



# TECHNICAL BULLETIN

## RE-HEALING™ Foam Fire Performance

### ***Introduction***


In September 2011, the Fire Fighting Foam Coalition (FFFC) issued an association newsletter entitled “AFFF Update”, which compared the firefighting performance of SOLBERG RE-HEALING RF6 (6%) fluorine-free foam concentrate, against two AFFF foam concentrates currently on the U.S. Military Specifications Qualified Products List (QPL), as contained in a report presented at the 2011 SUPDET Conference in Orlando, Florida by the U.S. Naval Research Laboratories (NRL). A copy of the complete U.S. Navy report is attached to this bulletin.

The Navy report is attached, because the FFFC selectively chose various quotations from the report, to include only quotations that would cast AFFF's in the best possible light, while at the same time not including quotations where SOLBERG RE-HEALING fluorine-free foam performed equal to or better than AFFF foams. Thus the purpose of this Technical Bulletin is to clarify the fire performance of RE-HEALING RF6 foam concentrate.

It is important to recognize that Solberg has never promoted RE-HEALING foams as Military Specification (MILSPEC) compliant, or meeting the fire performance criteria of the Military Specification. In addition, it is the official position of The Solberg Company that had this analysis been conducted between the two MILSPEC foam concentrates and a non-MILSPEC, commercial grade AFFF concentrates (available from any number of foam manufacturers), the fire test results would have been exactly the same. Non-Military Specification AFFF concentrates are not formulated for MILSPEC compliance, but do comply with other recognized industry standards, such as UL, EN, IMO, which is no different than for RE-HEALING RF6 foam concentrate.

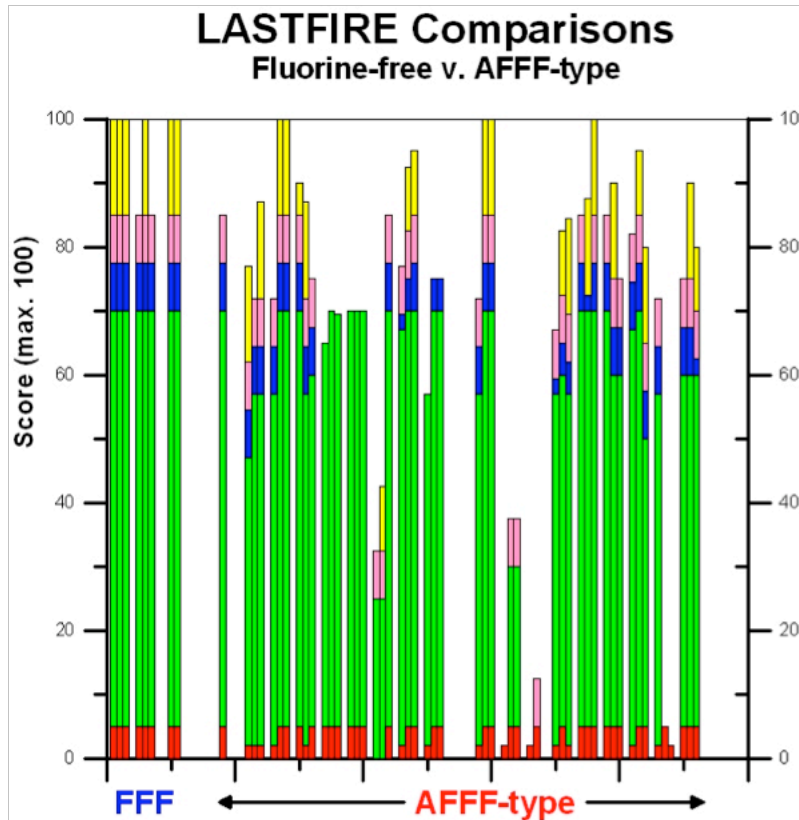
### ***RE-HEALING Foam Fire Performance***

SOLBERG RE-HEALING foam has been tested and accepted by numerous test agencies around the World. In addition, RE-HEALING foam has been tested to the LASTFIRE test protocol. LASTFIRE is a consortium of 16 oil companies, initiated in the late 1990s to review the risks associated with large diameter (greater than 40m [130 ft]) open top floating roof storage tanks. LASTFIRE stands for “Large Atmospheric Storage Tank Fires” and is managed by Resource Protection International (UK) on behalf of the oil companies.



***Solberg is a global company that is a one-stop resource for firefighting foam concentrates and custom-designed foam suppression systems hardware, offering both traditional and innovative firefighting foam technology. [www.solbergfoam.com](http://www.solbergfoam.com)***

The following chart is a summation of data collected during LASTFIRE testing on a full range of fluorinated AFFF concentrates, and fluorine-free concentrates, including fluorine-free concentrates available from SOLBERG. LASTFIRE evaluates the fire performance of firefighting foams, using a point scale, where 0 is a poor performing product, and 100 is the best score achievable.



A review of the LASTFIRE test results shows that AFFF foam concentrates are not superior to the firefighting performance of RE-HEALING foam. As this chart shows, there are numerous fluorine containing foams that are poor performing, achieving very low scores (some with single digit scores), while fluorine-free foams such as those from SOLBERG routinely out-performed their fluorinated counterparts, with several achieving perfect scores of 100.

We encourage our customers to read the full U.S. Navy report. In doing so the reader will see many examples of quotes where SOLBERG RE-HEALING foam compared very favorably to their fluorinated counterparts. There are numerous quotes from the U.S. Navy report, shown in this bulletin, that are positive to Solberg products including:

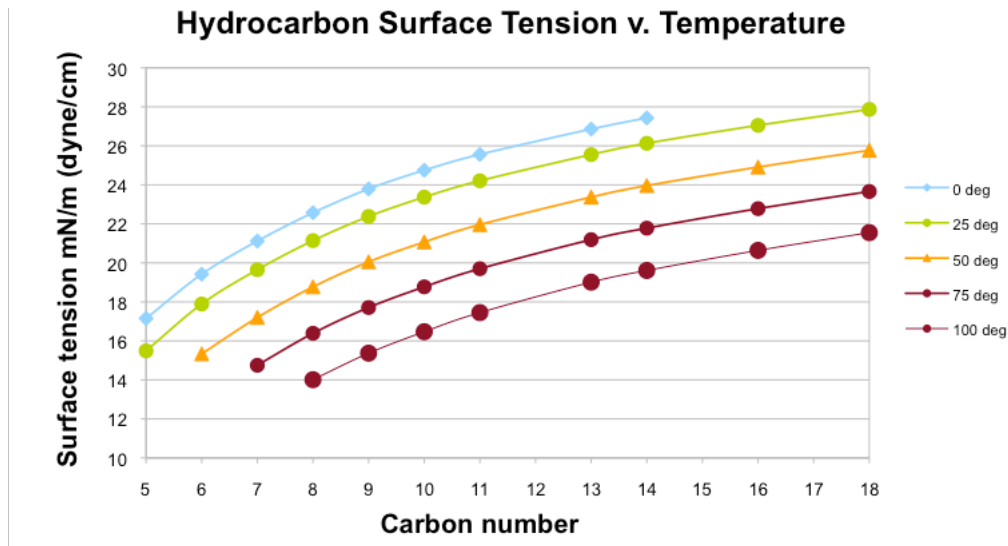
*“We observed that the AFFFs had diminished fire extinguishment performance with fire extinction times of 5 to 12 seconds longer in cases where they could not form film. The non-fluorinated foam performed as good as or better than the AFFFs on iso-octane.”*



One of the reasons for this performance is that not all fuels require film formation for extinguishment or vapour control. Additionally, AFFF foam concentrates have problems extinguishing or controlling low surface tension hydrocarbons such as gas condensate in the oil and gas industry (mainly  $=<C5$ ). AFFF's are also not effective on gasohol containing greater than 10% ethanol, or on fuels at elevated temperatures. As for the Military Specification, there is a revision under discussion to change the test fuel from gasoline to heptane, which will have an effect on the surface tension parameters for testing.

**Effects of Surface Tension vs. Temperature**

The following chart shows the effect of fuel temperature on the fuel's surface tension. In order for AFFF foam concentrates to form a film, the fuel surface tension must be greater than the AFFF surface tension – a positive spreading coefficient. This chart shows that at elevated temperatures, the fuel surface tension is less than the AFFF solution surface tension (a value of 17 dyne/cm is commonly referenced). In these cases of elevated fuel temperature, AFFF foam concentrates will not form a film as this leads to a negative spreading coefficient.



This statement in the U.S. Navy report summarizes one of the many advantages of SOLBERG RE-HEALING foam:

*“Fluorosurfactants, however, are environmentally persistent, and their use in firefighting foams has led to environmental concerns.”*

Table I from the U.S. Navy report is included below. SOLBERG RE-HEALING foams do not require elevated expansion levels for use, RE-HEALING foam provides excellent performance at low expansion rates. Please note, during the Navy testing expansion ratios are all in the 10:1 range, the same expansion rate as the tested fluorinated AFFF's.





**Table I: Expansion Ratios and 25% Drainage Times of Foams (Mixed at Nominal Strength in Fresh Water) and Tested According to MIL-F-24385F**

Foam	Expansion Ratio	25% Drain Time (s)
Foam X	9.0	262
Foam Y	9.4	360
Solberg (3M) RF6	10.3	>720 (no drainage observed)

*Note: commercial names of MILSPEC AFFF's removed*

It is important to note that the MILSPEC AFFF foam concentrates showed 25% drain times in the range of 262 seconds (4 minutes, 22 seconds) to 360 seconds (6 minutes). For SOLBERG RE-HEALING foam, after 12 minutes, no drainage was observed. Longer drain times lead to greater burn back resistance, which leads to greater firefighter safety.

The U.S. Navy report includes this statement, which is favorable to SOLBERG RE-HEALING foam:

*“The ability for film formation does not appear to increase burnback time”*

The report also includes the following information; addressing the issue of film formation of the tested AFFF agents.

*“On heptane, the \_\_\_\_\_ formed a film; the \_\_\_\_\_ was able to form a film after 60 seconds, but not after 5 seconds. Therefore, although it is technically film-forming on this fuel, a film might not be able to form on the time scale relevant to the extinguishment tests.”*

*“On iso-octane, the \_\_\_\_\_ did not form film. The \_\_\_\_\_ was able to prevent ignition in some, but not all trials. Therefore we consider the \_\_\_\_\_ AFFF as being marginal in terms of film formation for this fuel. Like the \_\_\_\_\_ on heptane, film formation may not occur on the time scale relevant to fire suppression.”*

*Note: commercial names of MILSPEC AFFF's removed*

This is important, as these two quotes call into question the premise that film formation is critical to control and extinguishment. According to the U.S. Navy report, film formation is not occurring on a time scale relevant to fire suppression!

*“MIL-F-24385F specifies a fire extinction time for a standard gasoline fire of no more than 30 seconds under these test conditions. Both of the MILSPEC qualified AFFFs met this requirement easily, extinguishing the fire in slightly over 20 seconds. The RF6 foam did not meet the 30 second requirement, although it did achieve a reasonably close value of 35 seconds.”*

We are including this quote, because as stated earlier, the company has never implied that SOLBERG RE-HEALING foam is MILSPEC compliant. We again restate that there are numerous AFFF commercial foam concentrates on the market that will also not achieve a 30 second extinguishment because, like SOLBERG RE-HEALING foam, they are formulated to a different test standard.



The report references other test scenarios where SOLBERG RE-HEALING foam performed well:

*“On iso-octane fuel, on which none of the foams were able to seal well, the AFFFs did not perform any better than the non-fluorinated RF6 foam.”*

From the U.S. Navy report, the below quote concurs with our earlier statement that AFFF foam concentrates are adversely affected by elevated fuel temperatures, and how elevated fuel temperature reduces the surface tension, which then hinders film formation:

*“Although not an objective of the test series, it was noted, particularly in the concurrent series of tests comparing gasoline and heptane as test fuels for the MIL-F-24385F protocol, that extinguishment performance of AFFFs on heptane fires was adversely affected by elevated fuel and ambient temperatures that were encountered during testing. Due to different temperature dependences of the surface and interfacial tensions of the AFFF/fuel system, the spreading coefficient tends to decrease slightly with temperature. Since film formation on heptane fuel is hampered by its low surface tension compared to gasoline (the spreading coefficient is close to zero [3]), even a slight further decrease with increasing temperature might hinder film formation.”*

Also from the Navy report, a quote showing SOLBERG RF6 exhibiting superior fire performance to the tested AFFF's:

*“For iso-octane, the non-fluorinated foam had shorter extinguishment times than the two AFFFs and was the only foam to achieve an extinguishment time under 30 seconds.”*

*“It is not surprising that the AFFFs tested show decreased performance on fires of fuels on which they cannot easily form film. Since their intended mode of operation assumes film formation, one would expect decreased performance in cases where film formation does not occur. The non-fluorinated, non film-forming RF6 foam, however, is designed to have mechanical properties of foam which compensate for the lack of film formation. In particular, the rate of water drainage is reduced and the foam has a lower yield stress. The shorter extinguishment times of iso-octane fires by the non-fluorinated foam compared to the AFFFs indicates that extinguishment performance in the absence of film formation can be improved by optimization of other properties of foam.”*

Lastly, the Navy report includes this conclusion, as number one:

The Navy report is attached, because the FFFC selectively chose various quotations from the report, to include only quotations that would cast AFFF's in the best possible light, while at the same time not including quotations where SOLBERG RE-HEALING fluorine-free foam performed equal to or better than AFFF foams. Thus the purpose of this Technical Bulletin is to clarify the fire performance of RE-HEALING RF6 foam concentrate.

*“Conclusions: For the AFFF foams which were intended to work via formation of an aqueous film, fire extinction times were lengthened considerably in cases where film formation was made difficult by the low surface tension of the fuel. For the non-filming fluorine-free foam, however, no such performance decrement was observed, and the fire extinction times on the lowest surface tension fuel were lower than for fuels with higher surface tensions, and within the 30 second time limit specified (on gasoline) by MIL-F-24385F.”*





In closing, attached is a copy of the U.S. Navy report, which served as the basis for the FFFC “AFFF Update” of September 2011. The Solberg Company is issuing this bulletin to provide a more balanced view of the content reported in the referenced newsletter.

The Solberg Company remains steadfast in its commitment to invest heavily in the continual progressive development of new generation of high performance firefighting foam concentrates, namely RE-HEALING RF foam concentrates, as RE-HEALING foam offers superior fire performance to AFFF under many scenarios, is environmentally responsible in that it does not contain ingredients that take decades to degrade, and RE-HEALING foam offers superior burn-back resistance and drainage times compared to AFFF foam concentrates.

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**AMERICAS**

THE SOLBERG COMPANY  
1520 Brookfield Avenue  
Green Bay, WI 54313  
USA  
Tel: +1 920 593 9445

**EMEA**

SOLBERG SCANDINAVIAN AS  
Radøyvegen 721 - Olsvollstranda  
N-5938 Sæbøvågen  
Norway  
Tel: +47 56 34 97 00

**ASIA-PACIFIC**

SOLBERG ASIA PACIFIC PTY LTD  
3 Charles Street  
St Marys NSW 2760  
Australia  
Tel: +61 2 9673 5300

## **Extinguishment and Burnback Tests of Fluorinated and Fluorine-free Firefighting Foams with and without Film Formation**

Bradley Williams,<sup>1</sup> Timothy Murray,<sup>1\*</sup> Christopher Butterworth,<sup>1\*</sup> Zachary Burger,<sup>1\*</sup> Ronald Sheinson,<sup>1†</sup> James Fleming,<sup>1</sup> Clarence Whitehurst,<sup>2</sup> and John Farley<sup>2</sup>

<sup>1</sup>Combustion Dynamics, Code 6185 and <sup>2</sup>Shipboard and Field Operations, Code 6186  
Navy Technology Center for Safety & Survivability, Chemistry Division  
Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375 USA

**Abstract:** The fire extinguishment and burnback performance of three foams were tested on four low flash point fuels: gasoline, commercial grade heptane, iso-octane (2,2,4-trimethylpentane), and methylcyclohexane. The final three fuels have flash points in a range between -9°C and -4°C, compared to gasoline which has a typical flash point of -40°C. Gasoline and heptane represent, respectively, the current and the possible future fuels for the MilSpec qualification test for AFFF. Iso-octane and methylcyclohexane were chosen because they have similar flash points but different surface tensions; AFFFs have difficulty forming film on iso-octane but can easily form film on methylcyclohexane. We observed that the AFFFs had diminished fire extinguishment performance with fire extinction times of 5 to 12 seconds longer in cases where they could not form film. The non-fluorinated foam performed as good as or better than the AFFFs on iso-octane. Significant differences were found between fuels in burnback performance (the time for fire to spread across a foam-covered pool). These fuel differences in burnback were consistent for all three foams studied, and did not correlate with fuel flash point or film formation. Other properties of the fuels, and their interaction with foam components, must be responsible for the differences in fire suppression performance. The rate of fuel passage through the foam layer measured in laboratory studies correlates with burnback performance.

\*NRL Student Temporary Employment Program

† Nova Research, Inc. and Sheinson Associates, LLC

## **Introduction**

Aqueous film-forming foam (AFFF) is widely used for fire protection against liquid fuel fires. AFFF is a type of low expansion foam, having an expansion ratio typically between 5-10. It is applied to a burning liquid pool and covers the fuel surface, inhibiting vaporization of the fuel and acting as a physical barrier between fuel and air. AFFF was initially developed for Navy aircraft carriers, and is also used extensively in civilian airports.

The film-forming property of AFFF is made possible by the presence of fluorosurfactants, which lower the surface tension enough to allow a water layer to form on top of the fuel surface. It is thought that the water layer contributes to fire extinguishment by inhibiting evaporation of fuel and percolation of fuel through the foam. Other types of surfactants are not able to achieve surface tensions as low as fluorosurfactants, and aqueous film formation has not been demonstrated for any fire fighting foams which do not contain fluorosurfactants.

Fluorosurfactants, however, are environmentally persistent, and their use in fire fighting foams has led to environmental concerns [1]. The extent to which film-forming ability is necessary for optimal fire suppression has major implications for future development of more environmentally friendly fire-fighting foams. If filming ability is critical in achieving good performance, then the only recourse for achieving the best performance is to search for fluorosurfactants which are more environmentally benign. If it is not so critical, then other options are open.

In the 2010 SUPDET, we compared AFFF behavior on fuels with flash points below and above ambient temperature. Here, we investigate the contribution of film formation to extinguishment. In a 28 ft<sup>2</sup> circular fire, following the U.S. DoD MilSpec [2] procedure, we compared two MilSpec-qualified AFFF formulations and a non-fluorinated non-film-forming foam, on fuels which have different surface tensions, so that the effect of film formation on fire extinguishment performance could be separated from other properties of AFFF.

## **Test Procedures and Materials**

Tests were performed at the Naval Research Laboratory's Chesapeake Bay Detachment test facility during July and August, 2010. The tests conducted for this ONR program were performed in conjunction with a series of tests for NAVSEA (the AFFF warrant holder), which compared AFFF performance on gasoline with commercial grade heptane, which is under consideration as a replacement fuel for gasoline in the AFFF MilSpec qualification tests. The conjunction of the two test series allowed additional comparisons to be made between fuels for the same AFFF formulations.

All fire tests described here were performed inside a large burn room, using a 28 ft<sup>2</sup> circular pan which is used in MIL-F-24385F [2] qualification tests. The tests used a ten second preburn time (the interval between lighting the fuel and commencement of foam application) and a 2.0 gallons/minute foam application rate. Both of these parameters are identical to the MIL-F-24385F testing protocol.



The only testing parameter that was changed from the MilSpec protocol, other than the fuels used, was the total time of foam application, prior to beginning the burnback test. The MIL-F-24385F protocol calls for a total foam application time of 90 seconds, including the time for fire extinguishment. For the fuels used in this test series, this length of foam application was found to produce an unreasonably long and highly variable burnback time. Therefore, the foam application time was reduced to 60 seconds.

In addition to conjunction with the field tests, laboratory measurements of surface tension were conducted using a Du Nuöy Ring tensiometer.

### **Fuels Tested**

The following fuels were used in the field tests.

*Gasoline* (non-ethanol containing, unleaded)

This is the fuel currently used for MIL-F-24385 qualification tests. It typically has a flash point near -40°C. The measured surface tension of this fuel at an ambient temperature of 23°C was 23.7 dynes/cm.

*Iso-octane* (2,2,4-trimethylpentane, 99% minimum, Chevron-Phillips)

This fuel has a very low surface tension (measured value of the fuel as tested was 18.7 dynes/cm at 23°C) and it is difficult for even MilSpec AFFFs to film on it. The flash point of this compound is -7°C.

*Methylcyclohexane* (MCH, 99% minimum, Chevron-Phillips)

This fuel has a relatively high surface tension (measured value of the fuel as tested was 23.6 dynes/cm at 23°C), so AFFFs will easily film on it. The flash point of this compound is -4°C.

*Heptane* (commercial grade, isomeric mixture, Shell)

This fuel is used for AFFF qualification under the UL testing protocol, and is being considered for use in the MIL-F-24385 testing. The sample used in the field tests had a measured surface tension of 20.0 dynes/cm at 23°C. The flash point of the material used (manufacturer's data for the lot) is -9°C.

### **Foams Tested**

Three foam formulations were used in testing. For all tests, the foam concentrate was mixed at its nominal concentration (6% for Type 6, 3% for Type 3) in fresh (tap) water.

*-National Foam (now sold by Kidde Fire Fighting) Aer-O-Water 6-EM:* A Type 6 AFFF concentrate (intended to be mixed at 6% concentrate and 94% water) which has been qualified against the MilSpec MIL-F-24385F.

*-Buckeye Fire Equipment Company BFC-3MS AFFF:* A Type 3 AFFF concentrate (intended to be mixed at 3% concentrate and 97% water) which has been qualified against the MilSpec MIL-F-24385F.

-Solberg (originally 3M) RF6 Foam: A non-fluorinated, and hence non-film forming, foam which NRL has previously tested. On gasoline it takes a slightly longer time for flame extinguishment than AFFF (about 40 seconds, compared to 30 seconds MilSpec requirement) [3]. Comparing the performance of this foam to that of the AFFFs on isooctane, on which none of the foams form a film, allows us to assess whether the AFFFs have other properties, besides film formation, that contribute to suppression.

**Table I: Expansion Ratios and 25% Drainage Times of Foams (Mixed at Nominal Strength in Fresh Water) and Tested According to MIL-F-24385F**

Foam	Expansion Ratio	25% Drain Time (s)
National Foam 6-EM	9.0	262
Buckeye BFC-3MS	9.4	360
Solberg (3M) RF6	10.3	>720 (no drainage observed)

Properties of the foams produced by the concentrates when discharged through the "standard" nozzle used in MIL-F-24385F testing have been measured in previous testing in our laboratory. The measurement procedure to determine the expansion ratio (foam volume/volume of liquid contained in the foam) and drainage time (time for 25% of the liquid contained in the foam to drain) of foams is specified in MIL-F-24385F. For the three concentrates mixed at their nominal concentrations in fresh water, the expansion ratio, and 25% drainage times measured according to this procedure are given in Table I. The minimum values required for qualification are an expansion ratio of 5:1 and a drain time of 150 seconds. All three foams used in this test series have similar expansion ratios near 10:1. The RF6 foam has a much slower drainage than the AFFFs, due to the presence of polysaccharides in the concentrate.

### Film Formation and Sealability Test Results

The ability of AFFF to form an aqueous film on a hydrocarbon pool is governed by the spreading coefficient [4]:

$$\text{Spreading Coefficient} = \sigma_{\text{fuel}} - \sigma_{\text{AFFF}} - \gamma_{\text{fuel-AFFF}}$$

where  $\sigma_{\text{fuel}}$  and  $\sigma_{\text{AFFF}}$  are the surface tensions of the fuel and the AFFF solution, respectively, and  $\gamma_{\text{fuel-AFFF}}$  is the interfacial tension between the two. The two surface tensions are on the order of 15-20 dynes/cm, while the interfacial tension is in the range of 2-4 dynes/cm. The MilSpec protocol requires determination of the numerical value of the spreading coefficient (must be at least 3 dynes/cm on cyclohexane fuel), as well as a "practical" test of film formation. In MIL-F-24385F [2], cyclohexane is the fuel used for both tests.

Film formation and sealing tests (from the MIL-F-24385F protocol, Section 4.7.6) were conducted on the fuel/foam combinations. The test procedure involves covering a fuel surface with foam, then displacing the foam by inserting a wire screen funnel and scooping out residual

foam, so that the fuel surface can be covered by an aqueous film layer (if one is present), but no foam. After waiting 60 seconds, the operator attempts to ignite the fuel surface with a small butane flame that is placed approximately ½ inch above the surface. An inability to ignite the fuel surface indicates successful film formation (which inhibits fuel vaporization). If the fuel surface can be ignited, this means that a film has not formed.

For MIL-F-24385F qualification testing, cyclohexane is the fuel used. Cyclohexane has a high surface tension (24.5 dynes/cm, higher than any of the fuels tested here). Therefore, use of cyclohexane as the fuel is not a very stringent test of an AFFF's film forming ability. In the present study, heptane, methylcyclohexane, and iso-octane were used. Whether the foams are able to form film on the test fuel is important at interpreting the fire extinguishment data given below.

An additional test conducted, if film formation after 60 seconds were successful, was to disturb the fuel surface to disrupt the film layer, then attempt ignition after approximately five seconds. This indicated how rapidly a film layer could form--60 seconds is twice the allowable extinguishment time for full strength AFFF in the MIL-F-24385F protocol. The ability of AFFFs to form film after a longer length of time, but not after a short time interval is a consequence of dynamic surface tension. In a surfactant solution, the surface tension slowly approaches the equilibrium value (the static surface tension). An AFFF with a spreading coefficient which is only very slightly positive on a given fuel may not be able to form a film [5,6] if its dynamic surface tension is not able to approach the equilibrium value quickly enough.

The results of the film formation and sealability tests, as well as surface tension measurements for the fuels, are given in Table II. In these tests, ignition means that film did not form; no ignition means that film did form. As expected, the non-fluorinated RF6 foam was unable to form a film on any of the fuels tested. Both of the AFFF foams formed film on MCH, which has a high surface tension. On heptane, the Buckeye Type 3 formed a film; the National Type 6 was able to form a film after 60 seconds, but not after 5 seconds. Therefore, although it is technically film-forming on this fuel, a film might not be able to form on the time scale relevant to the extinguishment tests.

<b>Table II: Film Formation and Sealability Test Results</b>				
<b>Fuel</b>	<b>Fuel Surface Tension (dynes/cm)</b>	<b>Foam</b>		
		<b>National Type 6</b>	<b>Buckeye Type 3</b>	<b>RF-6 (Type 6)</b>
<b>Iso-octane</b>	18.7	No film	Marginal <sup>1</sup>	No film
<b>Heptane</b>	20.0	Marginal <sup>2</sup>	Film	No film
<b>MCH</b>	23.6	Film	Film	No film
<b>Gasoline</b>	23.7	Film Expected	Film Expected	No Film Expected

<sup>1</sup> Fuel was ignited on some, but not all, attempts.

<sup>2</sup> No ignition occurred after waiting 60 seconds for film to form, but ignition occurred after a 5 second wait time.

On iso-octane, the National Type 6 did not form film. The Buckeye Type 3 was able to prevent ignition in some, but not all trials. Therefore we consider the Buckeye AFFF as being marginal in terms of film formation for this fuel. Like the National Type 6 on heptane, film formation may not occur on the time scale relevant to fire suppression.

### Fire Suppression Test Results

The times required to extinguish the fire by foam application are shown in Table III. Two values on a particular entry in the Table indicates multiple tests were performed. The fire fighting protocol followed the MIL-F-24385F procedure. The foams were mixed at their nominal strength in fresh (municipal) water and the mixture was applied at a flow rate of 2.0 gallons/minute from the nozzle specified by MIL-F-24385F, following a 10 second preburn interval between ignition and the beginning of foam application.

MIL-F-24385F specifies a fire extinction time for a standard gasoline fire of no more than 30 seconds under these test conditions. Both of the MilSpec qualified AFFFs met this requirement easily, extinguishing the fire in slightly over 20 seconds. The RF6 foam did not meet the 30 second requirement, although it did achieve a reasonably close value of 35 seconds on one of the tests. In general, the non-fluorinated foam tended to show more test to test variability in fire out times than the AFFFs. This is consistent with the lack of film formation making the extinguishment of the last remnant of the fire more difficult (flames tend to flare up again if the firefighter's technique is not optimal). This greater sensitivity can be attributed to the lack of a film, which suppresses fuel volatilization in areas uncovered by foam.

Based on the ability of the two AFFFs to qualify for the MilSpec and the measured surface tension of the gasoline sample, we expect the National and Buckeye AFFFs, but not the RF6 foam, to be able to form a film on gasoline.

<b>Table III: Fire Out Time (s)</b>				
		<b>Foam</b>		
<b>Fuel</b>	<b>Fuel Surface Tension (dynes/cm)</b>	<b>National Type 6</b>	<b>Buckeye Type 3</b>	<b>RF-6 (Type 6)</b>
<b>Iso-octane</b>	18.7	32,33 (no film)	32,33 (marginal film)	29,30 (no film)
<b>Heptane</b>	20.0	23,28 (marginal filming)	25 (film)	43 (no film)
<b>MCH</b>	23.6	22,23 (film)	19,20 (film)	33, 46, (no film)
<b>Gasoline</b>	23.7	22 (film expected)	21 (film expected)	35,41 (no film)

All of the tests performed on fuel/foam combinations on which good sealing occurred showed fire out times of no more than 25 seconds. By contrast, with one exception (National Type 6 on heptane), all of the tests performed on fuel/foam combinations where no, or only marginal,

sealing occurred, showed fire out times of at least 29 seconds. On iso-octane fuel, on which none of the foams were able to seal well, the AFFFs did not perform any better than the non-fluorinated RF6 foam. Thus it appears that film formation does indeed contribute to good AFFF fire extinguishment performance by 20%.

There does not appear to be a significant influence of flash point on foam suppression performance between the fuels tested. National and Buckeye AFFFs both had similar extinguishment times for MCH and gasoline, in spite of a large difference in flash point. It should be noted that all of these fuels have flash points significantly below ambient temperature, so this trend will not necessarily apply to fuels with flash points above room temperature.

### **Burnback (Re-ignition) Test Results**

Burnback tests were conducted according to the procedure described in MIL-F-24385F. After extinguishment is achieved in the tests described above, the foam application is continued, building up a foam layer that will be challenged for reignition. For the standard MIL-F-24385F tests on gasoline, the total time of foam application (including the time to extinguish the fire) is 90 seconds. After completion of the foam application, a 1 ft. diameter pan filled with burning fuel is placed in the middle of the 6 ft diameter burn pan. Fig. 1 shows the firefighter placing the starter pan at the beginning of the burnback test.



**Figure 1: Firefighter placing the started pan in the foam-covered fuel at the beginning of the burnback test**

There is no direct contact between the starter pan fuel and the fuel or foam in the main burn pan. Heat release from the starter pan fire erodes the foam and in the case of low flash point fuels, ignites vapors which penetrate the foam layer. Eventually, the fire ignites outside the starter pan and spreads across the main burn pan. When the fire is judged to be self-sustaining outside the starter pan, the starter pan is removed. The burnback time is defined as the time interval from

placement of the starter pan until the fire re-involves 25% of the main burn pan. The MIL-F-24385F requirement for burnback is a time of at least 360 seconds for full strength AFFF.

In comparing test results for heptane done for the re-baselining of the MilSpec test procedure done concurrently with the tests reported here, it was discovered that heptane fires exhibit a much longer burnback time than gasoline. In order to give a reasonable and reproducible test result for the burnback time, it was decided that the foam application time for heptane fires should be reduced to 60 seconds from 90 seconds. The burnback times observed for heptane at 60 seconds foam application were longer than for gasoline at 90 seconds foam application. Comparison of two tests with National Foam AFFF with 90 second and 60 second application times show a burnback time approximately 80 seconds longer for the 90 second foam application.

Because iso-octane and methylcyclohexane have similar flash points to heptane, a 60 second foam application was used on these fuels as well (with the exception of one test of RF-6 foam in which a 45 second foam application was used). Results of the burnback tests are given in Table IV.

Fuel	FOAM		
	National Type 6	Buckeye Type 6	RF-6 (Type 6)
Iso-octane	767	820	789 <sup>1</sup>
Heptane	878 <sup>1</sup> , 758	674	563
MCH	522	499	503
Gasoline	652 <sup>2</sup>	657 <sup>2</sup>	512 <sup>2</sup>

<sup>1</sup> 45 second foam application

<sup>2</sup> 90 second foam application

All three foams displayed longer burnback times on heptane than on gasoline even for a foam application time that was 30 seconds shorter. There were also substantial differences in burnback between fires of heptane, iso-octane, and methylcyclohexane, even though these three fuels have very similar flash points. MCH fires exhibited the shortest burnback times for all three foams tested, and iso-octane the longest. This large difference in burnback times was unexpected, given the similarity in flash points. Also, the burnback times do not correlate with filming ability. Isooctane has the lowest surface tension among the fuels tested but exhibited longer burnback times than methylcyclohexane or gasoline, which have higher surface tension and filming ability. It suggests that the key factor governing burnback times for fuels with flash points below ambient temperature may not be either the flash point or the filming ability, but rather other differences between fuels which influence the rate of vapor penetration through the foam.

### **Discussion of Field Test Findings**

Extinguishment times for gasoline and methylcyclohexane fires by AFFF were about 20 seconds for AFFF solution at nominal strength, using fresh water. This compares to a requirement of 30 seconds under MIL-F-24385F. The similar extinguishment times for these two fuels indicate

that the lower flash point of gasoline compared to MCH does not greatly affect extinguishment times.

On the other hand, fuel/foam combinations on which filming did not occur or was difficult (the non-fluorinated foam formulation for all fuels, and iso-octane with the two AFFF foams), showed extinguishment times ranging from approximately 30-40 seconds. On heptane, the AFFFs formed film, although in one case sealing did not occur within a few seconds. In terms of extinguishment, heptane was found to be an intermediate case, giving extinguishment times a few seconds longer than for gasoline fires, but shorter than the iso-octane fires, for both AFFFs tested.

Although not an objective of the test series, it was noted, particularly in the concurrent series of tests comparing gasoline and heptane as test fuels for the MIL-F-24385F protocol, that extinguishment performance of AFFFs on heptane fires was adversely affected by elevated fuel and ambient temperatures that were encountered during testing. Due to different temperature dependences of the surface and interfacial tensions of the AFFF/fuel system, the spreading coefficient tends to decrease slightly with temperature. Since film formation on heptane fuel is hampered by its low surface tension compared to gasoline (the spreading coefficient is close to zero [3]), even a slight further decrease with increasing temperature might hinder film formation.

For iso-octane, the non-fluorinated foam had shorter extinguishment times than the two AFFFs and was the only foam to achieve an extinguishment time under 30 seconds. Based on this observation, it is tempting to ascribe a major role in extinguishment to film formation. There appear to be other factors at work, however. The non-fluorinated foam had substantially better performance on iso-octane than on any of the other fuels. This is not explained by film formation, which did not occur for any of the fuels for this foam.

It is not surprising that the AFFFs tested show decreased performance on fires of fuels on which they cannot easily form film. Since their intended mode of operation assumes film formation, one would expect decreased performance in cases where film formation does not occur. The non-fluorinated, non film-forming RF6 foam, however, is designed to have mechanical properties of foam which compensate for the lack of film formation. In particular, the rate of water drainage is reduced and the foam has a lower yield stress. The shorter extinguishment times of iso-octane fires by the non-fluorinated foam compared to the AFFFs indicates that extinguishment performance in the absence of film formation can be improved by optimization of other properties of foam.

An unexpected observation was the substantial difference in burnback times between the fuels. Since all of the model fuels (heptane, iso-octane, and methylcyclohexane) have very similar flash points, it was expected that they were likely to show similar burnback behavior to one another, but somewhat longer burnback times than for fires of gasoline, which has a lower flash point.

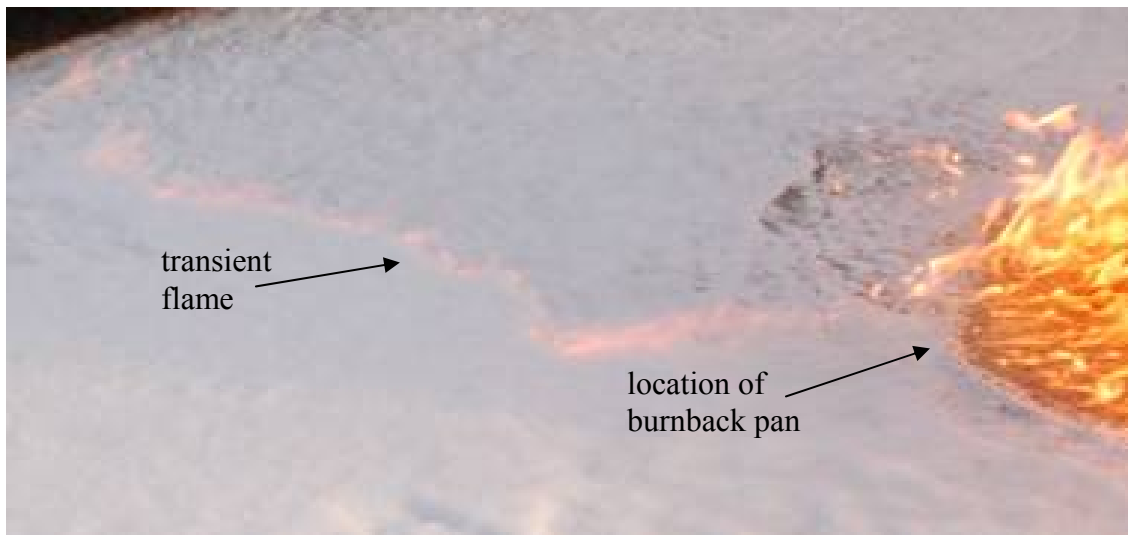
In fact, methylcyclohexane had similar burnback performance to gasoline, while the other two fuels had much longer burnback times, indicating better foam performance. This trend, while varying somewhat in magnitude, was consistent across all three foams tested. The ability for film formation does not appear to increase burnback time. In fact, iso-octane, on which film

formation is the most difficult, had the longest burnback times of any of the fuels tested. The present series of tests do not provide an immediate explanation for this finding. Laboratory studies to measure the rate of fuel transport through the foams were carried out to determine whether fuel differences in vapor penetration could account for the observed differences in burnback times.

### **Laboratory Studies of Vapor Penetration Through Foams**

One of the roles of foam in preventing reignition, particularly on fuels with flash points below ambient temperature, is to prevent / inhibit the vaporization of fuel to form a flammable mixture with air that can be reignited. That fuel passage through the foam contributes to reignition is apparent from field tests in which transient flames sweep across the foam during burnback, indicating a flammable vapor concentration, but not maintained in steady state. (Fig. 2).

Previously, Moran et al. investigated fuel vaporization suppression by AFFF aqueous film in the absence of foam [6]. Schaefer et al. [7] compared the time for a flammable mixture to form above foams of RF6, other non-fluorinated formulations, and an AFFF formulation. Previous studies have not included a systematic comparison between fuels. The significant differences observed in burnback times in the field tests discussed above indicates that fuel differences are significant in foam performance.



**Fig 2: Transient flames observed during burnback test, demonstrating a flammable air/fuel mixture created by fuel vapor passage through the foam.**

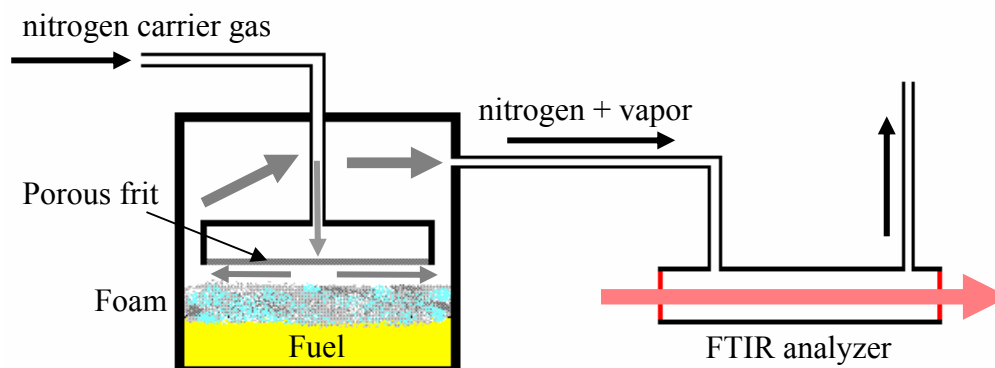
In the present series of tests, we investigate the rate of steady state fuel vapor transport through the three foams investigated in the field tests, on iso-octane, heptane, and methyl-cyclohexane.



## Experimental Setup and Methodology

To quantify vapor passage through foam for different fuel/foam combinations, we constructed a laboratory apparatus to study the passage of vapor through foams and aqueous films. The design, shown in Fig. 2, largely follows the design of Leonard and Burnett [4]. A nitrogen carrier gas passes through a porous frit in a stagnation flow geometry into a container containing fuel covered by film and/or foam. The nitrogen carrier gas picks up fuel vapor, and the mixture is analyzed in real-time by an FTIR spectrometer (Midac Corp.), which monitors the concentration of the fuel in the carrier gas.

For data collection, the foam is prepared and covers the fuel. The foam is generated by air



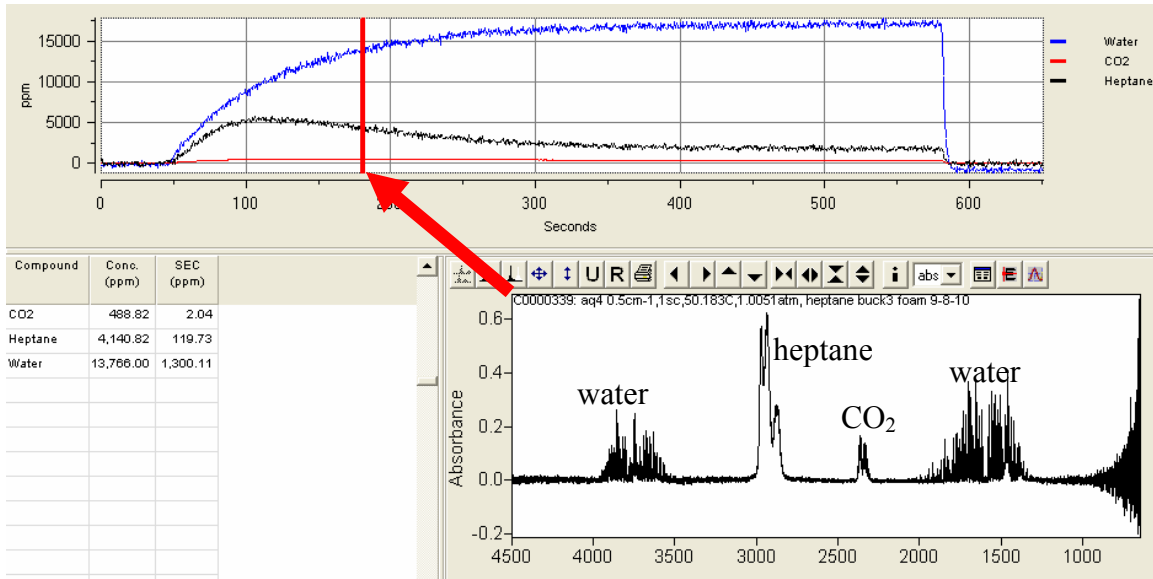
**Fig. 3: Schematic of Vapor barrier test set-up.**

sparging, rather than by the aspirated nozzle used in the field tests. Due to the small volume of foam required for the laboratory studies, the nozzle used in the field tests would not be practical. The expansion ratios of the foams generated by air sparging used for the vapor penetration studies were, however, similar to the values obtained with the field equipment given in Table I.

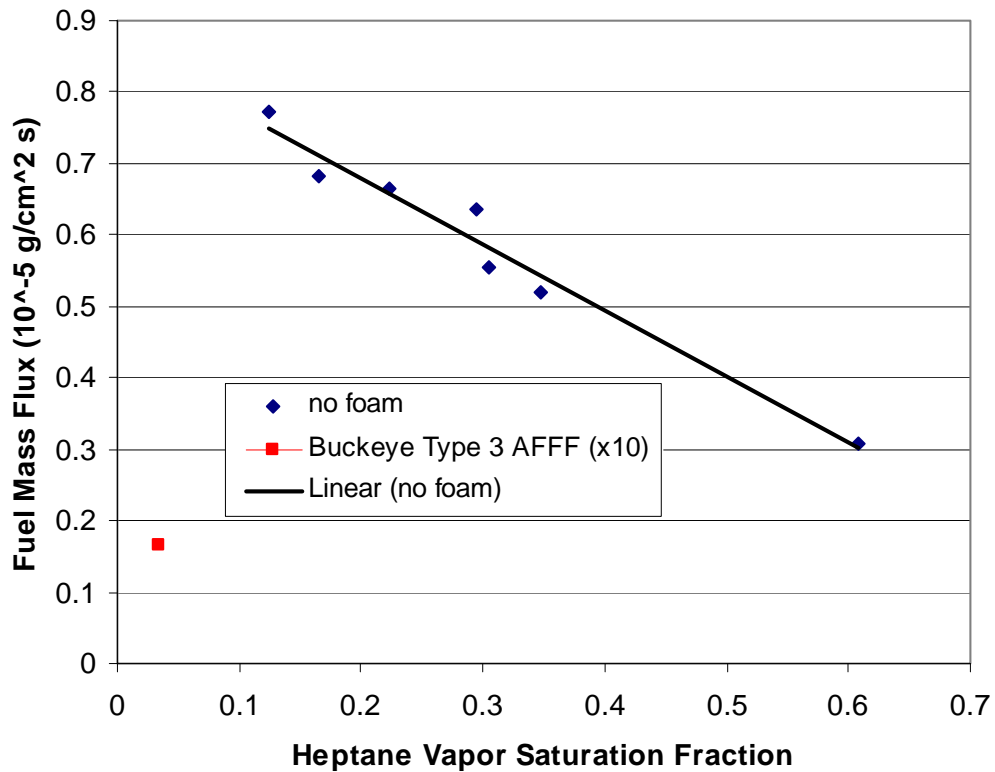
Data from a typical run, using heptane fuel, foam produced from Buckeye Type 3 AFFF, and nitrogen carrier gas, are shown in Fig. 4. The IR spectrum, which contains absorption features due to heptane, water and carbon dioxide, is shown, along with a concentration vs. time plot of the analytes.

The data are analyzed by taking the steady state equilibrium concentration as a function of the carrier gas flow rate. At steady state, the amount of fuel vapor passing into the IR cell (vapor concentration  $\times$  total gas flow rate) is equal to the fuel mass transfer rate from the pool to the gas. The data are plotted (Fig. 5) as the vaporization rate per unit area ( $\text{gm}/\text{cm}^2\text{-s}$ ) vs. the ratio of the actual vapor concentration compared to the saturated vapor concentration. The measurements give a linear relationship, which reaches zero for saturated vapor, and can be extrapolated to the evaporation rate at a negligible vapor concentration.

Fig. 5 also compares the rate of fuel volatilization in the presence of Buckeye Type 3 AFFF foam to the rate in the absence of foam. Under this test condition, the fuel volatilization rate is reduced by approximately a factor of 50 by the presence of the foam.



**Fig. 4: IR spectrum and concentration versus time plot of heptane vapor penetrating through AFFF. Line on concentration graph indicates time corresponding to spectrum**



**Fig. 5: Comparison of mass flux rates in the presence and absence of foam. The foam reduces the fuel volatilization by approximately a factor of 50.**

## Results for Different Fuel/Foam Combinations

We measured the reduction in fuel volatilization by foams for all the fuel/foam combinations investigated in the field tests described in Sections 2 and 3. These measurements clarify the role of fuel penetration through foams in explaining the differences in burn back times observed for fuels with similar volatilities.

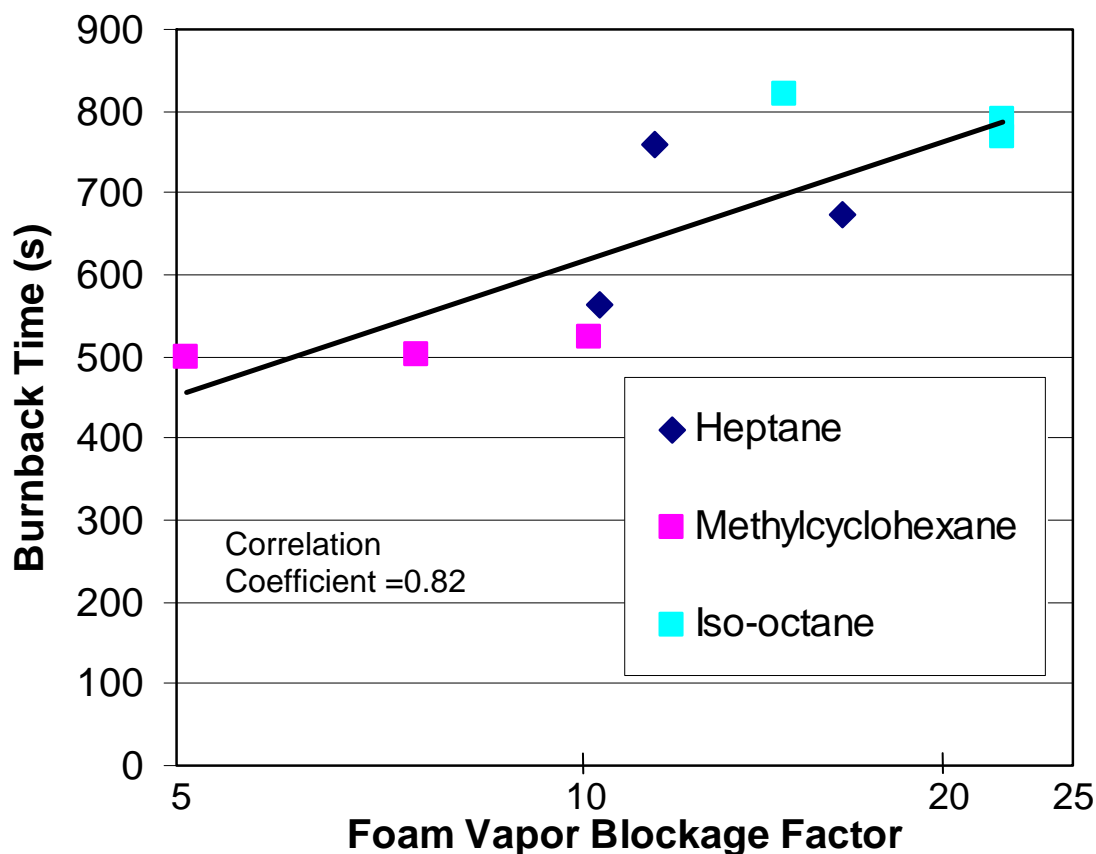
Results for the steady state vaporization rate for the different foam/fuel combinations, and for each fuel without foam, are given in Table V. The porous plug standoff distance, and carrier gas flow rate, are held constant in this series of experiments. The effect of each foam inhibiting fuel volatilization is characterized by a Foam Blockage Factor (ratio of vaporization rate without foam to rate with foam). A blockage factor of one means the foam does not inhibit volatilization at all; a factor of infinity means that no vapor penetrates the foam.

The blocking factors range from roughly 5 to 20, with significant differences between fuels. Methylcyclohexane has the lowest blocking factor for all foams, and iso-octane the highest for two of the three. It is noteworthy that the ordering of the fuels by blocking factor is the same as the fuels' ordering by burnback times in the field tests.

Figure 6 plots the burnback times observed in the field tests (60 seconds foam application except in the case of the RF6/iso-octane combination, which had a 45 second foam application). The correlation coefficient between the two quantities is 0.82, indicating that the rate of fuel vapor transport through the foam has a significant influence on burnback.

**Table V: Steady State Vapor Concentrations and Foam Blockage Factors**

Foam	Fuel					
	Iso-octane		Heptane		Methylcyclohexane	
	vapor conc.	blockage factor	vapor conc.	blockage factor	vapor conc.	blockage factor
none	20900		28800	---	14600	---
National	950	22.0	2450	11.8	1400	10.5
Buckeye	1400	14.9	1750	16.5	2850	5.1
RF6	950	22.0	2700	10.7	1900	7.7



**Fig. 6 Dependence of burnback time in field tests on the foam vapor blockage factor (ratio of steady state fuel vapor concentration without and with foam) measured in laboratory experiments.**

## Conclusions

For the AFFF foams which were intended to work via formation of an aqueous film, fire extinction times were lengthened considerably in cases where film formation was made difficult by the low surface tension of the fuel. For the non-filming fluorine-free foam, however, no such performance decrement was observed, and the fire extinction times on the lowest surface tension fuel were lower than for fuels with higher surface tensions, and within the 30 second time limit specified (on gasoline) by MIL-F-24385F.

An unexpected observation was the substantial differences in burnback times between fuels, which were fairly consistent across foams. Since all of the model fuels (heptane, iso-octane, and methylcyclohexane) have very similar flash points, it was expected that they were likely to show similar burnback behavior to one another, but somewhat longer burnback times than for fires of gasoline, which has a lower flash point.

In fact, methylcyclohexane had similar burnback performance to gasoline, while the other two fuels had much longer burnback times, indicating better foam performance. This trend, while

varying somewhat in magnitude, was consistent across all three foams tested. The ability for film formation does not appear to increase burnback time. Iso-octane, on which film formation is the most difficult, had the longest burnback times of any of the fuels tested.

Laboratory studies to measure the rate of fuel transport through the foams indicate that foam/fuel systems which better inhibit fuel passage through the foams are associated with longer burnback times. This finding intuitively makes sense, because the primary mechanism of burnback for low flashpoint fuels is vapor passing through the foam layer. However, the mechanisms of fuel transport through the foam, and the influence of fuel and foam composition, remain to be determined.

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