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ENHANCEMENT OF FLUORINE-FREE FIREFIGHTING AGENTS FOR COMPRESSED AIR FOAM APPLICATIONS

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Contents

1. List of Figures.....	ii
2. List of Tables	iii
3. Abstract.....	3
4. Objective.....	3
5. Background.....	3
5.1. Candidate Foams for Evaluation.....	9
5.2. Additional Additives	9
6. Materials and Methods	12
6.1. Drain time.....	12
6.2. Surface Tension (SFT) and Interfacial Tension (IFT)	13
6.3. Refractive index and pH.....	13
6.4. Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Biodegradability.....	13
6.5. Fire Testing	13
7. Results and Discussion	14
Drain Time and	22
7.1. Fire Testing – Low concentration	22
8. Conclusions and Implications for Future Research.....	26
9. Works Cited.....	27
10. Appendices.....	29
LIST OF ABBREVIATIONS AND ACRONYMS	29

1. List of Figures

Figure 1. Gelest product DMS-A11 and acidified with phosphoric acid in pH neutral conditions.	5
Figure 2. A foaming surfactant made with DMS-A11 and phosphoric acid in a phosphate buffer.	6
Figure 3. Gelest product MCR-A11 and acidified with phosphoric acid in pH neutral conditions.	7
Figure 4. Gelest product SIA0604.5 and acidified with phosphoric acid in pH neutral conditions.	8
Figure 5. Gelest product DMS-N12 and acidified with phosphoric acid in pH neutral conditions.	9
Figure 6. Trisiloxane-(poly)ethoxylate,, a super spreader known as Silwet-L77.	10
Figure 7. Aluminum 2-ethylhexanoate, a fuel-thickening agent.	10
Figure 8. Triethanolamine Stearate	11
Figure 9. Alginic Acid	11
Figure 10. Synthesis of carboxylato-alumoxane with boehmite and gluconic acid.	12
Figure 11. Twenty-five percent drain time for Avios Green and BioEx with additives added individually.	15
Figure 12. Surface tension for Avios Green and BioEx with additives added individually.	15
Figure 13. Interfacial Tension of Avios Green and BioEx with additives added individually.	16
Figure 14. Refractive index for Avios Green and BioEx with additives added individually.	16
Figure 15. Hydrogen ion concentration (pH) for Avios Green and BioEx with additives added individually.	17
Figure 16. 90% Control time for Avios Green with formulations from table 2.	19
Figure 17. Total extinguishment time for Avios Green with formulations from table 2.	20
Figure 18. Burn-back time for Avios Green formulations from table 2.	20
Figure 19. 90% control time for BioEx.	21
Figure 20. Time to extinguish for BioEx.	21
Figure 21. Burn-back test for BioEx.	22
Figure 22. Drain time for Avios Green and BioEx with individual additives at 1%.	23
Figure 23. 90% control time for Avios Green.	24
Figure 24. Time to Extinguish for Avios Green.	24
Figure 25. Burn back time for Avios Green.	25
Figure 26. 90% control time for BioEx.	25
Figure 27. Time to extinguish for BioEx.	26
Figure 28. Burn back time for BioEx.	26

2. List of Tables

Table 1. Samples tested for Drain-time, SFT, and IFT.....	14
Table 2. Formulas used for testing Avios Green with multiple additives.	17
Table 3. Formulas used for testing BioEx with additives.....	18
Table 4. Results for formulations of Avios Green for biological oxygen demand, chemical oxygen demand and biodegradability.	18
Table 5. Results for BioEx for biological oxygen demand, chemical oxygen demand and biodegradability.	18
Table 6. Concentrate formulations with Avios Green and BioEx with 1% additives.	22

3. Abstract

Two commercial PFAS free suppression agents (PF_FSA) were blended with three novel poly dimethyl siloxane surfactants synthesized here at Tyndall AFB. The list of additives grew to include a siloxane super-spreader (Silwet L-77), a fuel-thickening agent (aluminum 2-ethylhexanoate), solid nanoparticles (silica and several forms of boehmite), foam stabilizer (triethanolamine stearate), and a hydrogel biopolymer (alginic acid).

These additives were tested with the PF_FSAs by MIL-PRF-24385F standard for drain time, surface tension, interfacial tension, refractive index, pH, biodegradability and fire testing. The fire testing was done on a small-scale fire test apparatus with compressed air foam. This allowed us to compare extinguishment time and burn back performance of the PF_FSA samples to determine the effect of the additives.

The siloxane surfactants did not enhance the fire suppressing performance. The siloxane super-spreader, solid nanoparticles, and the foam stabilizer did not either. However, the hydrogel biopolymer and the fuel-thickening agent showed a reduction in extinguishment time for one of the PF_FSAs. These materials may warrant further study.

4. Objective

Since the 1970s, the US Air Force (USAF) has been using aqueous film forming foam (AFFF) as a firefighting agent for the suppression of combustible and flammable liquid fuel fires, particularly in the area of aircraft rescue and firefighting (ARFF). Legacy C8 and C6 AFFF, however, contains per- and polyfluoroalkyl substances (PFAS)—primarily perfluorooctanoic acid (PFOA), perfluorooctyl sulfonate (PFOS) perfluorohexanesulfonate (PFHxS), and perfluorohexanoic acid (PFHxA)—fluorinated surfactant compounds that persist in the environment and are not readily degraded by natural processes. Additionally, PFOA and PFOS are classed as ‘emerging environmental contaminants’ because they do not have established regulatory standards, but research and historical studies have identified an associated risk for exposure. However, fluorinated surfactants do provide inherent advantages to AFFF fighting fires particularly in extinguishment times and long burn back times. The objective of the work proposed here is to design a PFAS-free fire suppression agent (PF_FSA) by using siloxane-based surfactants that are currently approved for use in medicine and cosmetics blended with other environmentally friendly ingredients. The findings will also be used to further expand the body of knowledge as to how to design PF_FSA.

5. Background

AFFF is a water-based firefighting agent used by military and civilian firefighting agencies to combat fires involving hydrocarbon fuels. Historically, AFFF concentrates contained long chain fluorosurfactants and per- and polyfluorinated substances (PFASs) including PFOA and PFOS. These chemicals present a risk to the environment and human health due to their persistence,

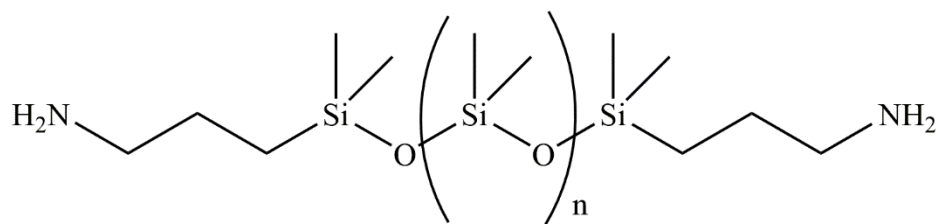
bioaccumulation, and potentially harmful properties (1). Even the new C6 (PFHxA and PFHxS based) AFFFs persist in the environment, and it is unknown what their long-term impact will be. The Air Force has recently placed a moratorium on any AFFF use except in emergencies—resulting in a mission critical limitation on firefighter training and testing of equipment. Commercial and research entities have developed numerous PF_FSA, however, none meet the firefighting performance criteria required in MIL-PRF-24385F needed for DoD approval. For the DoD to comply with environmental regulations and maintain long-term sustainability, alternatives to fluorinated surfactant foams with adequate firefighting performance are urgently needed. The firefighting community is understandably cautious with identifying a suitable replacement for AFFF, reluctant to sacrifice performance in lieu of environmental stewardship.

Preliminary testing in our facilities at AFCEC indicates that modified foam delivery techniques such as compressed air foam (CAF) significantly improves the performance of AFFF in burn back and extinguishment time (2). Under two ongoing ESTCP projects (WP19-5299 and WP20-5335), the Battelle/Air Force Civil Engineer Center (AFCEC)-Tyndall Air Force Base (AFB) Team has conducted Mil-SPEC testing, employing a standard air-aspirating nozzle, for more than 10 commercial-off-the-shelf (COTS) PF_FSA products, but none have so far met the fire performance standards, especially with respect to fire extinguishment time. To improve the performance, Battelle/AFCEC have demonstrated, at the MIL-SPEC scale, that CAF can provide a marked (40%) improvement (decrease) in extinguishment time, on average, and a substantial (25%) improvement (increase) in burn back time when compared to conventional, air-aspirating nozzles (3).

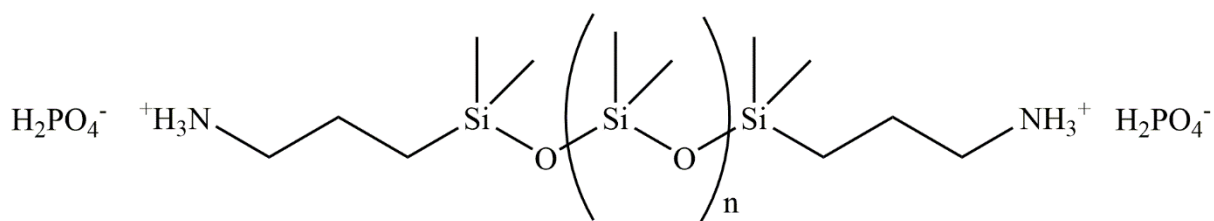
By adding a water-based film-forming siloxane surfactant formulation, we hypothesize that the firefighting performance of PF_FSA in combination with CAF can be strategically enhanced. The approach used in this study was: 1) development of a fluorine-free siloxane surfactant formulation that will be validated for fire suppression performance, and 2) evaluation of the formulation as an additive that enhances foam properties when used with CAF application technologies. It is important to clarify that the intent was not solely a new formulation of PF_FSA, but instead, a siloxane surfactant admixture (SSA) that can be blended with a COTS PF_FSA formulations in order to improve fire performance metrics. The SSA formulations were rationally designed to impart physical and chemical characteristics that improve foam stability, spreadability, and drain time, and thereby enhance fire performance (burn back and extinguishment times), as this is where most formulations fall short of MIL-SPEC requirements. The addition of SSA extends the use of CAF to new PF_FSA formulations that may not otherwise transition to field-testing.

The project was designed to identify environmentally friendly additives that may enhance the performance of PF_FSA. The PF_FSA that have been developed do not currently pass the MIL-PRF 24385F. Several fluorine free foams extinguish the fire but do not pass the burn back test.

The original proposal included amine-modified siloxane compounds that are available from Gelest Morrisville, PA. These compounds were combined with phosphoric acid in the presence of a phosphate buffer to form an amino phosphate cationic head group. The cationic head group, when combined with the non-polar siloxane portion of the molecule, will form a surfactant.



Gelest product DMS-A11



DMS-A11phosphate salt

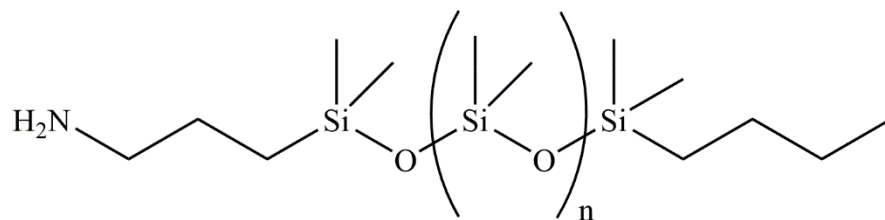
Figure 1. Gelest product DMS-A11 and acidified with phosphoric acid in pH neutral conditions.

Preliminary proof of concept tests of this approach indicated that the molecule synthesized as a surfactant produced a foam as was observed in Figure 2.

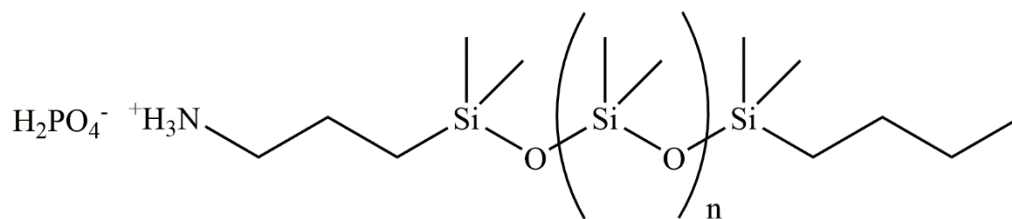


Figure 2. A foaming surfactant made with DMS-A11 and phosphoric acid in a phosphate buffer.

The success of a surfactant is determined by the ratio of polar and non polar portions of the molecule (4). To assure that we were getting a broad overview of the performance of this class of molecule, the same procedure of producing an aminophosphate headgroup on a siloxane bearing molecule was repeated with several siloxane tail lengths as seen in Figure 1, Figure 3, Figure 4, and Figure 5. All of these compounds were purchased from Gelest and used as received.

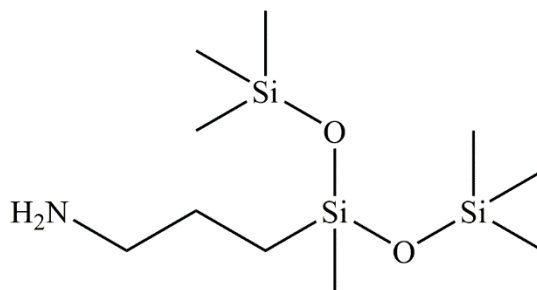


Gelest product MCR-A11

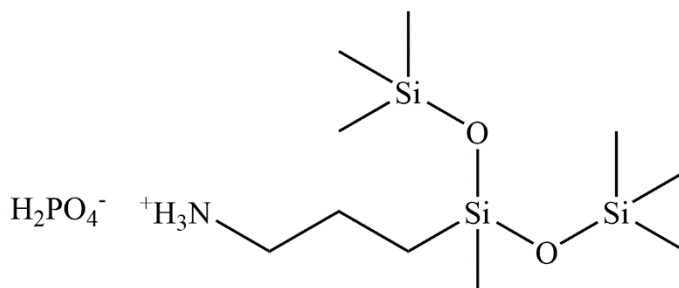


MCR-A11 phosphate salt

Figure 3. Gelest product MCR-A11 and acidified with phosphoric acid in pH neutral conditions.

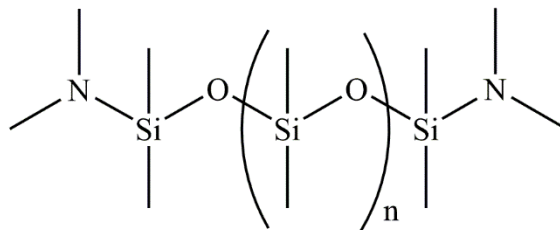


Gelest product SIA0604.5

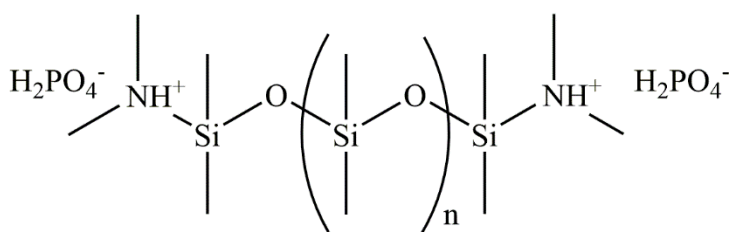


SIA0604.5 phosphate salt

Figure 4. Gelest product SIA0604.5 and acidified with phosphoric acid in pH neutral conditions.



Gelest product DMS-N12



DMS-N12 phosphate salt

Figure 5. Gelest product DMS-N12 and acidified with phosphoric acid in pH neutral conditions.

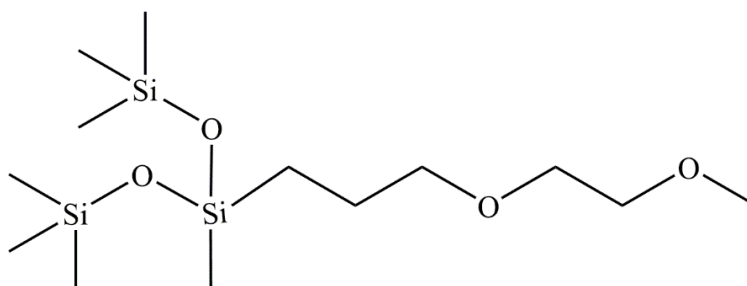
5.1. Candidate Foams for Evaluation

Two commercial off the shelf (COTS) PF_FSA, specifically BioEx and National Foam Avios Green foams were selected and evaluated with the additives made herein. These foams were selected as they performed well in parallel studies without additives and have low viscosity. High viscosity foams were not selected in this preliminary study, as there was concern that the additives that we were using would not incorporate well with a foam concentrate that is difficult to handle and will not stir. There was also concern that high viscosity foams may not be compatible with the CAF system. The testing of high viscosity foams can be revisited if any of the additives show promise.

5.2. Additional Additives

The original proposal included four siloxane-based surfactants, but we also included an assessment of alternative concepts such as fuel-thickening agents, solid nanoparticles, and spreading agents. Preliminary literature research indicated a beneficial effect of additives other than surfactants themselves. Additives can be used to enhance spreading, stabilize the lamellae, or form a gel with gasoline and prevent it from breaking through the foam. Thus, we added several new materials to our testing with COTS foams; including three additional additives:

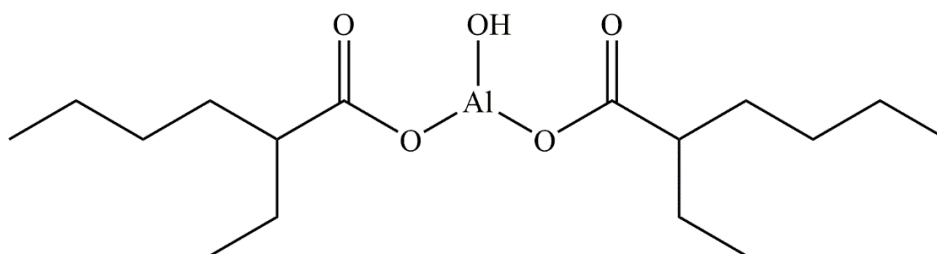
Silwet L-77[®] as seen in Figure 6 is a spreading agent used in the agriculture industry to enhance the delivery of fertilizers and pesticides. (5) This compound has shown to enhance the foamability and increase the drain time of sodium dodecyl sulfate (6). Trisiloxanes have also shown the ability to enhance spreading of aqueous solutions across hydrophobic substrates (7). It was thought that adding this compound could benefit the PF_FSA COTS foams that we were testing by enhancing their ability to spread across a fuel fire and reduce the surface tension between the aqueous surfactant mixture and the fuel.



Silwet L-77

Figure 6. Trisiloxane-(poly)ethoxylate,, a super spreader known as Silwet-L77.

The presence of the fuel is known to reduce the stability of the foam (8). Aluminum 2-ethylhexanoate (herein referred to as “Al soap” for brevity) is a fuel-thickening agent used to increase the viscosity and reduce the vapor pressure of gasoline (9) and (10). Though it has never been used in a firefighting foam before, we speculated that by adding this compound it would reduce or prolong the penetration of fuel vapors through the foam layer and thus increase the burn-back time.



Aluminium 2-ethylhexanoate
CAS 30745-55-2

Figure 7. Aluminum 2-ethylhexanoate, a fuel-thickening agent.

It has been noted that fluorine free foams are less stable in the presence of hydrocarbons than their fluorinated counterparts are (11). This is due to the fluorinated surfactants ability to form a film over the surface of the hydrocarbon fuel. In the oil industry, lightweight hydrocarbons are

used with surfactant foams to extract oil and gas. Hydrophilic silica nanoparticles are used to stabilize surfactant foams in the presence of these hydrocarbons (12), (13) and (14). We used silica nanoparticles (5-20 nanometers) to stabilize the lamella and provide durability in the presence of gasoline.

As the project progressed and there were indications that the siloxane surfactants were not yielding the desired results, we expanded the field of candidate additives to include; triethanolamine stearate (Figure 8). This compound is used in shaving cream to produce stable foams with small consistently uniform bubbles. Alginic acid (Figure 9) is a hydrogel biopolymer and thickening agent used to produce stable foams for medical applications.

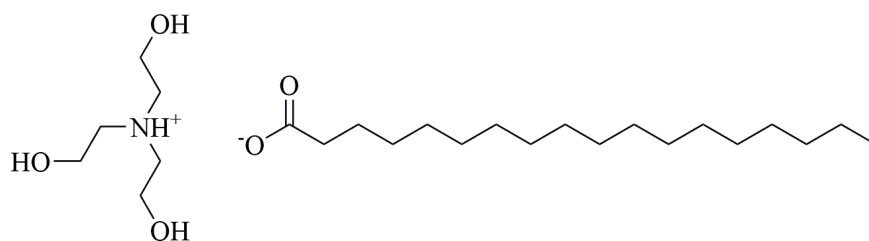


Figure 8. Triethanolamine Stearate

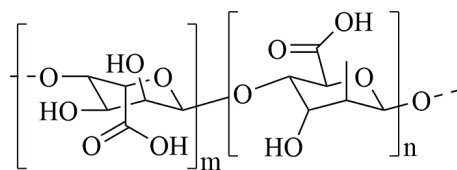


Figure 9. Alginic Acid

In addition to the unmodified silica nanoparticles, we also added two boehmite nanopowders, Catapal and Dispal (from Sasol Ltd.) These powders were used to stabilize the lamella of the foam and increase the drain time (14). These alumina powders were chosen for their ability to stay in suspension in plain RO water for an extended period without settling out at a concentration of 1%. We also made an additive that combined boehmite (Catapal-200) with a gluconic acid molecule to enhance the materials hydrophilicity. The synthesis was done in-house (Figure 10) to form a carboxylate-alumoxane (15). For brevity, we will refer to this compound as Gluconic Catapal.

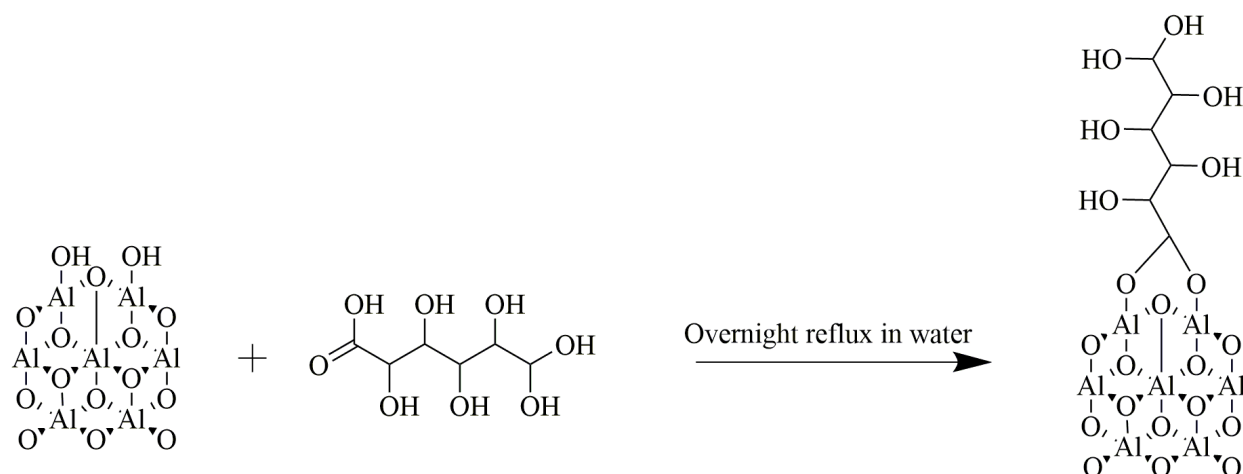


Figure 10. Synthesis of carboxylato-alumoxane with boehmite and gluconic acid.

6. Materials and Methods

The first Gelest product that was synthesized into a phosphate salt was DMS-A11 shown in Figure 1. The DMS-A11 was stirred in a phosphate buffer at a pH of 6.8 while dilute phosphoric acid (10% in DI water) was slowly dripped in. Care was taken to balance the pH as close to seven as possible. This was monitored by a pH meter. The same procedure was used to form the amine-siloxanes to a surfactant seen in Figure 3, Figure 4, and Figure 5.

When we attempted to produce a surfactant by titrating DMS-N12 (Figure 5) with phosphoric acid the result was a firm gel that was not soluble in water, or miscible with either of the foam concentrates that we were testing. We did not proceed with any further with this candidate formulation.

Standard laboratory processes referencing the corresponding MIL-SPEC standards were performed in accordance to ASTM International (West Conshohocken, PA); formerly American Society for Testing and Materials or EPA (Environmental Protection Agency, Columbus, OH). Standards Operating procedures were produced from Standard Methods for the Evaluation of Water and Waste Water (22nd Edition). All measurements were made using calibrated equipment.

For drain time, pH, refractive index, interfacial tension (IFT) and surface tension (SFT) the Avios Green and BioEx foams were mixed with one additive in a portion that did not reduce the foam quality. Each portion of 15 grams of foam was mixed with an additive and diluted to 500 grams with RO water to give a 3% solution.

6.1. Drain time

Samples were made by mixing ingredients with either Avios Green or BioEx individually. The test compound was weighed into a 500 mL bottle and the foam concentrate was added to bring the total mass up to 15 g. RO water was added to bring the total mass up to 500 g.

Drain times were measured by diluting the samples to 3% and blending 200ml in a blender for 30 seconds. A stopwatch was used to determine how long it took for 25% of the liquid to settle to the bottom of the blender.

6.2. Surface Tension (SFT) and Interfacial Tension (IFT)

Surface tension and interfacial tension were measured according to MIL-SPEC 4.7.4.1 and MIL-SPEC 4.7.4.2 respectively. A Krüss K100C tensiometer and the Wilhelmy plate method was used to measure dynamic surface tension (SFT). Samples ($n=3$) were prepared in 1L aliquots of 3% solutions (in DI water), as listed in ASTM D1331. IFT was measured according to MIL-SPEC 4.7.4.2. The samples were all run in triplicate ($n=3$) on 3% solutions (in DI water) using cyclohexane as the hydrocarbon substrate for standard comparison.

6.3. Refractive index and pH

Solution refractive indices were measured according to MIL-SPEC 4.7.1. Three drops of the sample were placed on a VeeGee C10 refractometer (VeeGee Scientific, Vernon Hills, IL) (25 °C). The line of refraction was determined by unaided visual inspection. Samples were tested in triplicate for each sample.

Hydrogen ion concentration (pH) was measured according to MIL-SPEC 4.7.3. The sample foam was placed in contact with glass electrode while stirring and measured against reference electrode, using Orion Star A211 pH meter (Fisher Scientific, Pittsburgh, PA), ($n=3$, 25 °C).

6.4. Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Biodegradability

When testing the biodegradability the foam formulations we tested them as they were intended to be used in the field. BOD was measured according to MIL-SPEC 4.7.12.3. Sample dilutions at 1%, 0.1%, 0.01% and 0.001% (wt:vol in DI water) made in accordance with Standard Methods 5210B were initially screened. A 5-day test was performed utilizing Hach BOD nutrient pillows (Hach Company, Loveland, CO). Assays were measured in triplicate and results were reported as an average with standard deviation. COD was measured according to MIL-SPEC 4.7.12.2. 50 mL samples of FFF concentrates were prepared at 1–3% concentration; COD was recorded in g/L using Hach TNT (test in tube) 824 Ultra high range COD kit on a Hach DR3900 Spectrometer. Biodegradability was calculated from test data using the formula below.

BOD_{20}/COD

BOD_{20} is derived from the 5-day BOD results and COD, both expressed as mg/L.

6.5. Fire Testing

We used a scaled-down version of the 28 square foot fire test described in MIL-PRF-24385F section 4.7.13.1. The foam concentrate was mixed with water at 3% concentration in a five-gallon bucket. A hose leading to the compressed air nozzle was placed in the foam-water mixture and pumped at a rate of 80 mL/min. The liquid was mixed with compressed air set to 0.85 L/s. The CAF system was allowed to run until it stabilized. The expansion ratio was measured by filling a 1L cylinder for one minute. The volume of foam was divided by the flow rate; in this case, 80 mL/min, thus 800 mL of foam in one minute equals a 10:1 expansion ratio.

A pan, approximately 19 cm in diameter and 12 cm deep was filled with 600 mL of water and 300 mL of ethanol free gasoline. The gasoline was ignited and allowed to burn for 30 seconds before the pan was slid under the flowing CAF nozzle. The time to gain 90% control over the fire and the time to extinguish were recorded. The burn-back pan was approximately 4 cm in diameter. It was filled with approximately 5-10 mL of gasoline and ignited. The flaming fuel was dropped into the extinguished fuel/foam mixture and the time to reignite the fuel pan was recorded. All fire testing was done in triplicate.

7. Results and Discussion

Table 1. Samples tested for Drain-time, SFT, and IFT.

500 mL bottle		
Avios Green (15 g)	Control	
Avios Green (15 g)	silwet (500 uL)	3%
Avios Green (15 g)	SiNPs (0.5 g)	3%
Avios Green (15 g)	Al soap (0.75 g)	5%
Avios Green (15 g)	DMS-A11 (1.5 g)	10%
Avios Green (15 g)	MCR-A11 (1.5 g)	10%
Avios Green (15 g)	SIA0604.5 (1.5 g)	10%
BioEx	plain BioEx	
BioEx (15g)	silwet (500 uL)	3%
BioEx (15g)	SiNPs (0.5 g)	3%
BioEx (15g)	Al soap (0.75 g)	5%
BioEx (15g)	DMS-A11 (1.5 g)	10%
BioEx (15g)	MCR-A11 (1.5 g)	10%
BioEx (15g)	SIA0604.5 (1.5 g)	10%

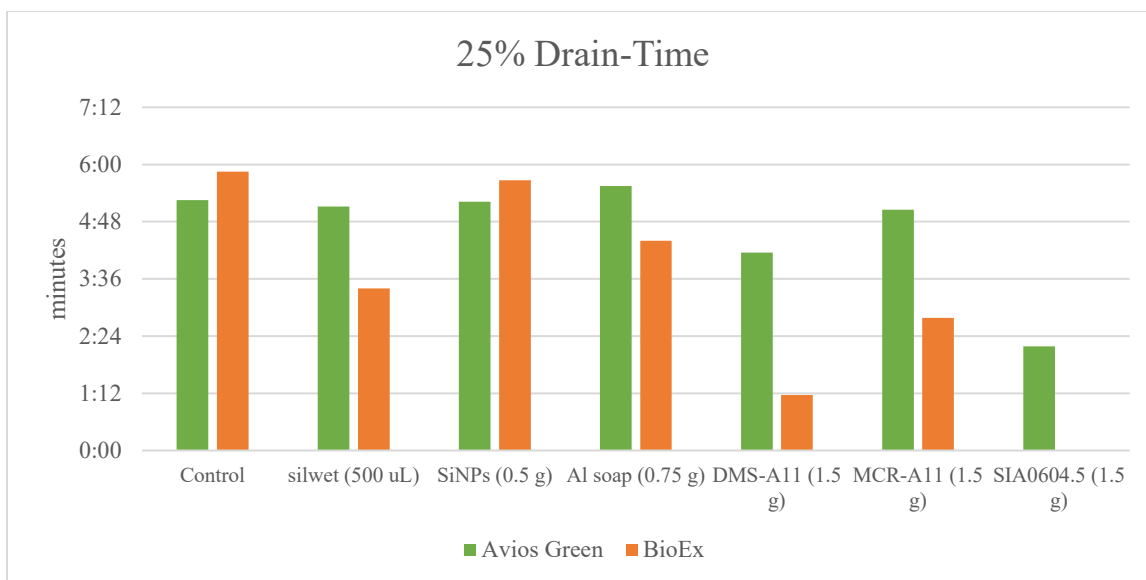


Figure 11. Twenty-five percent drain time for Avios Green and BioEx with additives added individually.

In Figure 11, the drain time of BioEx foam was adversely affected by all of the siloxane compounds including Silwet L-77. The Avios Green maintained a drain time similar to the control except when mixed with DMS-A11 and SIA0604.5

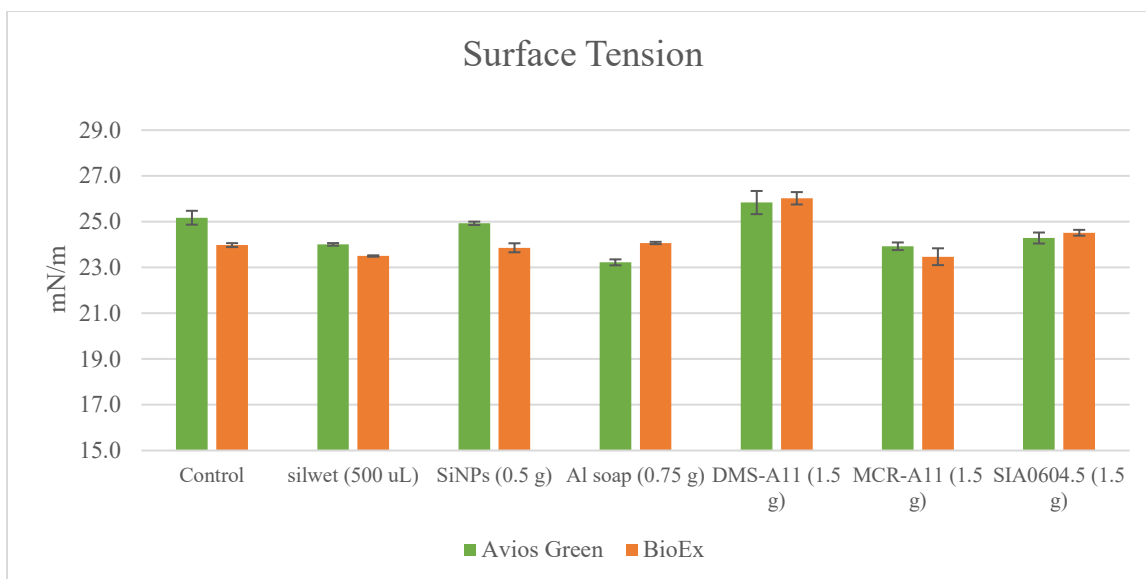


Figure 12. Surface tension for Avios Green and BioEx with additives added individually.

Figure 12 data indicates that the surface tension was minimally affected by the additives.

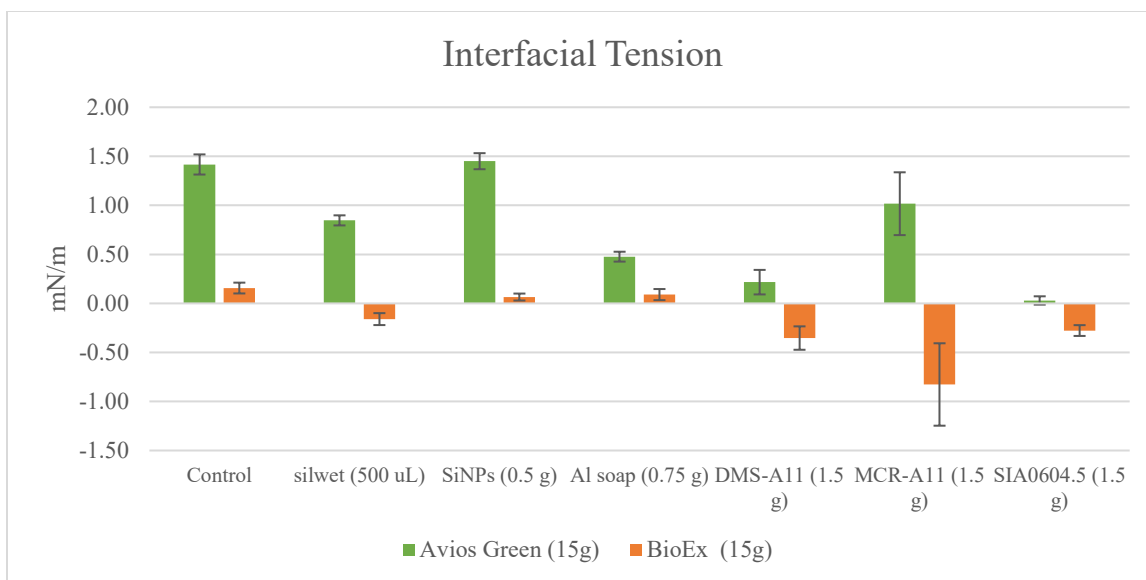


Figure 13. Interfacial Tension of Avios Green and BioEx with additives added individually.

The data from the interfacial tension tests in Figure 13 showed reduced values for several additives, most notably siloxane containing additives including Silwet L-77. It is not clear why negative values were obtained for interfacial tension. The test was repeated after recalibrating the instrument and retesting the control and confirmed that the negative values were accurate.

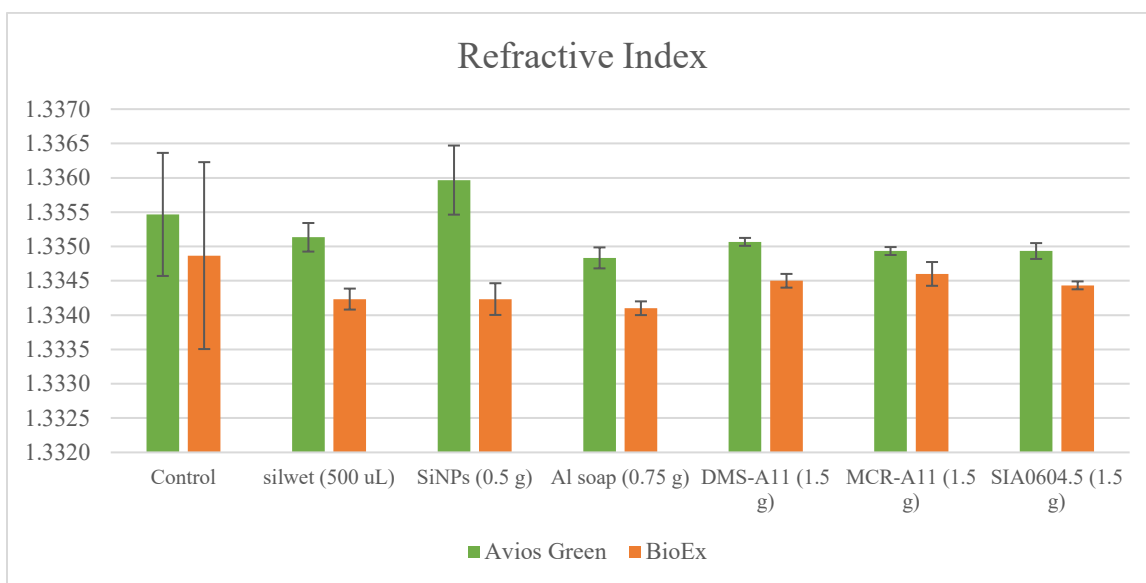


Figure 14. Refractive index for Avios Green and BioEx with additives added individually.

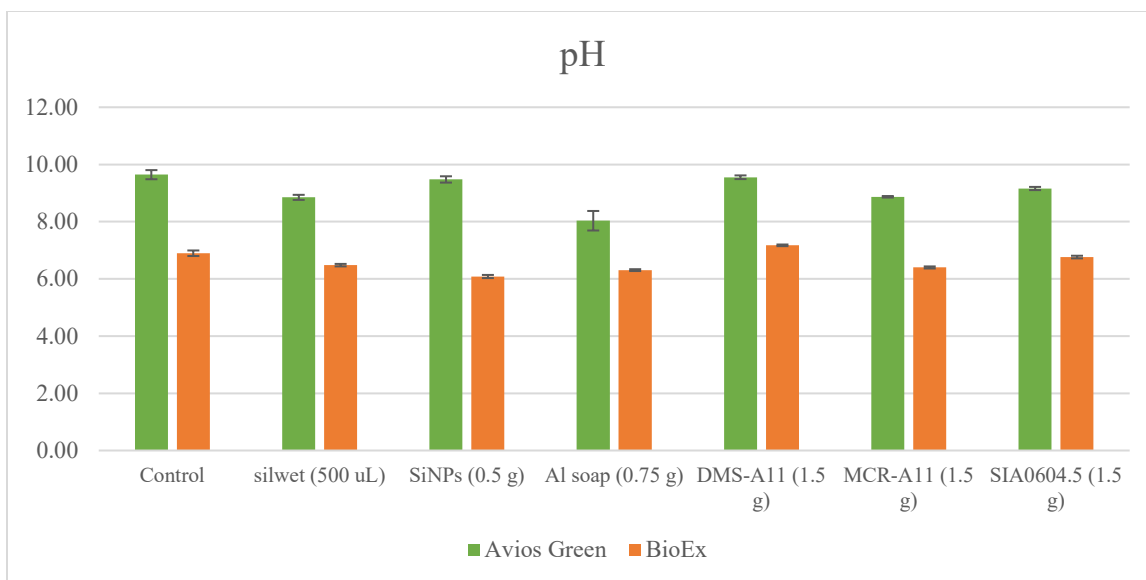


Figure 15. Hydrogen ion concentration (pH) for Avios Green and BioEx with additives added individually.

Overall, the BioEx had a lower pH value (6.9 for BioEx versus 9.64 for Avios Green control samples) Please note that the pH values for both control foams are outside of the range allowed in MIL-PRF-24385, which states that they must be between 7.0 and 8.5.

Table 2. Formulas used for testing Avios Green with multiple additives.

		Silwet L-77 (1%)	Al Soap (5%)	SiNPs (1%)	Siloxane Surfactant (10%)	Avios Green (g)
KMS11122020O	750 g total	7.5 g	37.5 g	7.5 g	75 g DMS-A11	622.5 g
KMS11122020P	750 g total	7.5 g	37.5 g	7.5 g	None	697.5 g
KMS11122020Q	750 g total	7.5 g	37.5 g	7.5 g	75g MCR-A11	622.5 g
KMS11122020R	750 g total	7.5 g	37.5 g	7.5 g	75 g SIA0604.5	622.5 g
Avios Green Control	750 g total	0 g	0 g	0 g	0 g	750 g

The formulas outlined in Table 2 were used to test BOD, COD, 90% control time, extinguishment time and burn back time for Avios Green. The percent of the additive relative to the base PF_FSA are given in the top row.

Table 3. Formulas used for testing BioEx with additives.

		Silwet L-77 (1%)	Al Soap (5%)	SiNPs (1%)	Siloxane Surfactant (10%)	BioEx (g)
KMS11122020S	750 g total	7.5	37.5	7.5	75 g DMS-A11	622.5
KMS11122020T	750 g total	7.5	37.5	7.5	None	697.5
KMS11122020U	750 g total	7.5	37.5	7.5	75g MCR-A11	622.5
KMS11122020V	750 g total	7.5	37.5	7.5	75 g SIA0604.5	622.5
BioEx control	750 g total	0 g	0 g	0 g	0 g	750 g

The formulas outlined in Table 3 were used to test BOD, COD, 90% control time, extinguishment time and burn back time for BioEx.

Table 4. Results for formulations of Avios Green for biological oxygen demand, chemical oxygen demand and biodegradability.

	BOD20	COD	BOD/COD	Type 3	Result
KMS111220-O	4248,593	888,300	4.782835	0.65	FAIL
KMS111220-P	9040,000	1,036,000	8.725869	0.65	FAIL
KMS111220-Q	1883,772	858,000	2.195539	0.65	FAIL
KMS111220-R	31,848	903,300	0.035258	0.65	PASS
Avios Green Control	263,761	984,000	0.26805	0.65	PASS

Table 5. Results for BioEx for biological oxygen demand, chemical oxygen demand and biodegradability.

	BOD20	COD	BOD/COD	Type 3	Result
KMS111220-S	82,929	575,300	0.14415	0.65	PASS
KMS111220-T	119,500	485,000	0.246392	0.65	PASS
KMS111220-U	87,961	500,000	0.175922	0.65	PASS
KMS111220-V	no data	no data	no data	no data	no data
BioEx control	118,871	378,600	0.313976	0.65	PASS

Sample V was not tested since it did not produce a foam.

Samples from Table 2 and Table 3 were mixed on November 12 2020 but were not fire tested until March 3 2021. The longer they sat in the lab the less foam they produced when shaken. This gradual degradation occurred over the course of four months. We speculate that the siloxane surfactants were hydrolyzing since we did not observe this phenomenon with sample P or T. Still, when the foam concentrates were diluted to 3% and used in the CAF nozzle, all of the samples except KMS11122020R reached the target expansion ratio of 10:1.

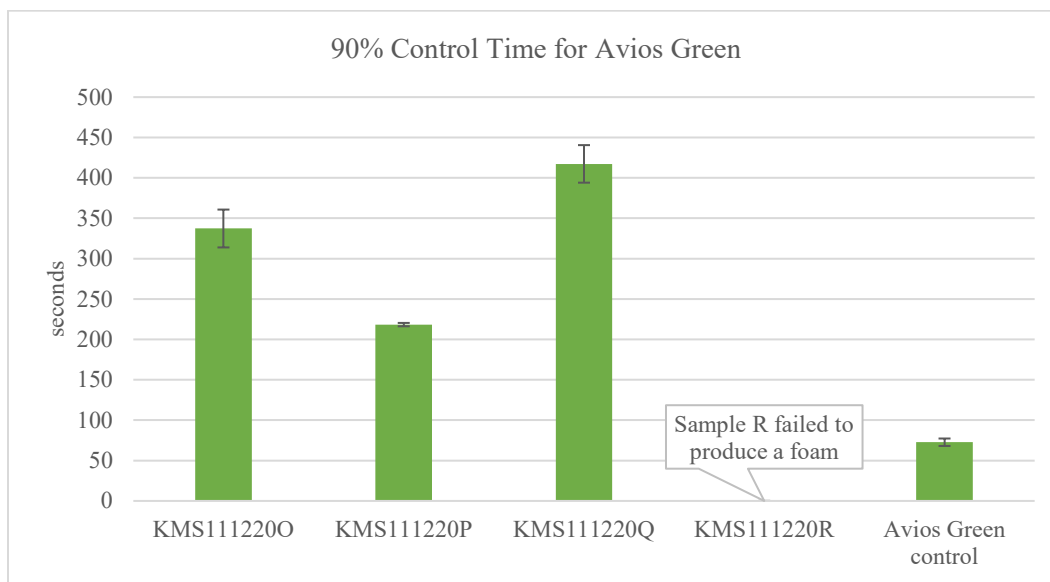


Figure 16. 90% Control time for Avios Green with formulations from table 2.

All of the samples tested in this experiment took significantly longer to suppress the fire than the control.



Figure 17. Total extinguishment time for Avios Green with formulations from table 2.

All of the samples tested in this experiment took significantly longer to extinguish the fire than the control.

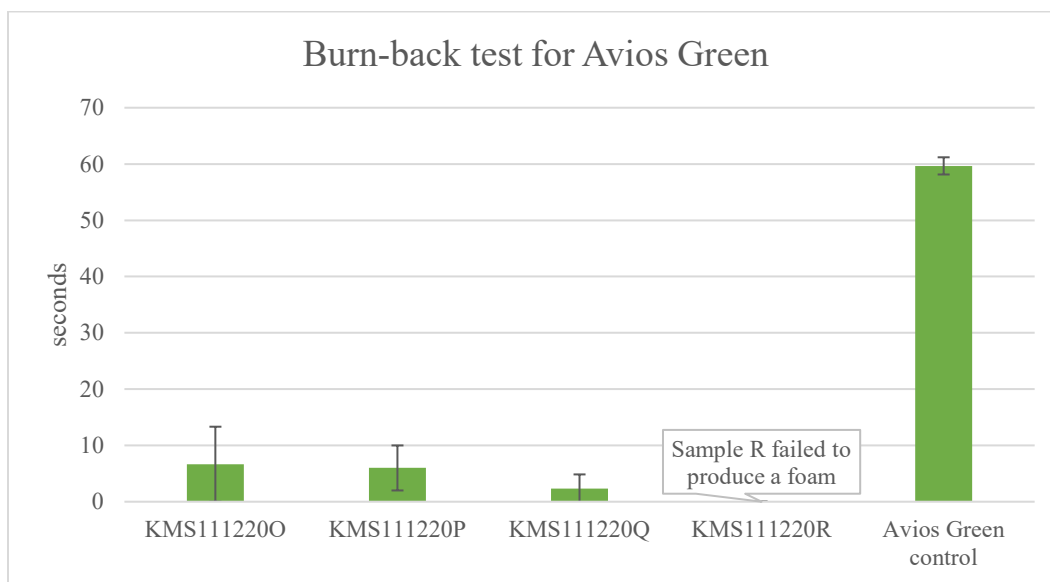


Figure 18. Burn-back time for Avios Green formulations from table 2.

The Avios Green control kept the fire suppressed for one minute. All of the samples tested had a shorter burn-back time than the control

As is apparent from the data, the additives used in the formulations were unsuccessful. Samples O, Q, and R contain siloxane-based surfactants and had the worst performance. Sample P did not have a siloxane-based surfactant but performed worse than the baseline, Avios Green. The

results are consistent and conclusive. The chosen siloxane based surfactants did not enhance the firefighting capabilities of Avios Green.

Samples that showed no improvement after 5 minutes were snuffed out. If the test were allowed to continue, all of the gasoline would burn off at approximately seven minutes.

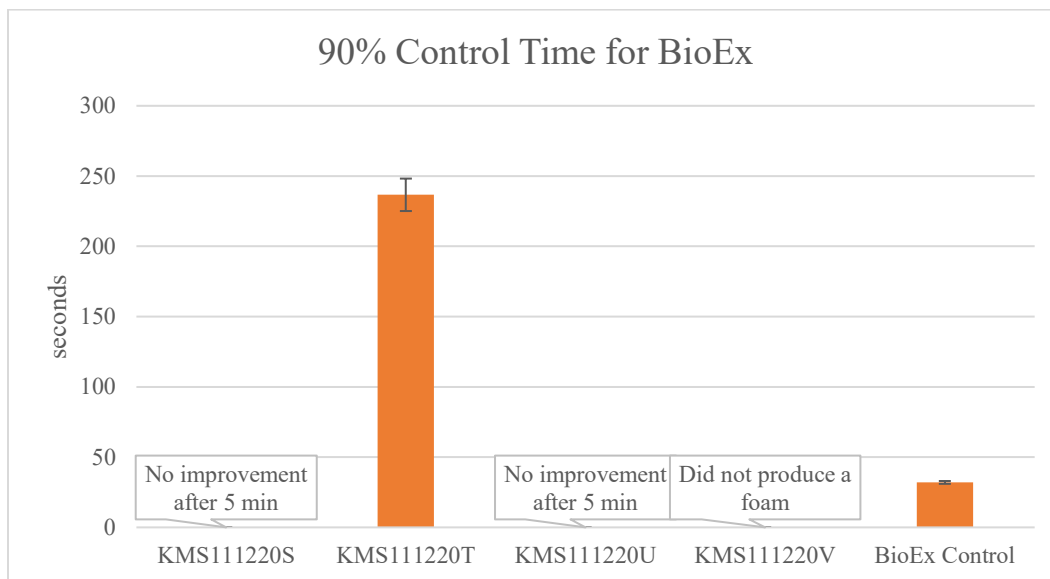


Figure 19. 90% control time for BioEx.

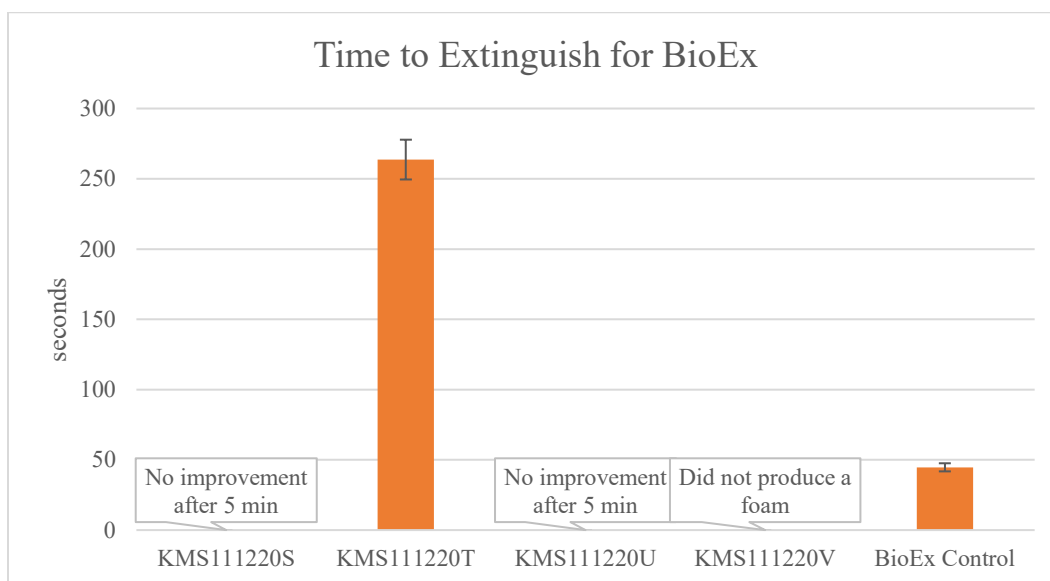


Figure 20. Time to extinguish for BioEx.

Sample T was the only foam that extinguished the fire at all. It was also the only sample that did not have a siloxane surfactant. Sample S (DMS-A11) and U (MCR-A11) were snuffed out after five minutes. Sample V (SIA0604.5) was not tested since it did not produce a foam.

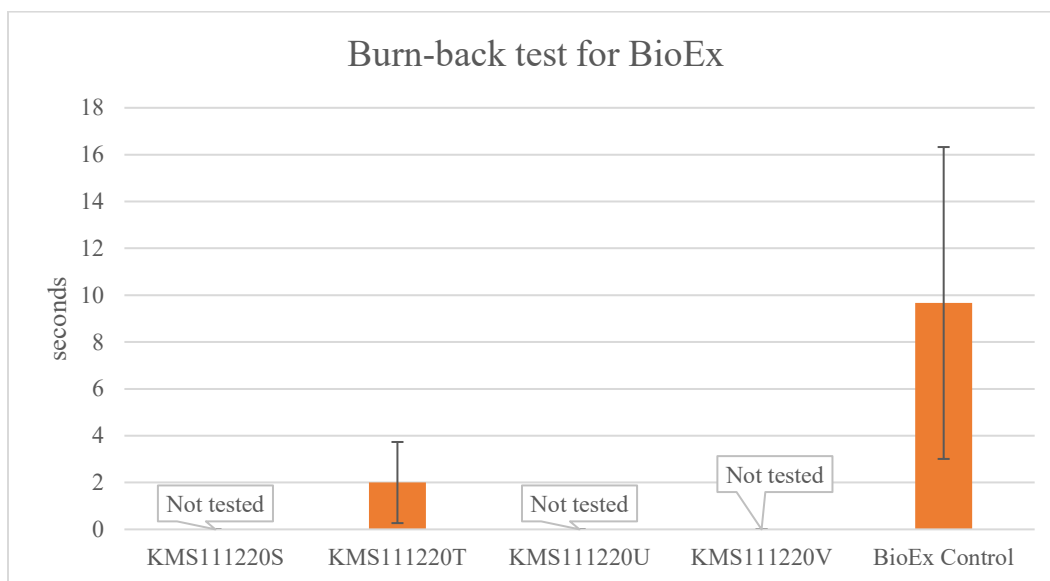


Figure 21. Burn-back test for BioEx.

Sample S, U, and V do not have a burn back data point since the fire had to be snuffed out.

7.1. Drain Time and Fire Testing – Low concentration

Since the fire testing done on the mixtures of the previous materials did not improve the performance of the firefighting foams, the second round of testing focused on drain time and fire performance with the components added individually and at lower concentrations. We did not retest the SIA0604.5 additive. Several additional candidate materials were also added. The concentrates were mixed with 1% of the additive into the foam concentrate and then diluted to 3% with water.

Table 6. Concentrate formulations with Avios Green and BioEx with 1% additives.

KMS03262021A	AviosGreen 495g	Dispal 23N-480	5g
KMS03262021B	AviosGreen 495g	Catapal-200	5g
KMS03262021C	AviosGreen 495g	Gluconic Catapal	5g
KMS03262021D	AviosGreen 495g	triethanolamine stearate	5g
KMS03262021E	AviosGreen 495g	alginic acid	5g
KMS03262021F	AviosGreen 495g	SiO ₂	5g
KMS03262021G	AviosGreen 495g	Silwet	5g
KMS03262021H	AviosGreen 495g	Al soap	5g

KMS03262021I	AviosGreen 495g	DMS-A11	5g
KMS03262021J	AviosGreen 495g	MCR-A11	5g
Avios Green Baseline		control	
KMS03262021K	BioEx 495g	Dispal 23N-480	5g
KMS03262021L	BioEx 495g	Catapal-200	5g
KMS03262021M	BioEx 495g	Gluconic Catapal	5g
KMS03262021N	BioEx 495g	triethanolamine stearate	5g
KMS03262021O	BioEx 495g	alginic acid	5g
KMS03262021P	BioEx 495g	SiO2	5g
KMS03262021Q	BioEx 495g	Silwet	5g
KMS03262021R	BioEx 495g	Al soap	5g
KMS03262021S	BioEx 495g	DMS-A11	5g
KMS03262021T	BioEx 495g	MCR-A11	5g
BioEx Baseline		control	

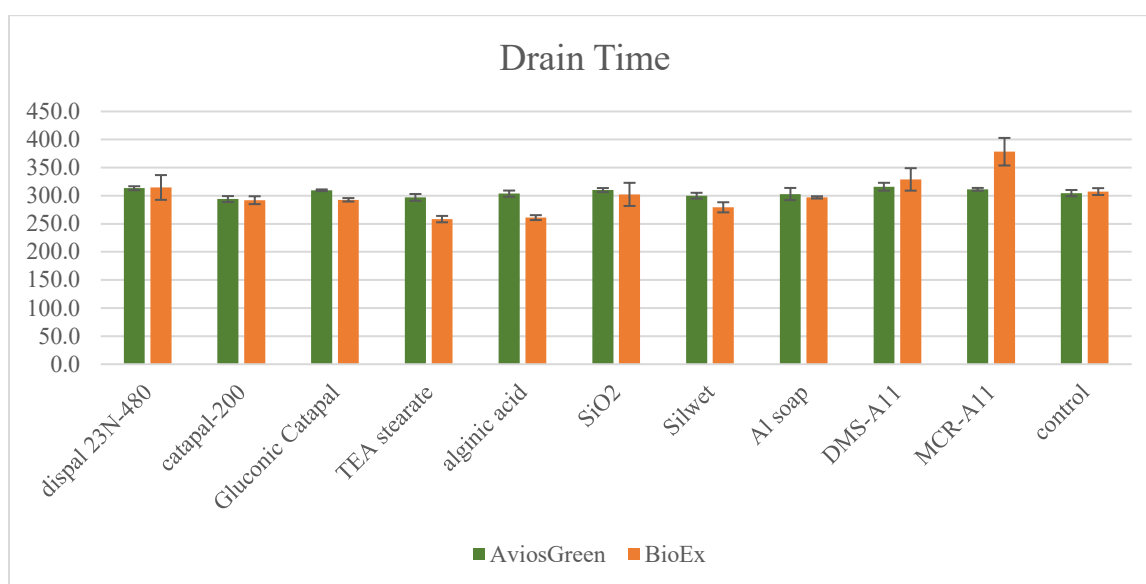


Figure 22. Drain time for Avios Green and BioEx with individual additives at 1%.

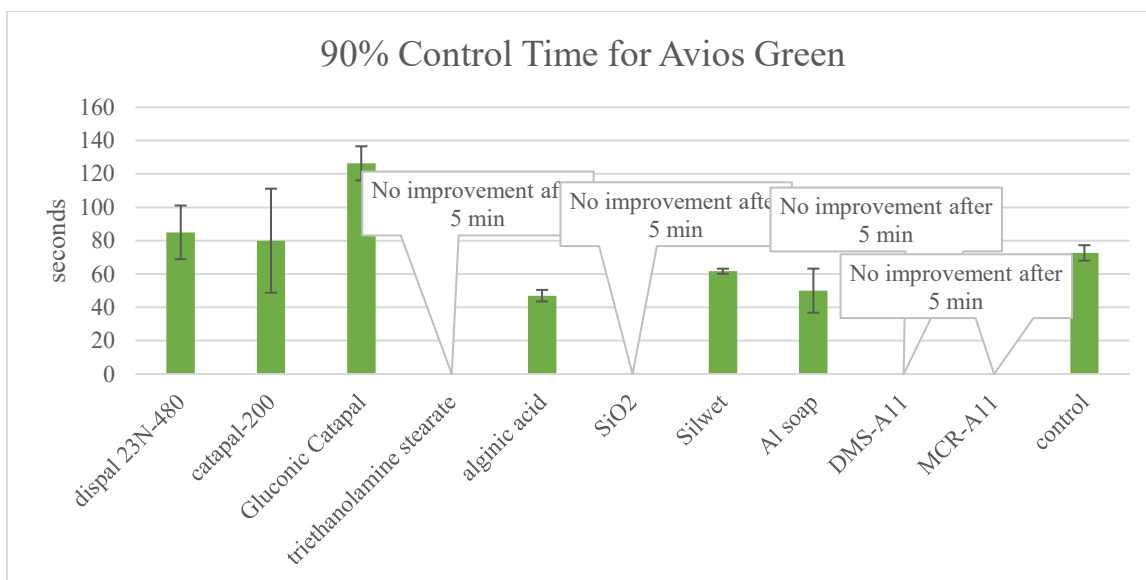


Figure 23. 90% control time for Avios Green.

In Figure 23, the sample with alginic acid showed the most improvement. The alginic acid reduced the extinguishment time relative to the Avios Green control. The Avios Green by itself took 125 seconds to extinguish the fire. By adding 1% alginic acid we were able to reduce this to 56 seconds.

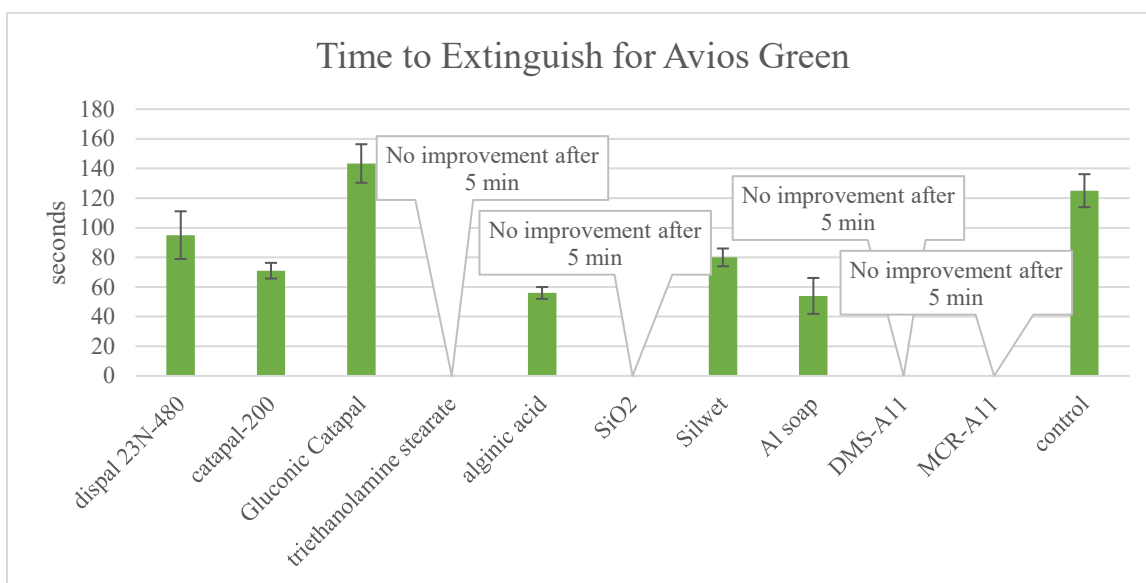


Figure 24. Time to Extinguish for Avios Green.

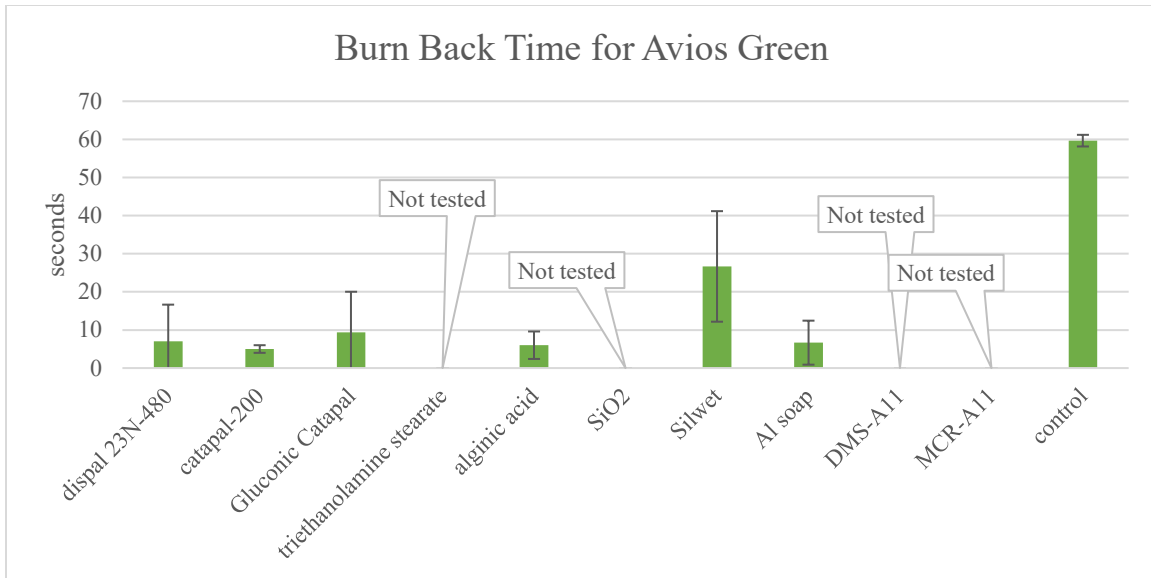


Figure 25. Burn back time for Avios Green.

The burn back times were longer for every additive tested against the Avios Green control. However, since the extinguishment times were shorter, there was less foam on the surface of the fuel when the burn back pan was lowered into the foam layer.

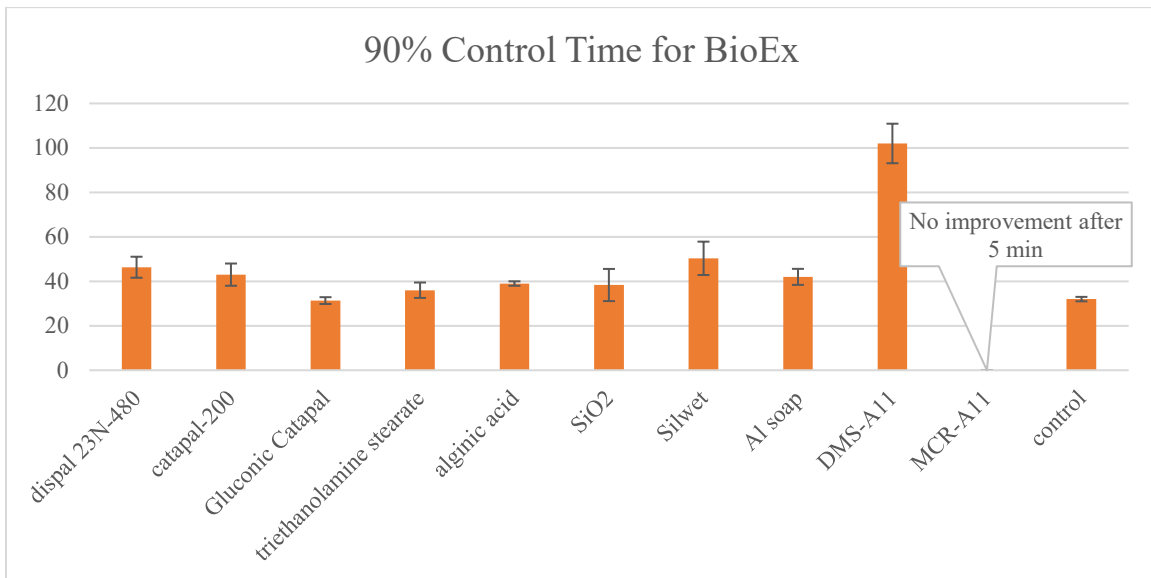


Figure 26. 90% control time for BioEx.

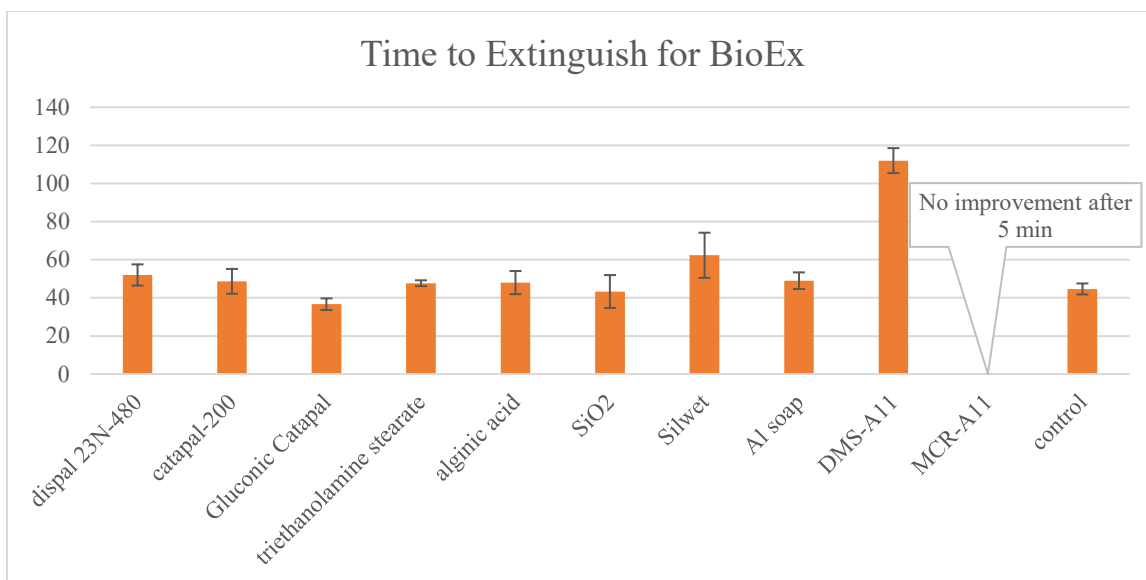


Figure 27. Time to extinguish for BioEx.

The 90% control time and time to extinguish performance for BioEx remained very similar to the control with all of the additives except DMS-A11 and MCR-A11. These were the siloxane surfactants and they made the BioEx performance worse.

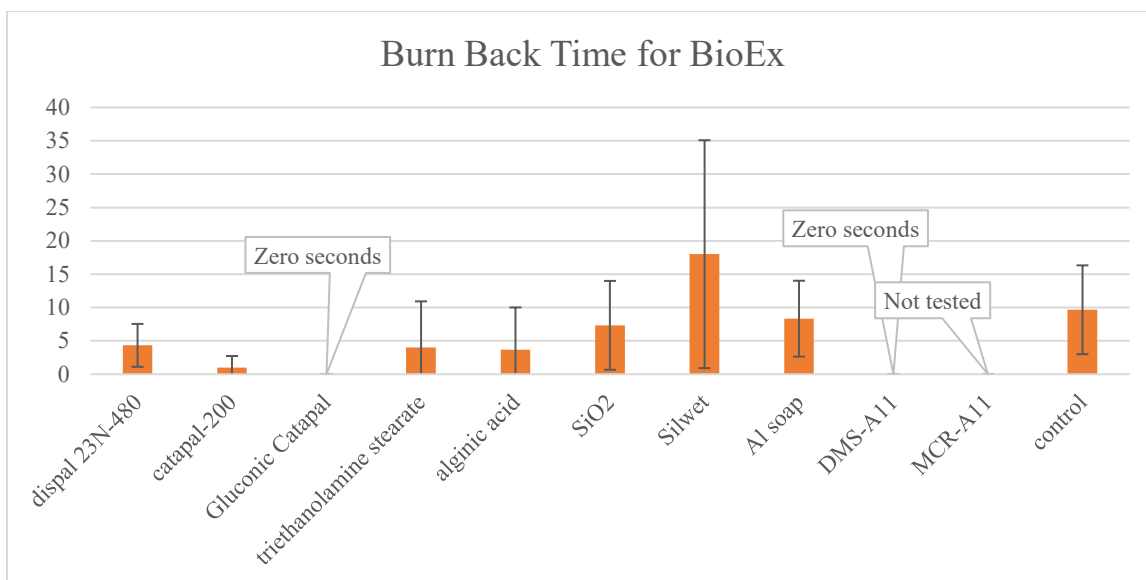


Figure 28. Burn back time for BioEx.

Silwet appears to increase the burn back time when blended at 1% with BioEx versus the BioEx control. However, it did not do so consistently.

8. Conclusions and Implications for Future Research

Our team here at Tyndall tested four amino phosphate siloxane surfactants. DMS-N12 produced an insoluble solid gel. SIA0604.5 did not produce a foam. MCR-A11 and DMS-A11 produced a

foam that hydrolyzed over the course of six months. The siloxane surfactants were revisited in a second fire test. They were tested at a lower concentration (1% versus 10%) and they were tested within two weeks of mixing with the base PF_FSA. They still did not enhance the ability of the COTS foams to extinguish a fire. In retrospect, this issue should have been addressed sooner since there is supporting literature (16) to indicate that hydrolysis of siloxanes could pose a problem during storage, especially at pH higher or lower than 7 or in the presence of water.

The Avios Green control took 125 seconds to extinguish a fire. When 1% alginic acid and 1% Al soap was mixed in, the time to extinguish was 56 and 54 seconds respectively. Future research should involve testing these additives at higher percentages.

The BioEx control extinguished the fire in 45 seconds. If some of the more promising additives were to be used at higher concentrations this may have been improved upon as it was with Avios Green.

Avios Green control took longer to extinguish the fire than the BioEx control but had a longer burn back time. Future research should focus on either enhancing the time to extinguish for Avios Green or lengthening the burn back time for BioEx.

There was an issue with the fire test that we would like to address before proceeding with any more samples. The fire pan is slid out from under the CAF nozzle immediately after the fire is extinguished. If a candidate foam extinguished the fire quickly, as was the case with the alginic acid samples, then there was less of a foam layer on top of the gasoline during the burn back portion of the test. This puts that sample at a disadvantage when evaluating its burn back capability. This test should be standardized to include 30 seconds of additional time to administer foam to the pan after the fire is extinguished.

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10. Appendices

LIST OF ABBREVIATIONS AND ACRONYMS

AFCEC/CXAE	Air Force Civil Engineer Center
AFFF	Aqueous Film Forming Foam
ASTM	American Society for Testing and Materials
BOD	Biological Oxygen Demand
CAF	Compressed Air Foam
COD	Chemical Oxygen Demand
COTS	Commercial Off the Shelf
DI	Deionized Water Ultra Pure 18MΩ
DoD	Department of Defense
EPA	US Environmental Protection Agency
FFF	Fluorine-free foam
FF_AFFF	Fluorine-free Aqueous Film Forming Foam
FF_FSA	Fluorine Free Fire Suppression Agent
IFT	Interfacial Tension
MIL-SPEC	Military Specification MIL-PRF-24385F(SH)
PF_FSA	PFAS Free Fire Suppression Agent
PFAS	Per- and Polyfluoroalkyl Substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate
RI	Refractive Index
RO	Reverse Osmosis purified water
SFT	Surface Tension
SSA	Siloxane Surfactant Admixture