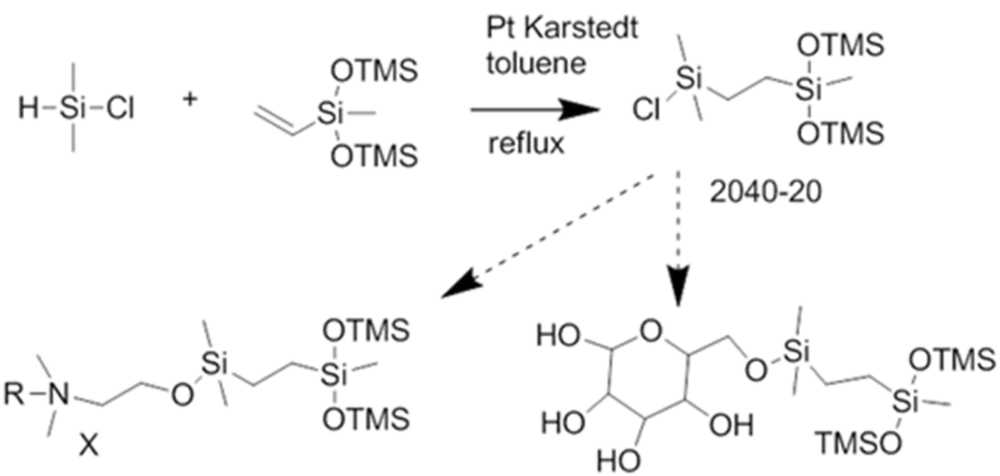
OTMS
Si
Cl
OTMS
2040-13
N
OH
TEA
THF
2040-21
heat
R-X
R
X
Choline

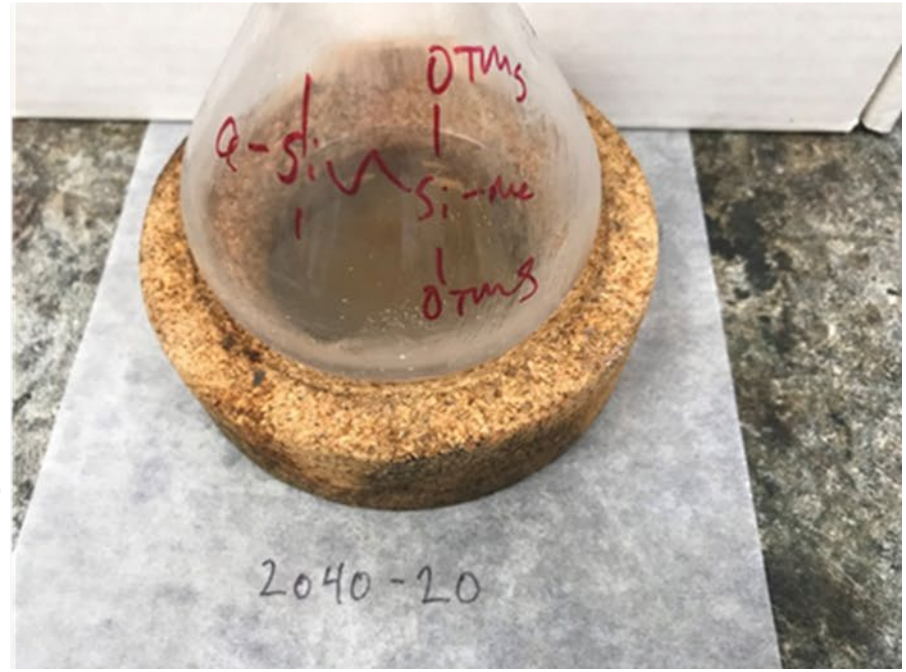


OTMS
Si
Si—Me
2040-21
OTMS
⊖ascorbate
surfactant

Results

Better water solubility with dimethyl silyl group?





Technology Transfer

- Presented Poster at SERDP Symposium
- Could submit research paper about results to technical journal

Key Points

- ♦ POSS was difficult to make into surfactant and had only weak activity
- ♦ Salts of aminoalkylsiloxanes appear to be good surfactants
- ♦ Carboxylate salts of aminoalkylsiloxanes had positive spreading coefficient on cyclohexane but could not extinguish heptane pool fire
- ♦ The aminoalkylsiloxane surfactants may have stability issues in water solution

Future Research

The ammonium alkylsiloxanes have good surface tension data and should be studied further

The aminoalkydisiloxane and aminoalkyltrisiloxane can be derivatized with alkylhalide to make many variations

The hydrolysis or decomposition of siloxane surfactants should be studied further to determine exact chemical reactions and by-products

Synergism of ammonium alkylsiloxanes and hydrocarbon surfactants may make 'stable' solutions similar to NRL findings

Run small scale pool fire experiments with the ammonium alkylsiloxanes with and without hydrocarbon surfactants (BASF Glucopons)

An additional $200K for 1 year should be enough to accomplish these studies

Publications

- Poster presented at the 2018 SERDP Symposium, Washington DC, Wednesday 28 November 2018.

Project Funding

	FY18	FYxx	FYxx
Funds received to date ($K)	200		
% Expended	200		
Funds Remaining ($K)	0		

WP18-1519: Surfactants with Organosilicate Nanostructures for Use as Fire-Fighting Foam (F^3)

Performers: Matthew Davis Ph. D. NAWC China Lake

Technology Focus

- *New Materials Useful for Hydrocarbon Pool Fire Fighting*

Research Objectives

- *Synthesize surfactants from POSS and aminoalkylsiloxanes with positive spreading coefficients on hydrocarbon fuels that can*
- *put out gasoline pool fires in 45 seconds.*

Project Progress and Results

- *POSS surfactant was not effective. Aminoalkylsiloxane carboxylates were good surfactants with positive spreading on cyclohexane but one example salt could not extinguish a heptane pool fire.*

Technology Transition

- *Ammonium alkylsiloxane surfactants are easy to synthesize and show promising surface tension data but may have hydrolysis issues which must be studied further.*