Synthesis and Testing of Hydrolysis Resistant Siloxane Surfactants as Additives for Pool Fire Suppression

SEED Project WP18-1519

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14. ABSTRACT
Perfluoroalkyl surfactants are the key ingredients in aqueous film forming foams (AFFF) which are used by the Department of Defense and others to fight hydrocarbon (Class B) pool fires. Perfluoroalkyl surfactants work extremely well for this application, however there are growing concerns about these materials because they are highly persistent in the environment and may be toxic to plants and animals or increase their risk to certain diseases. The objective of this project was to explore hydrolysis-resistant siloxane surfactants as replacements of perfluoroalkyl surfactants found in current aqueous film forming foam (AFFF) concentrates used in fire-fighting by the Department of Defense (DoD). The new, stable siloxane surfactants produced in this research will contain only the elements carbon, silicon, hydrogen and oxygen. Foams containing the new surfactants will extinguish small-scale, unleaded gasoline pool fire in 45 seconds or less as dictated by MIL-F-24385F.

15. SUBJECT TERMS
Fire fighting, Foam, Surfactants, Siloxanes, Fuels, Surface tension, Hydrolysis, Amines, Carbohydrates, Phosphorus, Silicon, Fluorine, Nucleophilic substitution, Nuclear magnetic resonance, Fire safety, Organic synthesis

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Prescribed by ANSI Std. Z39.18

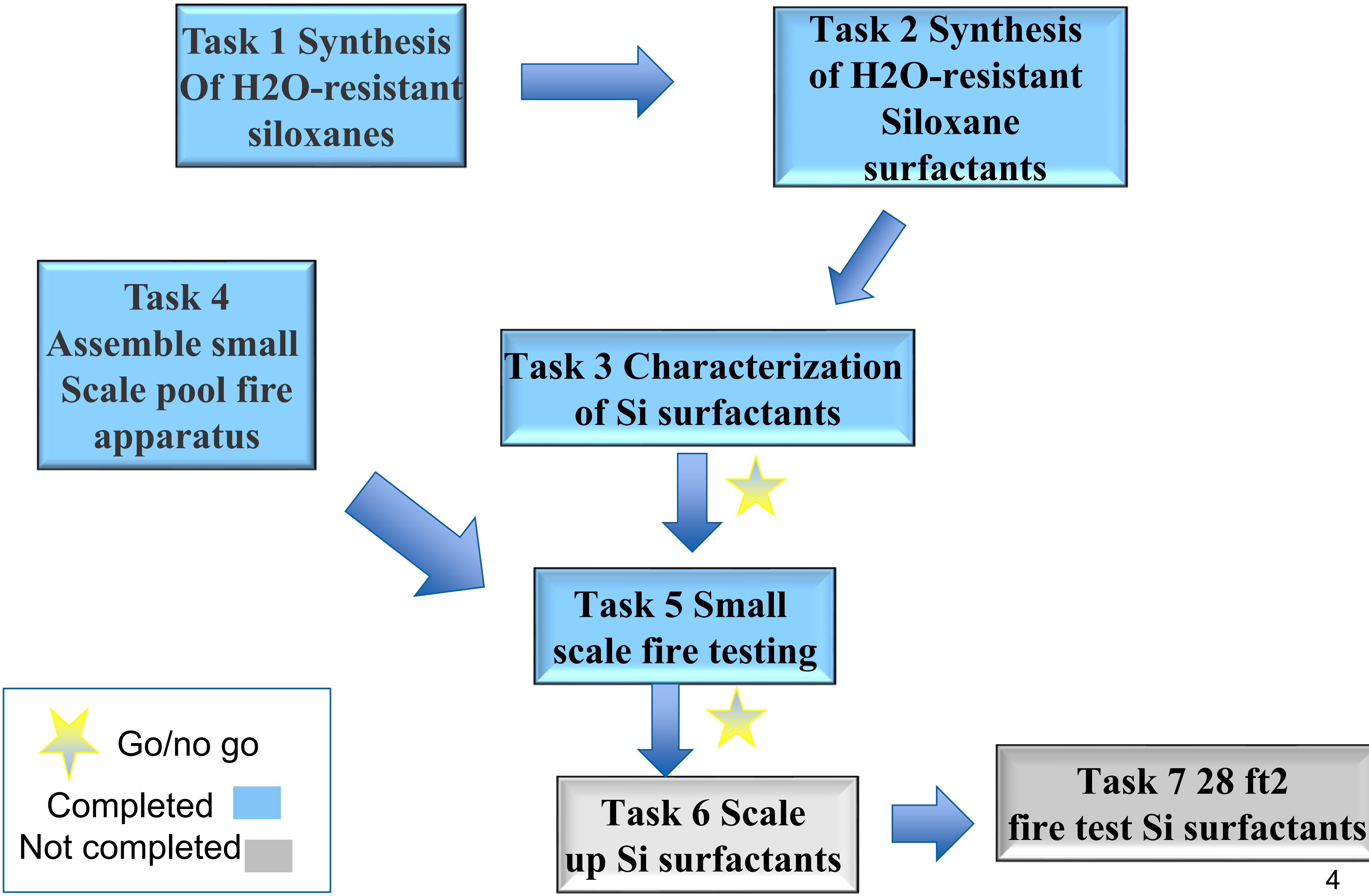
Background

- FY 2018
- Innovative Approaches to PFAS-Free Aqueous Film Forming Foam
- The objective of this limited-scope Statement of Need was to develop a fluorine-free surfactant formulation for use in aqueous film forming foam fire-suppression operations.

Technical Objectives

- The objective of this project was to create hydrolysis-resistant siloxane surfactants that could be mixed with inexpensive hydrocarbon surfactants to produce a fire-fighting foam able to extinguish hydrocarbon pool fires as effectively as the current perfluoroalkyl surfactant containing AFFF
- The project will determine the optimal degree of methyl-substitution necessary to achieve water stability of the siloxane surfactant.
- The concentration of siloxane surfactant in foam concentrate necessary to achieve an effect in fire extinguishment over control will be determined.

Technical Approach



Results

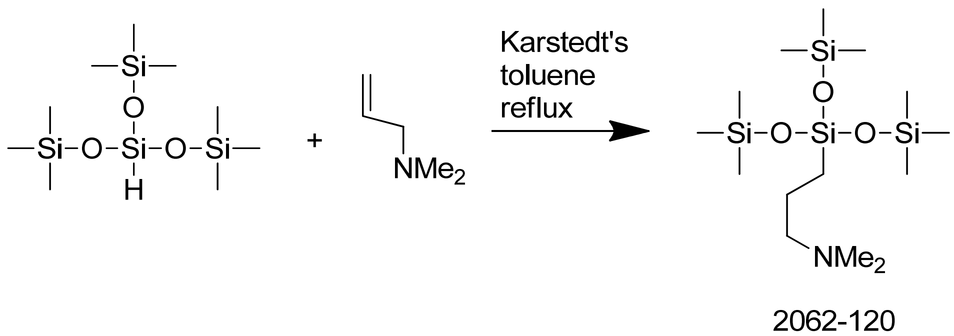


Figure 1 Hydrosilation reaction of silane and allylamine catalyzed by platinum catalyst.

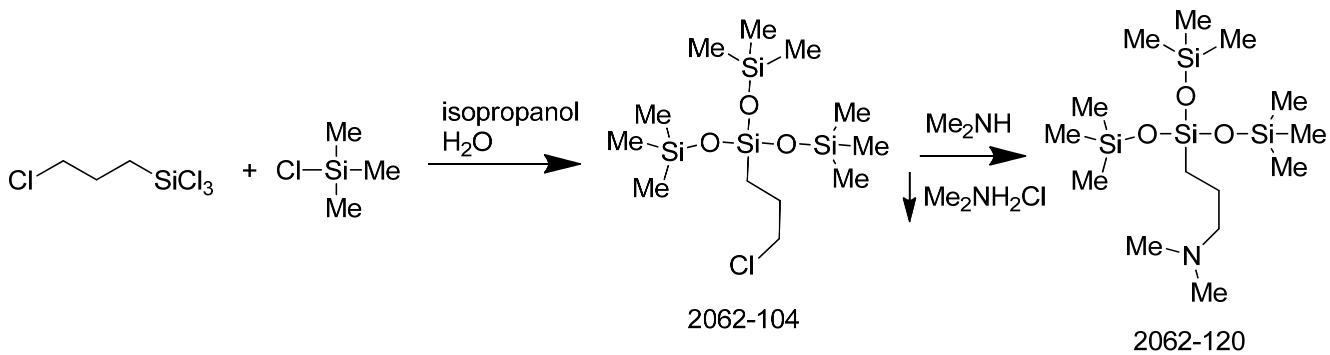


Figure 1 Two-step synthesis of the dimethylaminopropyltetrasiloxane using dimethylamine.

Results

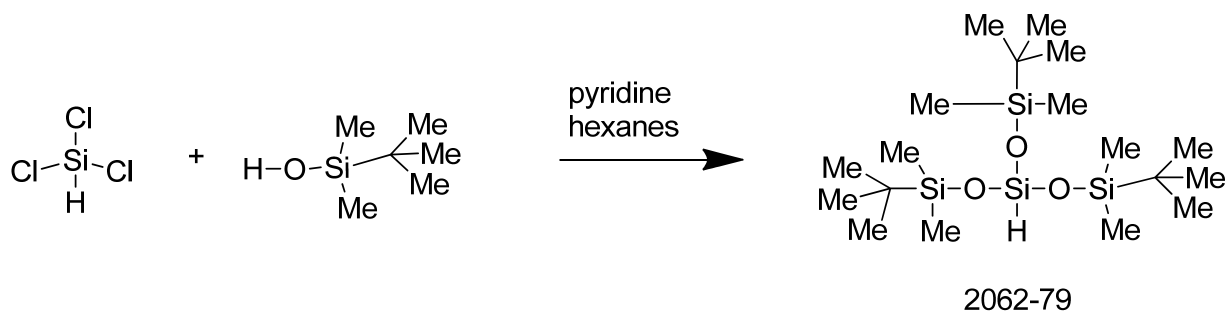


Figure 1 Relatively simple synthesis of tris(t-butyldimethylsiloxy)silane from trichlorosilane and the silanol.

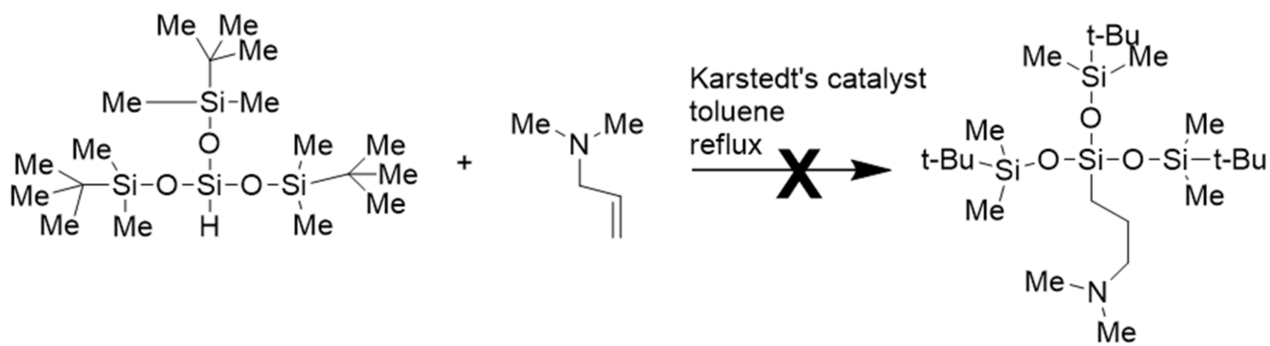


Figure 1 Failure to obtain the desired product from the platinum-catalyzed hydrosilation.

Results

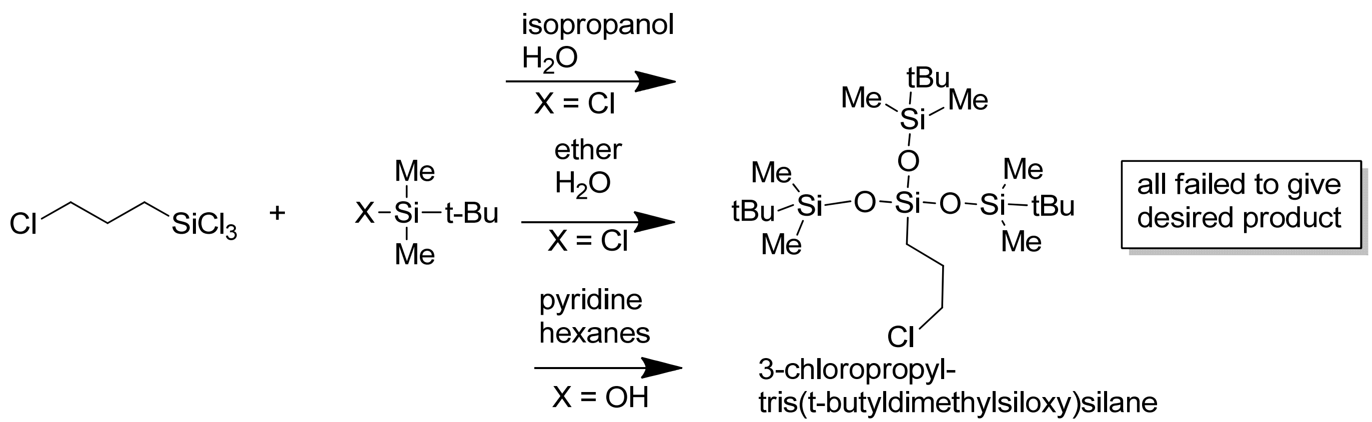
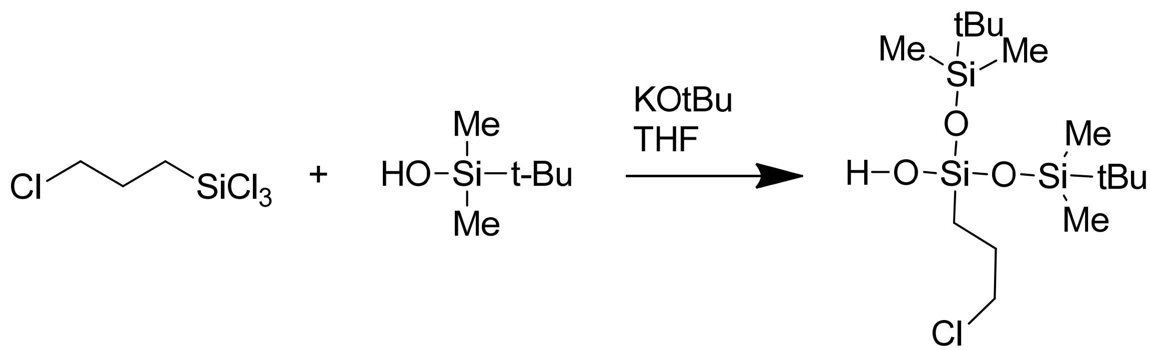


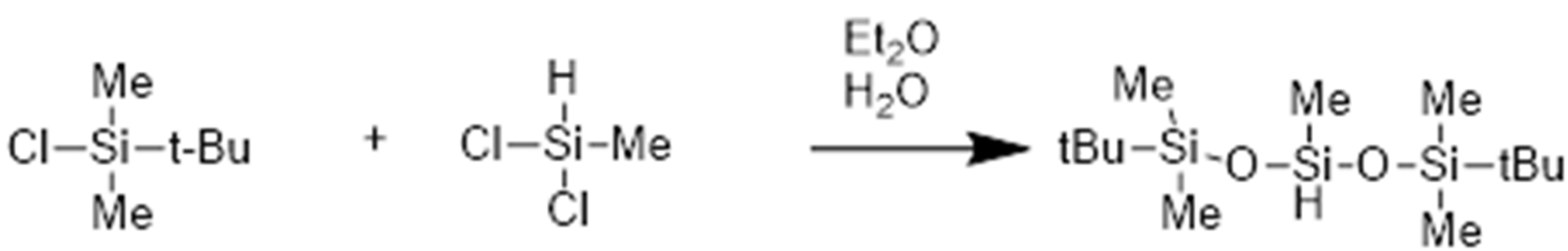
Figure 1 The simple standards methods for siloxane synthesis were unsuccessful.

RESULTS



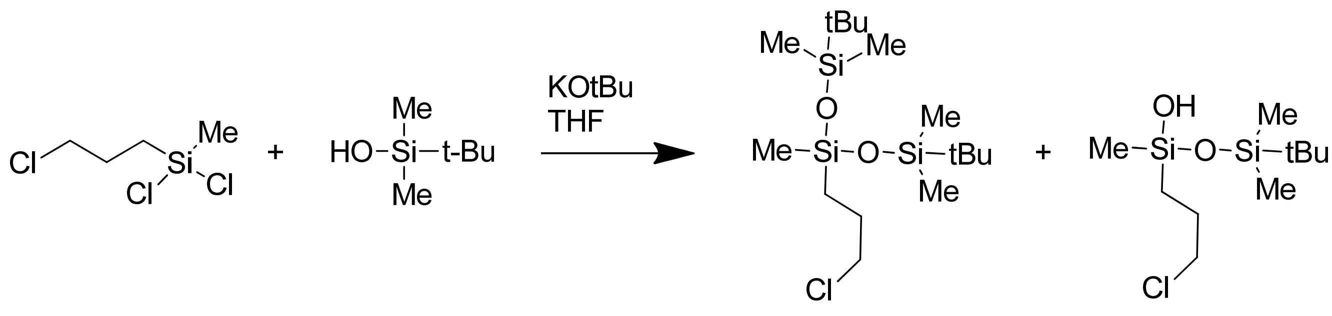
2062-136

Figure 1 Tert-butyldimethylsilanol was too bulky to achieve complete siloxylation.



2040-103

Results



2062-49

2062-149

Figure 1 The trisiloxane incorporating t-butyldimethylsilyl groups was synthesized using the strong base potassium tert-butoxide.

Results

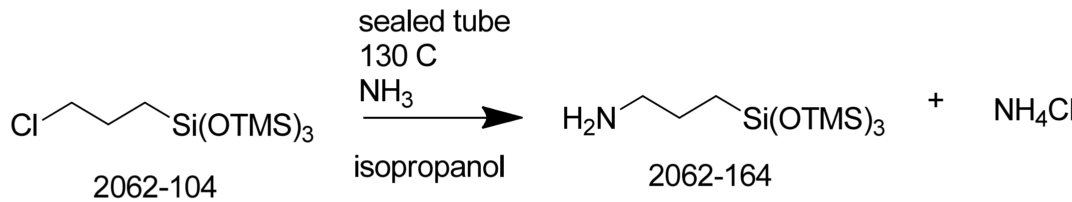


Figure 1 The simple amination with ammonia appeared to react as desired.

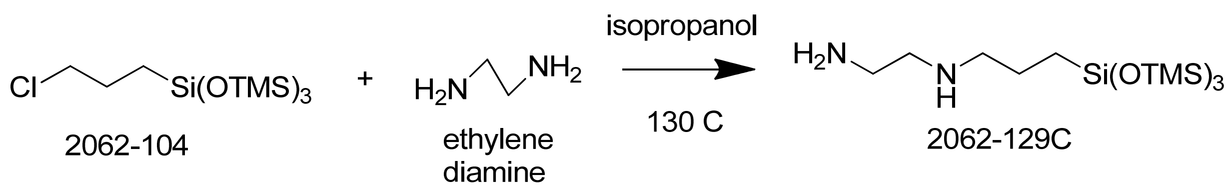


Figure 1 Amination of the chloropropyltetrasiloxane with ethylene diamine.

Results

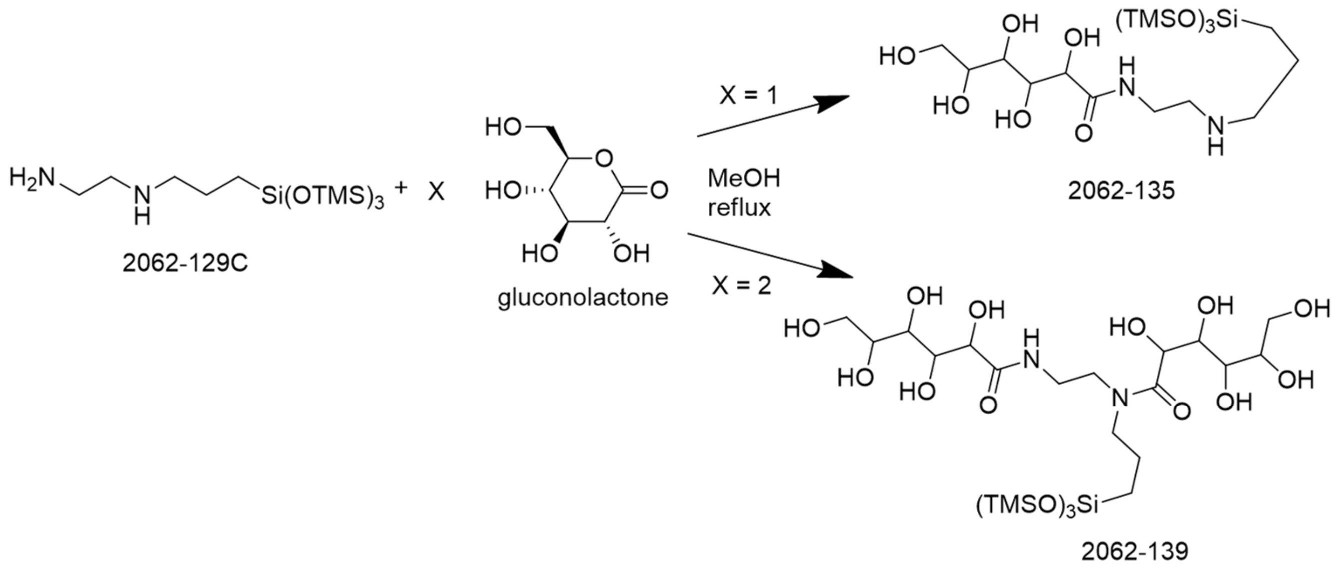


Figure 1 The diaminoalkyltetrasiloxane could be derivatized with sugar acid lactones.

Figure 2 The mono- and bis-gluconamides of diaminoalkylsiloxane 2062–129C and their empirical solubility in water after vigorous shaking.

RESULTS

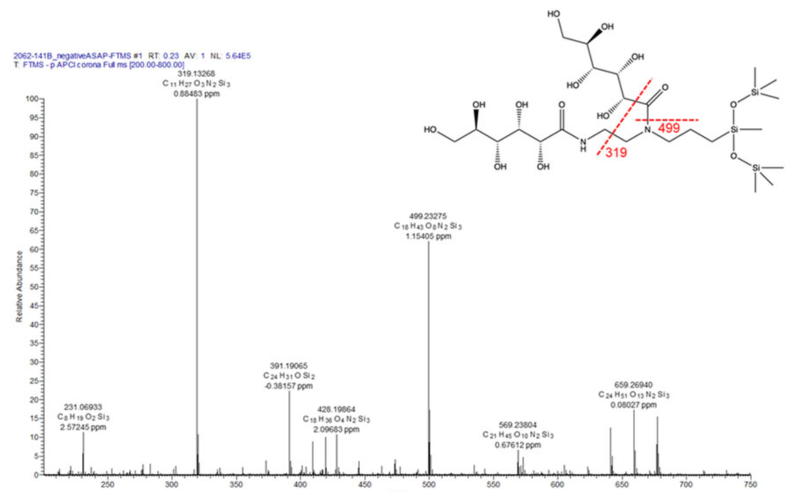


Figure 1 Negative-ion mode of ASAP mass spectrum of the 2062–141B confirming structure.

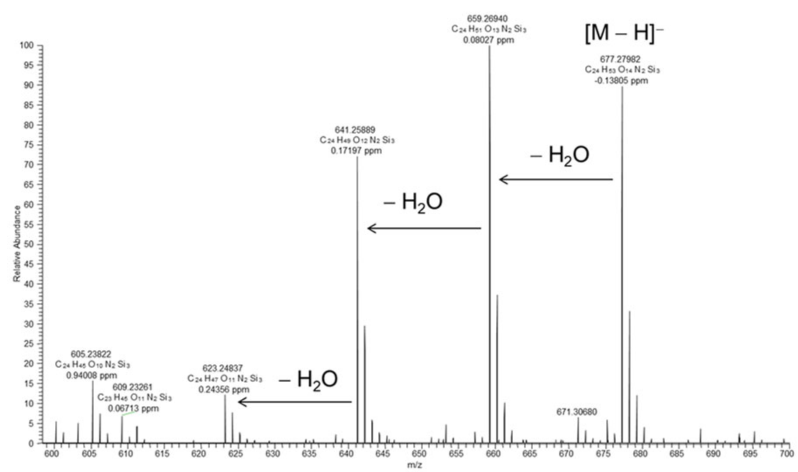
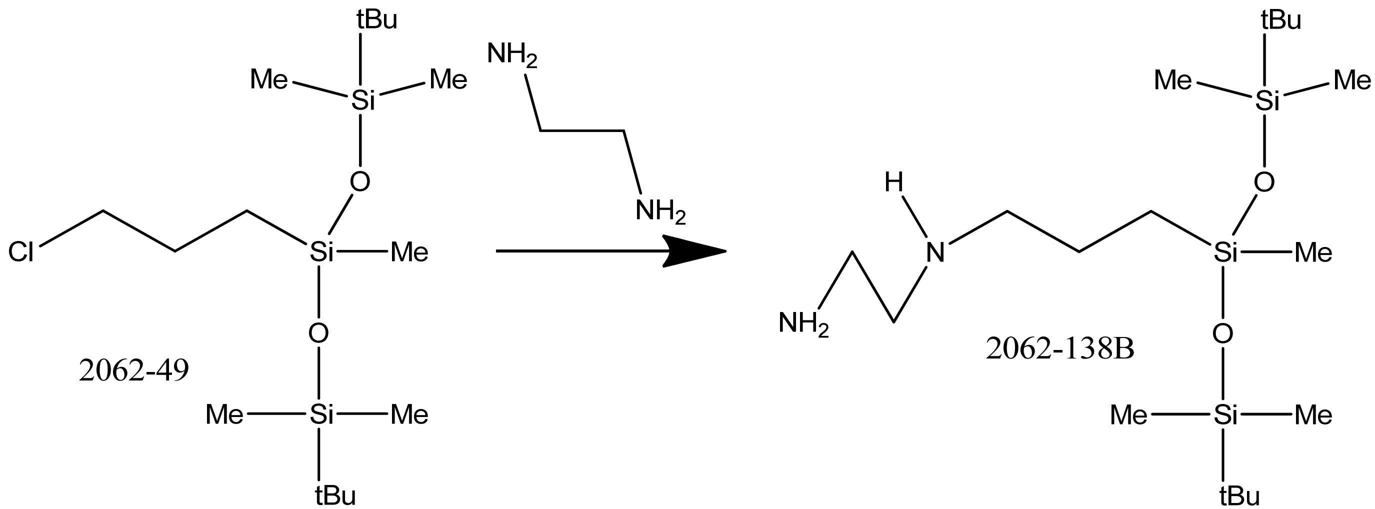


Figure 2 Close up view of the ASAP mass spectrum of the 2062–141B, the molecular ion has lost one proton by the MS ionization method.

RESULTS

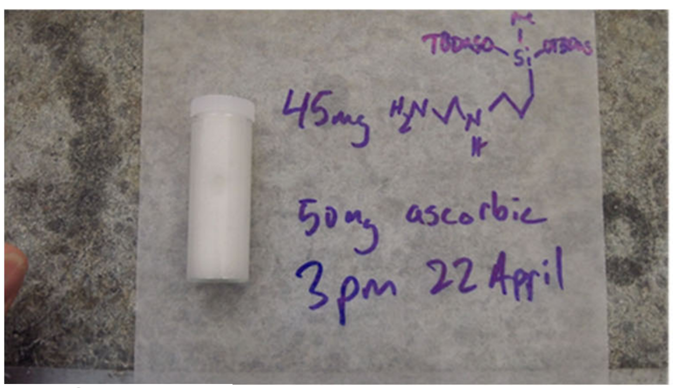


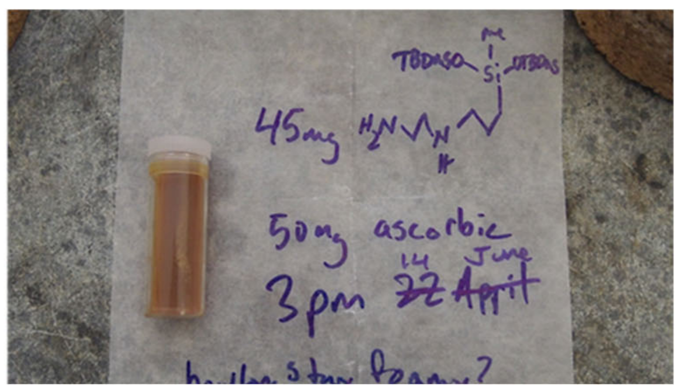
2062-49

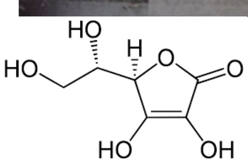
2062-138B

Organic acids

Figure 1 Amination of the tert-butyldimethylsilyl analog with ethylene diamine.

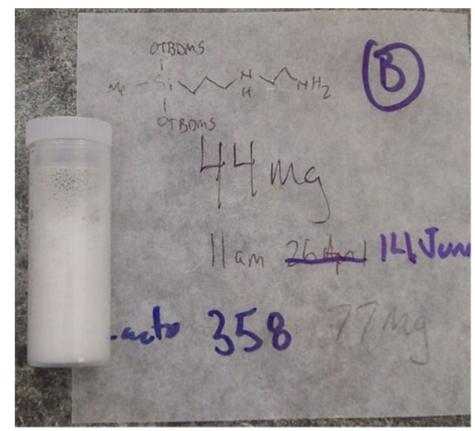


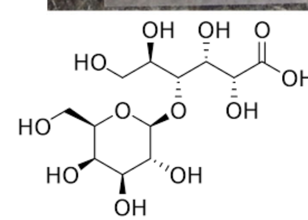




Ascorbic acid

50 days

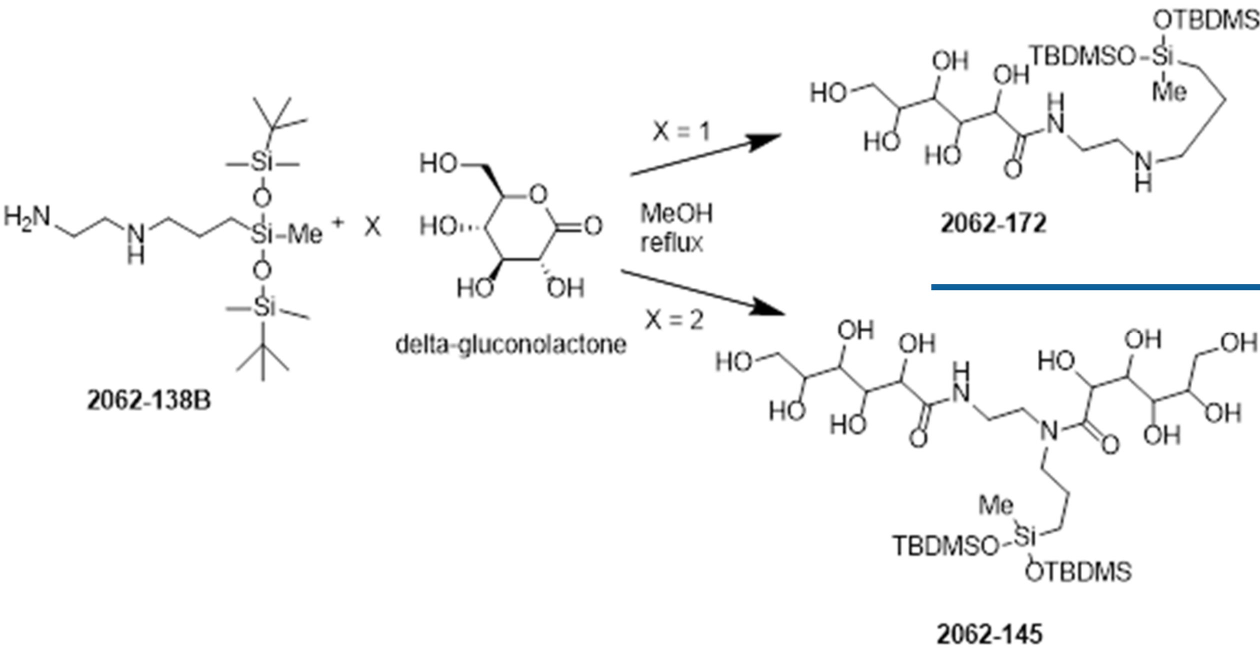




48 days

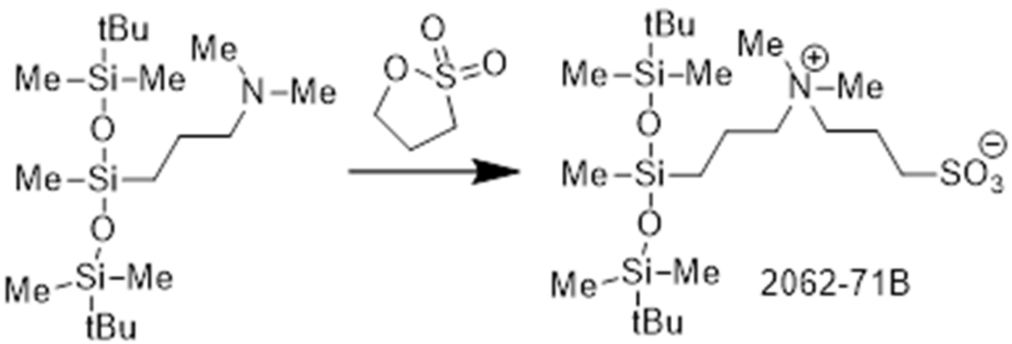
Lactobionic acid

RESULTS

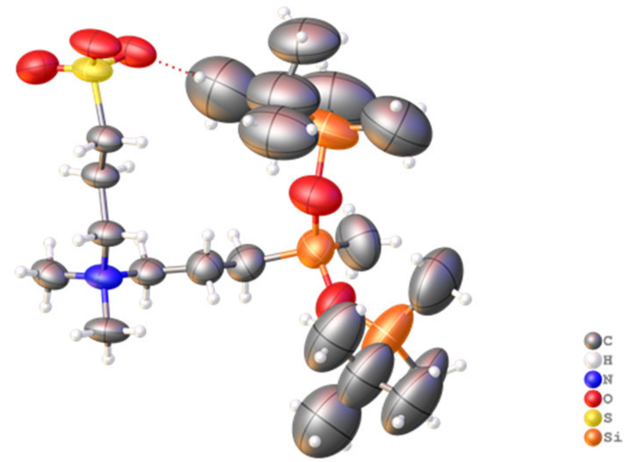

2062-138B
delta-gluconolactone
X = 1
X = 2
MeOH
reflux
2062-172
2062-145
OTBDMS
TBDMSO-Si
Me


2062-145
50MG
2062-145
9mL H2O

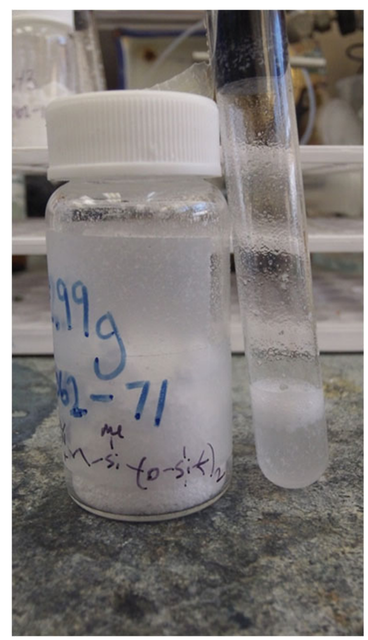
RESULTS



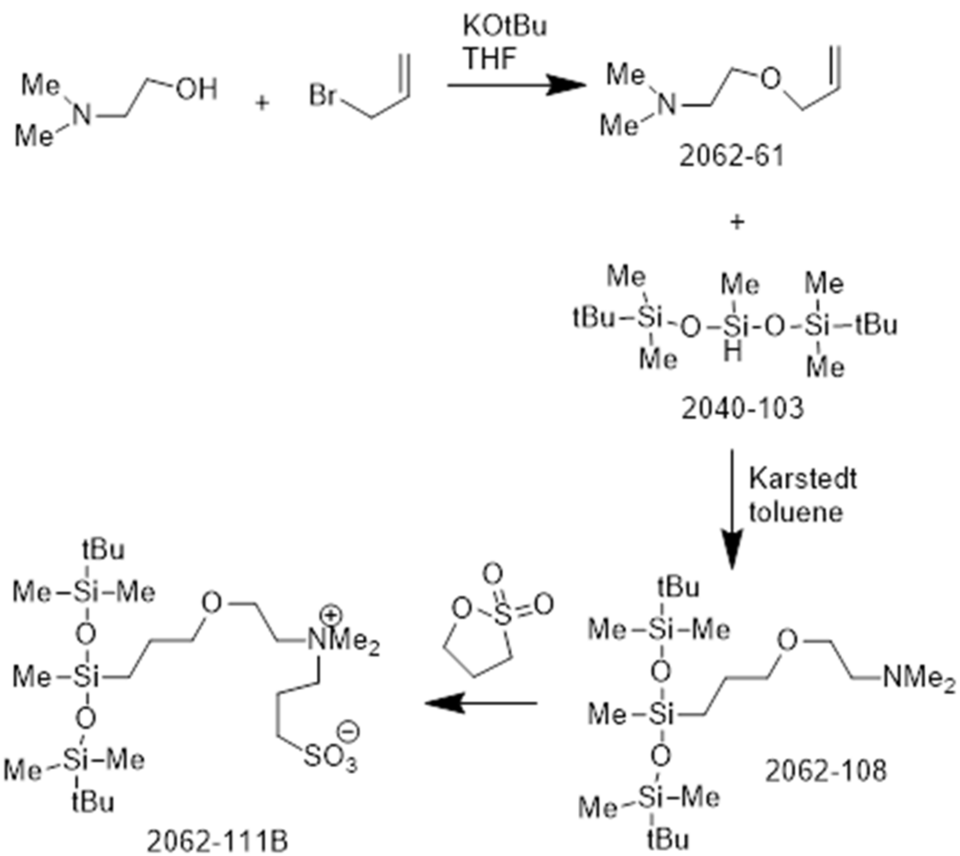
2062-158



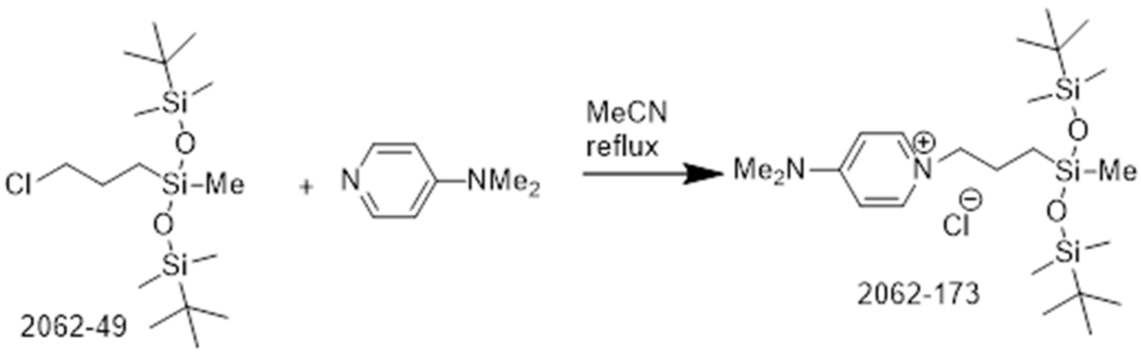
(solution courtesy of Greg Imler, NRL).



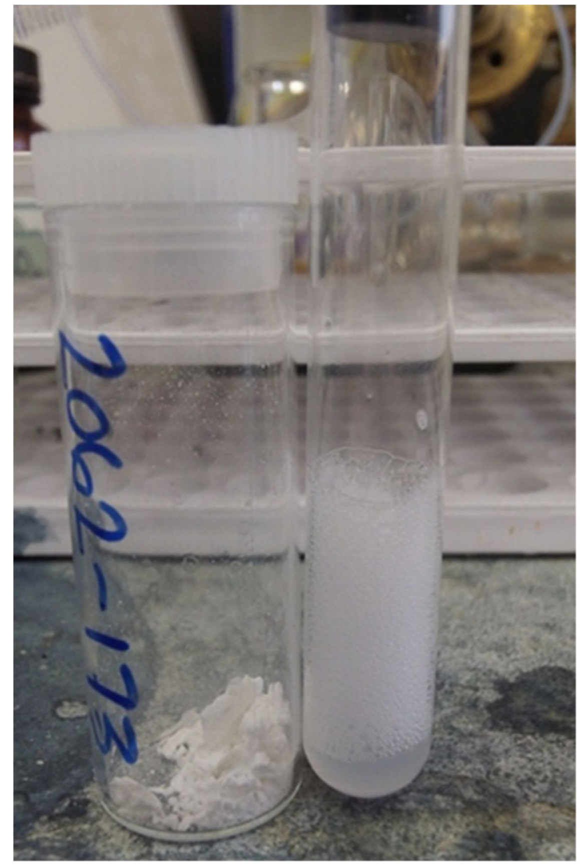
RESULTS


KOtBu
THF
2062-61
2040-103
Karstedt
toluene
2062-108
2062-111B

RESULTS

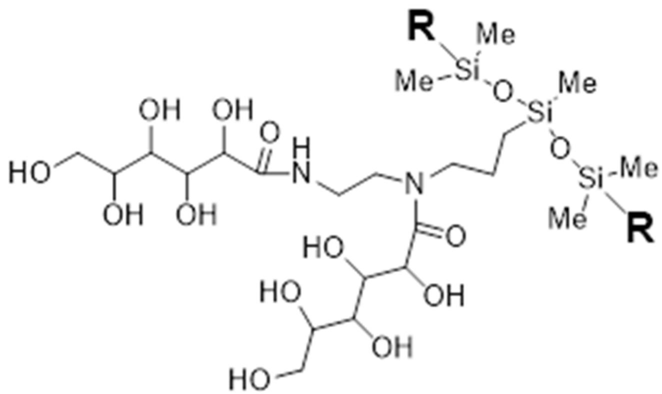


Cl
Si
O
Si-Me
O
Si
2062-49
N
NMe2
MeCN
reflux
Me2N
N
Cl
Si
O
Si-Me
O
Si
2062-173

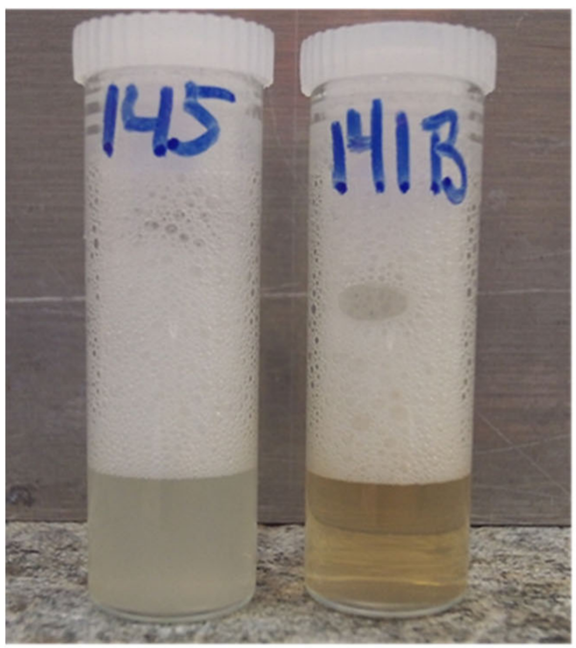


2062-173

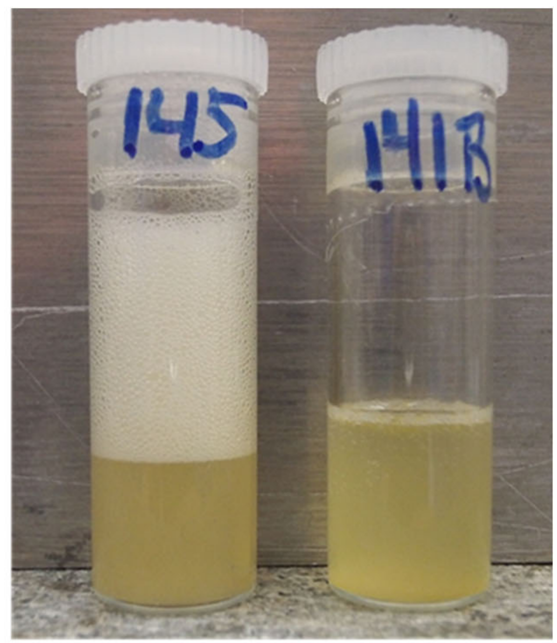
RESULTS



R = Me, 2062-141B
R = *t*Bu, 2062-145



Time Zero



After 29 days

RESULTS

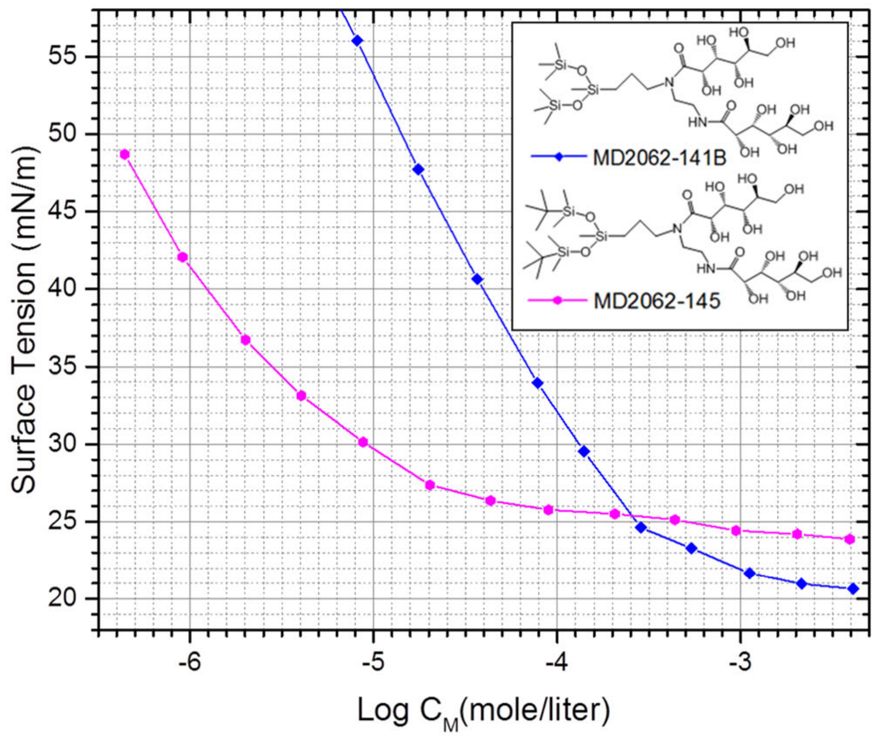


Figure 1 Surface tension data (mole/L) of 2062–141B and 2062–145.

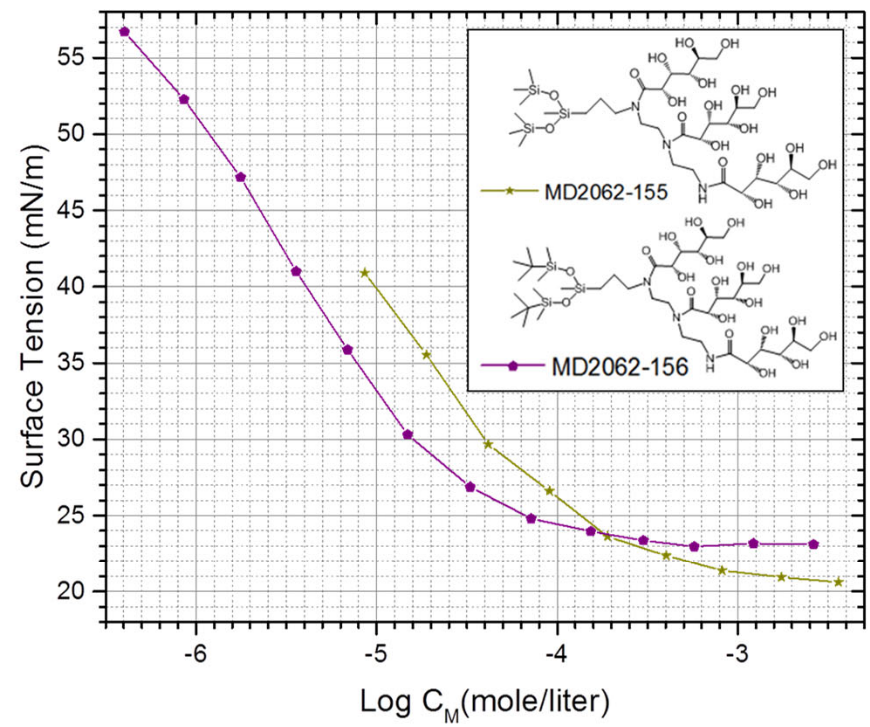


Figure 1 Surface tension data (mole/L) for 2062–155 and 2062–156.

Data provided by NRL

RESULTS

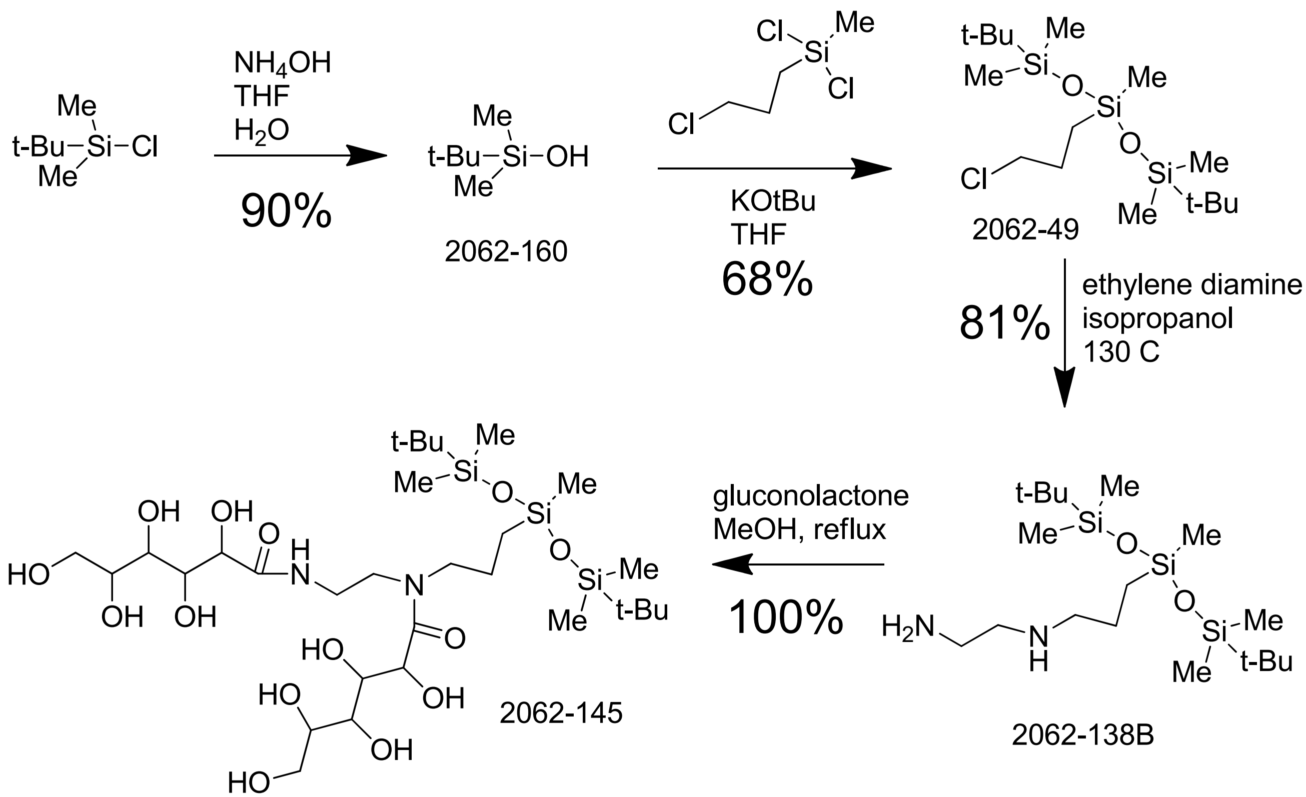
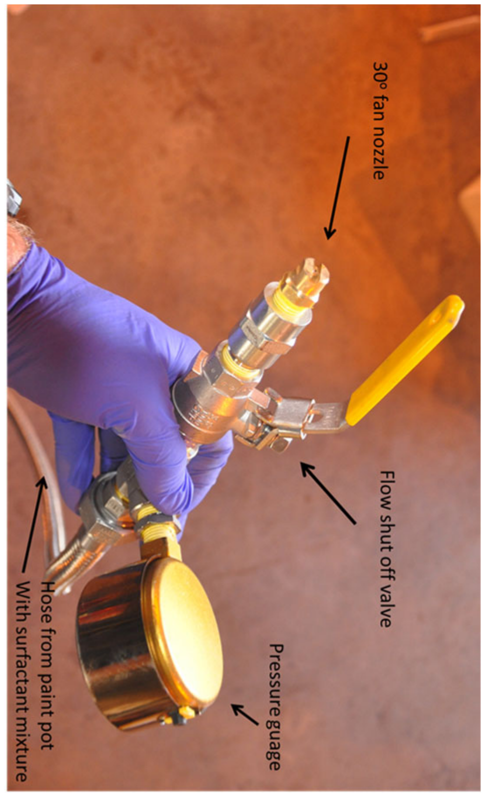


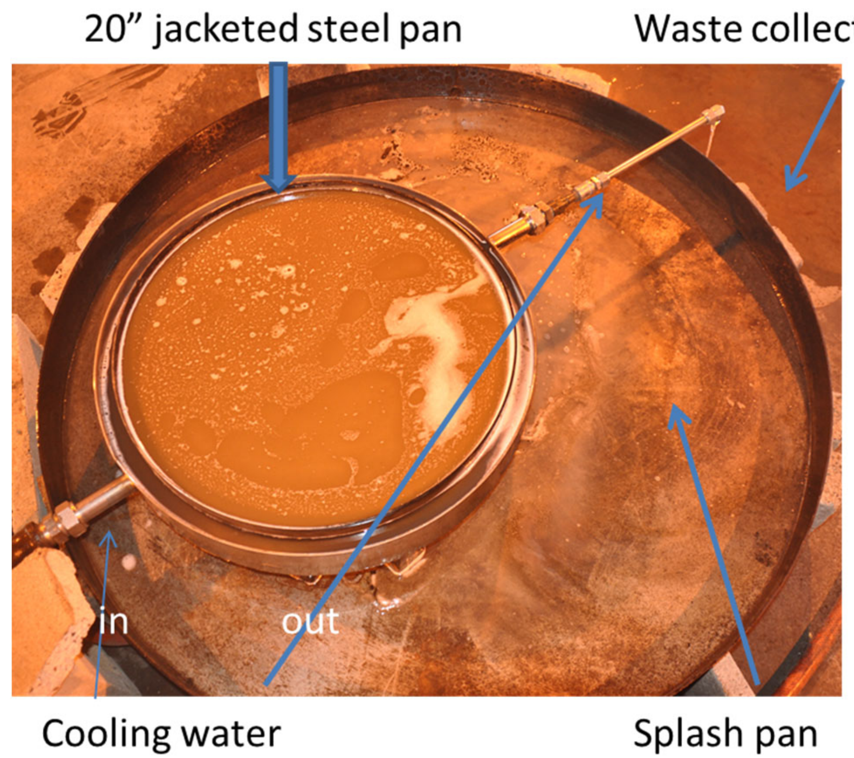
Figure 1 Overall synthe[...]cess and yields to scale-up 180 grams of siloxane surfactant 2062–145.

RESULTS

Premix foam reservior

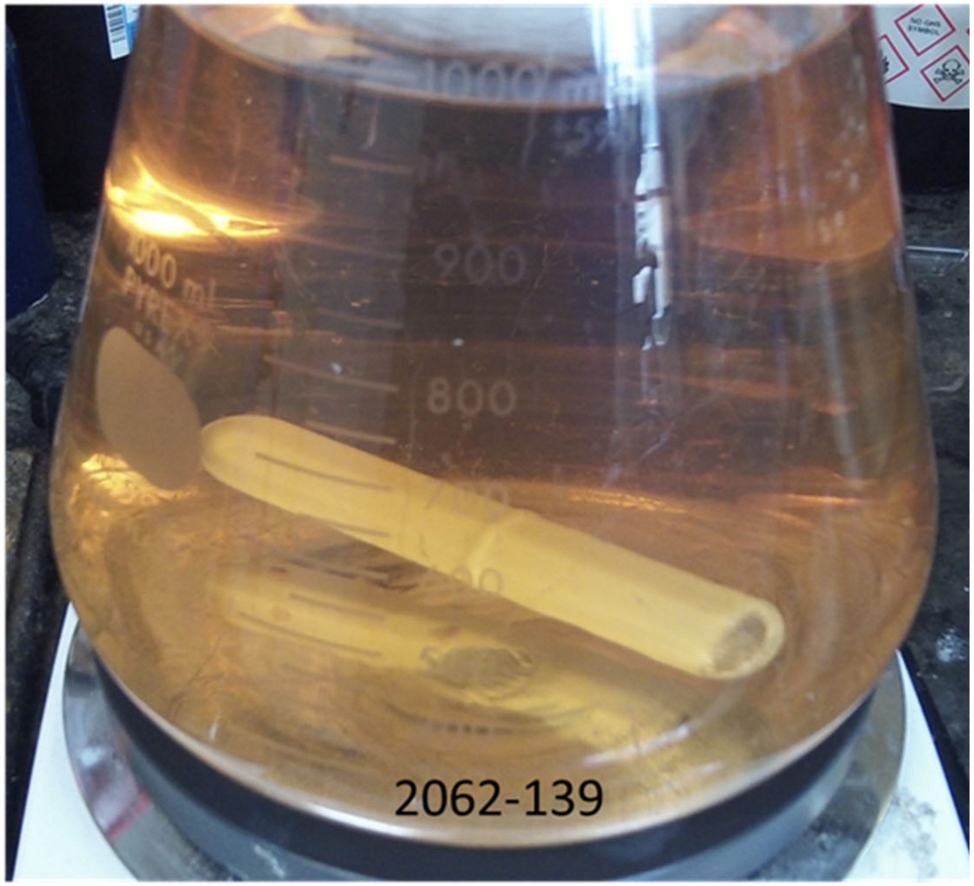


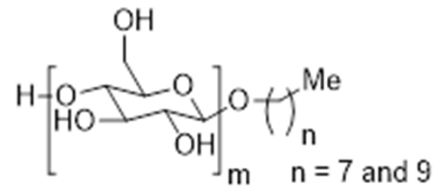
nozzle



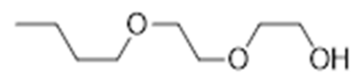
20 inch fire pan

RESULTS

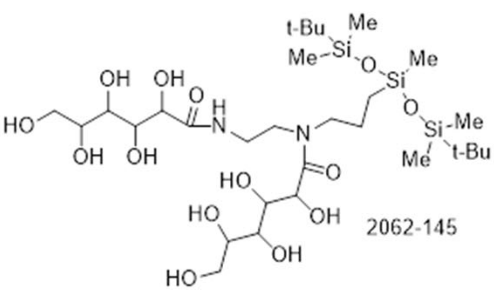




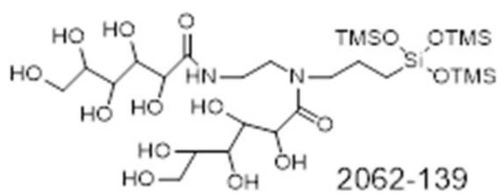
BASF Glucopon 225DK



DGBE



2062-145



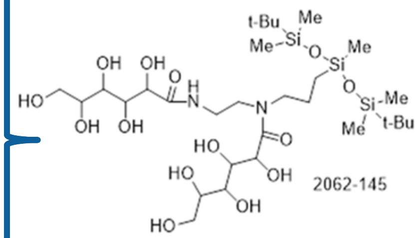
2062-139

RESULTS

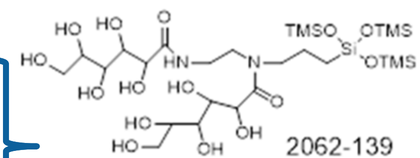
Agent and Specific Nozzle Hardware	Foam Expansion Ratio
AFFF w/o CAFS and with Spray Tip (ST)	2.98/1
AFFF w/ CAFS and ST	3.09/1
145/225DK/DGBE w/o CAFS and w/ ST	2.29/1
145/225DK/DGBE w/ CAFS and ST	2.58/1
225DK/DGBE w/ CAFS and ST	2.31/1

RESULTS F24 Jet Fuel Fire

Test Number	Agent	Nozzle type	Agent Flow Rate (GPM)	90% out (Sec.)	100% out (Sec.)	Application Rate (**AR**) *GPM/sq. ft.*	Application Density *AR*FF*	Room Temp °F Humidity (%)	Agent Temp °C
T1 Baseline	Mil Spec C6 AFFF 3%	FN025	0.153	12.5	15	0.07	0.017	102.1/12%	37.8
T2 Baseline	Mil Spec C6 AFFF 3%	FN025	0.173	6	7	0.079	0.009	104.8/12.2%	34.2
T3 Baseline	Mil Spec C6 AFFF 3%	FN025	0.153	6.5	9	0.07	0.01	89.2/21.7	32.8
T4 Baseline	Mil Spec C6 AFFF 3%	FN025	0.153	7	9	0.07	0.01	94.5/21.2%	34.2
ES1#1	145/225DK/DGBE	FN025	0.153	220	232	0.07	0.27	98.4/14.3%	34.8
ES1#2	145/225DK/DGBE	FN025	0.158	148	150	0.072	0.18	99.5/18.6%	33.5
ES1#3	145/225DK/DGBE	FN04	0.306	113	113	0.14	0.263	81.9/21.8%	28.1
ES1#4	145/225DK/DGBE	FN04	0.306	59	63	0.14	0.147	81.5/21.4%	28.1
ES1#5	145/225DK/DGBE	CAFS	0.153	150	158	0.07	0.184	93.8/21.2%	32.6
ES1#6	145/225DK/DGBE	CAFS	0.161	65	70	0.073	0.085	94.7/16.7%	32.6
ES1#7	145/225DK/DGBE	CAFS	0.161	40	51	0.073	0.062	95.5/15.4%	32.7
ES1#8	145/225DK/DGBE	CAFS	0.161	51	62	0.073	0.075	96.2/19.6%	33
ES2#9	225DK/DGBE	CAFS	0.161	0	0	0.073	0.324	86.9/29.3	30.5
ES2#10	225DK/DGBE	CAFS	0.161	0	0	0.073	0.324	90.6/29.6	30.5
ES4#15	145/2062-200/225DK/DGBE	CAFS	0.161	0	0	0.073	0.292	95.0/17.1	32.3
ES4#16	145/2062-200/225DK/DGBE	CAFS	0.161	0	0	0.073	0.292	96.8/14.9	32.3
ES5#17	139/225DK/DGBE	CAFS	0.161	9	11.7	0.073	0.014	95.2/14.1	33.7
ES5#18	139/225DK/DGBE	CAFS	0.161	9	10.3	0.073	0.012	99.5/14	33.8
ES5#19	139/225DK/DGBE	CAFS	0.153	8	10.5	0.07	0.012	99.8/14.9	33.8
ES5#20	139/225DK/DGBE	CAFS	0.161	11	12.09	0.073	0.014	100.1/16.1	33.9



2062-145



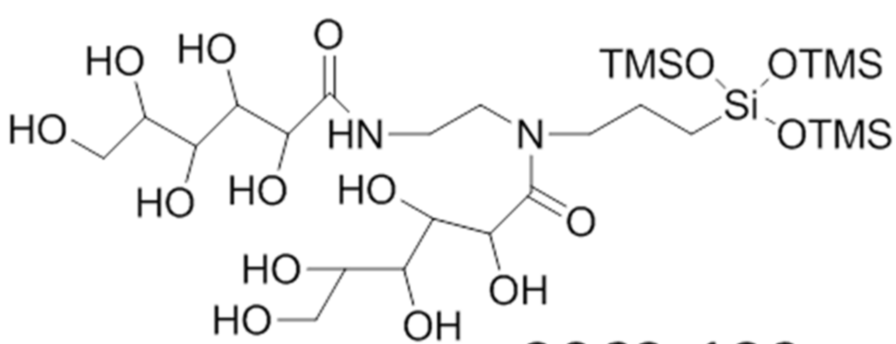
2062-139

RESULTS

Figure 1 Fire extinguishment experiment with 2062–139/225DK/DGBE in water. The mixture was able to extinguish the 20 square inch F24 pool fire in an average of 11 seconds.

Next Steps

- Scale up the synthesis of siloxane surfactant 2062-139
- Test 2062-139 versus gasoline pool fires
- Run pool fire test of 2062-139 at 28 ft2 level
- Understand hydrolysis mechanism and products of 2062-139
- Toxicity analysis of the new siloxane surfactants



2062-139

Key Points

- Hydrolysis resistance of siloxane improved by adding methyl groups
- Tert-Butyl dimethylsilanol convenient precursor hydrolysis resistant siloxanes
- Hydrolysis resistant siloxane surfactants were made from aldonic acid amides
- The siloxane surfactants from aldonamides were able to extinguish jet fuel pool fires

Publications

- Navy Case 210259US01 - Surfactants from Aldonic Acid Amides of Polyaminoalkylsiloxanes

Acknowledgements

Robin Nissan and Braxton Lewis SERDP

Eric Sievert, Jason Lint and Ross Davidson, Fire Science NAWC China Lake

WP18-1519: Synthesis and Testing of Hydrolysis Resistant Siloxane Surfactants as Additives for Pool Fire Suppression

Performers: Naval Air Warfare Center China Lake

NAVAIR

NAWC
Weapons Division
NAVAL AIR WARFARE CENTER

Technology Focus

- *Synthesis and testing of siloxane surfactants as additives to replace fluorinated AFFF in pool fire suppression*

Research Objectives

- *Identify water-resistant siloxane surfactants that can extinguish gasoline and jet fuel fires*

Project Progress and Results

- *Although water-resistant siloxanes were prepared, better activity in pool fire suppression was found with simple siloxanes*

Technology Transition

- *Scale-up of the lead siloxane surfactant 2062-139 for testing against gasoline at milspec 28 ft2*