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From: Commanding Officer, Naval Research Laboratory
To: Commander, Naval Sea Systems Command (Code 05P M. Hunstad)

Subj: COMPARISON OF COMMERCIAL GRADE HEPTANE WITH UNLEADED, ETHANOL-FREE GASOLINE AS FUELS FOR AFFF QUALIFICATION TESTING UNDER THE MIL-F-24385F PROTOCOL – FINAL REPORT

Encl: (1) One copy of subject report

1. Enclosure (1) is forwarded for your information and review.

2. This report documents the results of the Aqueous Film-Forming Foam (AFFF) fire tests comparing the fire extinguishing performance of AFFF products appearing on the MIL-F-24385F Qualified Products List (QPL) when using either heptane or gasoline as the test fuel. This project was sponsored by the Naval Sea Systems Command (NAVSEA) under the Cross Platform Systems Development Program, Task Number 3.13.10 / MILSPEC AFFF Re-Baseline.

3. The overall finding of this test series confirms the acceptability of changing the test fuel for AFFF MILSPEC qualification testing to commercial grade heptane with a boiling point range of 87-105 °C.

4. In addition to recommending changes to the AFFF MILSPEC fire test protocol, the AFFF Re-Baseline project also identified additional chemical and physical MIL-F-24385F requirements that could be modified including changes to Fish Toxicity testing, Halide Concentration testing, Biological Oxygen Demand (BOD) testing, Index of Refraction testing, Packaging and Shelf Life requirements.

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6180/0071A:JPF
28 March 2014

Comparison of Commercial Grade Heptane with Unleaded, Ethanol-Free Gasoline as Fuels for AFFF Qualification Testing under the MIL-F-24385F Protocol – Final Report

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COMPARISON OF COMMERCIAL GRADE HEPTANE WITH UNLEADED, ETHANOL-FREE GASOLINE AS FUELS FOR AFFF QUALIFICATION TESTING UNDER THE MIL-F-24385F PROTOCOL – FINAL REPORT

1.0 OBJECTIVE

Aqueous Film Forming Foam (AFFF) is an important component of Department of Defense (DoD) fire protection against liquid fuel fire threats, particularly on carrier flight decks, land-based aviation facilities and fuel storage depots.

MIL-F-24385F [1] is the current DoD qualification protocol for AFFF. "MILSPEC" qualified AFFFs are required for designated applications aboard Navy ships and other DoD facilities, and are also widely used in civilian applications, especially in airports and fuel storage facilities. NAVSEA Code 05P is the Technical Warrant Holder (TWH) for the MIL-F-24385F standard and the Qualified Products List [2] for MILSPEC AFFFs.

Currently, the fuel used for MIL-F-24385 testing is unleaded gasoline [1]. This fuel was chosen in part because it is commonly available and has a low flash point, typically about -40 °C. Most fuels which are common fire threats in DoD applications, such as JP-5, JP-8, and F-76 diesel, have much higher flash points; therefore testing the AFFF on a lower flash point fuel is believed to provide an additional safety factor. At the time the MILSPEC was first established, JP-4 (the military version of Jet-B) was in common use; this fuel also has a low flash point (typically around -18 °C). This may have been an additional motivation for the choice of gasoline as the AFFF MILSPEC test fuel.

Recently, use of unleaded gasoline for AFFF testing has been complicated by the addition of ethanol to gasoline in many areas. In designated areas, the addition of ethanol at the 10% level (E10) is mandated for environmental reasons. The NRL test facility at the Chesapeake Bay Detachment, in Chesapeake Beach, MD, is located in an area where ethanol is required to be added to gasoline. Although NRL has obtained an exemption from the Environmental Protection Agency (EPA) to purchase non-ethanol-containing gasoline for AFFF fire testing, locating suppliers who can provide such gasoline is made difficult by tax credits given for renewable fuels (including ethanol) which lead many distributors to supply E10 even in instances where its use is not mandated.

MILSPEC AFFF is not intended for use on water miscible fuels, as these fuels are known to disperse foam and interfere with AFFF's performance. Even a 10% ethanol concentration in gasoline might impact the performance of a candidate AFFF under the very stringent test protocol required for AFFF MILSPEC qualification. Therefore E10 cannot be used for MIL-F-24385 qualification testing.

Additionally, the flashpoint and vapor pressure of gasoline varies with the geographical location and time of year, as a compromise between ease of starting an engine and minimizing fugitive emissions. The issue of gasoline having variable properties which might influence AFFF performance in MIL-F-24385 qualification tests has been raised in the past by AFFF manufacturers.

Therefore, NAVSEA, in consultation with NRL, desired to explore the use of a different fuel for AFFF qualification testing. After considering possible fuel choices, commercial grade heptane has been identified as a candidate fuel as a replacement for gasoline in future AFFF qualification tests. Heptane is currently used as the test fuel in some commercial certification standards [3]. The present test report documents the results of the AFFF fire tests comparing the performance of AFFFs appearing on the MIL-F-24385F Qualified Products List (QPL) between heptane and gasoline.

2.0 TEST SERIES PROTOCOL AND MATERIALS

2.1 Test Methodology

In order to validate the viability of using commercial grade heptane in lieu of unleaded, ethanol-free gasoline as fuels for AFFF qualification testing under the MIL-F-24385F protocol, NAVSEA 05P directed that the fire test series be divided into two fire test phases. Phase one included fifty-four extinguishment and burnback fire tests in a 28 ft^2 (6 ft diameter) fire pan using both full strength fresh & seawater Type-3 AFFF solutions and half strength seawater Type-3 AFFF solutions. Table 1 provides an overview of the phase one fire test matrix.

Table 1 – Phase One Fire Test Matrix

Agent/Test	Fuel (Gasoline)	Fuel (Heptane)	Fire Size (ft^2)	AFFF (New/Aged)
National: Full Strength/Fresh	3	3	28	New
Chemguard: Full Strength/Fresh	3	3	28	New
Buckeye: Full Strength/Fresh	3	3	28	New
National: Full Strength/Seawater	3	3	28	New
Chemguard: Full Strength/Seawater	3	3	28	New
Buckeye: Full Strength/Seawater	3	3	28	New
National: Half Strength/Seawater	3	3	28	New
Chemguard: Half Strength/Seawater	3	3	28	New
Buckeye: Half Strength/Seawater	3	3	28	New

Phase two testing, which included an additional forty-two fire tests addressed half-strength freshwater Type-3 AFFF solutions, half-strength seawater Type-3 AFFF solutions using aged concentrate (both in the 28 ft^2 (6 ft diameter) fire pan, and full strength seawater Type-3 AFFF solutions conducted in a 50 ft^2 (8 ft diameter) fire pan. Table 2 provides an overview of the phase two fire test matrix.

Table 2 – Phase Two Fire Test Matrix

Agent/Test	Fuel (Gasoline)	Fuel (Heptane)	Fire Size (ft^2)	AFFF (New/Aged)
National: Half Strength/Fresh	3	3	28	New
Chemguard: Half Strength/Fresh	3	3	28	New
Buckeye: Half Strength/Fresh	3	3	28	New
National: Half Strength/Seawater	3	3	28	Aged
Chemguard: Half Strength/Seawater	3	3	28	Aged
Buckeye: Half Strength/Seawater	3	3	28	Aged
National: Full Strength/Seawater	1	1	50	New
Chemguard: Full Strength/Seawater	1	1	50	New
Buckeye: Full Strength/Seawater	1	1	50	New

2.2 Fuels

All fire tests were performed using ethanol-free gasoline, obtained from a local supplier, and commercial grade heptane (Shell Chemical). Heptane has a higher flash point than gasoline. Commercial grade heptane is not isomerically pure, but is defined by a certain boiling range, and can have a variable composition depending on the supplier. One manufacturer (Shell Chemical) specifies limits of 87-105 °C for the allowable boiling point range, and lists "typical values" of 93 - 99 °C. Typically n-heptane is a substantial component of the mixture. The measured closed cup flash point of the lot used in testing was -9 °C (manufacturer's data). Typical material properties of the Shell product from the manufacturer's data [4] (not product specifications) are shown in Table 3.

Table 3 – Selected Properties (Typical Values) of Commercial Heptane used in Testing

Property	Value
Initial Boiling Point	93 °C
50% Boiling Point	94 °C
Final Boiling Point	99 °C
Flash Point	<-7 °C
Vapor Pressure @ 20 °C	49 Torr
Composition:	
Aromatics	<0.1%
Cycloparaffins	10%
Paraffins	90%
n-Heptane	28%

2.3 AFFF Concentrate Formulations Used in Testing

COTS samples of three Type-3 AFFF concentrates were purchased and used for phase one and phase two testing. All foams used are on the current Qualified Products List [2]. Different COTS samples were used in the two series of tests. The AFFFs, lot numbers, and dates of manufacture are listed in Table 4.

Table 4 – Lot numbers and dates of manufacture of AFFFs in Phase 1 and Phase 2 testing

AFFF	Phase 1 testing		Phase 2 testing	
	Lot #	Manufacture date	Lot #	Manufacture date
National Foam 3EM	L11360	Oct. 2011	L13133	August 2013
Chemguard C-301MS	0923112	Sept. 2011	0708131	July 2013
Buckeye BFC-3MS	50285	Aug. 2011	120050	August 2012

3.0 PHASE ONE TEST RESULTS

Phase one fire extinguishment and burnback tests were conducted for the following conditions:

- AFFF at nominal strength, mixed with fresh water in 28 ft^2 fire pan
- AFFF at nominal strength, mixed with artificial sea water in 28 ft^2 fire pan
- AFFF at one-half nominal strength, mixed with artificial sea water in 28 ft^2 fire pan

3.1 Tests for AFFF Extinguishment at Full Strength, Mixed with Fresh Water in 28 ft^2 Fire Pan

Extinguishment and burnback times for the tested AFFF solutions at full strength in fresh water are provided in Table 5.

Table 5 – Extinguishment and 25% Burnback Times for 28 ft^2, Full Strength, Fresh Water Tests

Test #	Fuel Type	COTS MILSPEC AFFF Concentrate	Fire Out Time (s)	Foam Application Time Before Burnback (s)	25% Burnback Time (s)
MIL-F-24385F Requirement			**≤ 30**	**90**	**≥ 360**
01	Gasoline	National Type 3	26	90	501
02	Gasoline	National Type 3	28	90	501
03	Gasoline	National Type 3	27	N/A	n.d.
04	Heptane	National Type 3	25	90	690
05	Heptane	National Type 3	24	90	728
06	Heptane	National Type 3	29	N/A	n.d.
07	Gasoline	Chemguard Type 3	26	90	432
08	Gasoline	Chemguard Type 3	26	90	392
09	Gasoline	Chemguard Type 3	26	N/A	n.d.
10	Heptane	Chemguard Type 3	24	90	552
11	Heptane	Chemguard Type 3	25	90	529
12	Heptane	Chemguard Type 3	26	N/A	n.d.
13	Gasoline	Buckeye Type 3	22	90	919
14	Gasoline	Buckeye Type 3	22	90	704
15	Gasoline	Buckeye Type 3	23	N/A	n.d.
16	Heptane	Buckeye Type 3	26	90	726
17	Heptane	Buckeye Type 3	28	90	640
18	Heptane	Buckeye Type 3	28	N/A	n.d.

n.d.: test not performed; N/A: not applicable

3.2 Tests for AFFF Extinguishment at Full Strength, Mixed with Artificial Sea Water in a 28 ft^2 Fire Pan

Extinguishment and burnback times for the AFFF solutions tested at full strength, mixed with artificial sea water are provided in Table 6.

Table 6 – Extinguishment and 25% Burnback Times for 28 ft^2, Full Strength, Artificial Sea Water Tests

Test #	Fuel Type	COTS MILSPEC AFFF Concentrate	Fire Out Time (s)	Foam Application Time (s)	25% Burnback Time (s)
MIL-F-24385F Requirement			**≤ 30**	**90**	**≥ 360**
19	Gasoline	National Type 3	27	90	579
20	Gasoline	National Type 3	*31*	90	438
21	Gasoline	National Type 3	26	N/A	n.d.
22	Heptane	National Type 3	*33*	90	671
23	Heptane	National Type 3	30	90	667
24	Heptane	National Type 3	30	N/A	n.d.
25	Gasoline	Chemguard Type 3	30	90	492
26	Gasoline	Chemguard Type 3	29	90	521
27	Gasoline	Chemguard Type 3	29	N/A	n.d.
28	Heptane	Chemgurad Type-3	28	90	706
29	Heptane	Chemguard Type-3	27	90	598
30	Heptane	Chemguard Type-3	26	N/A	n.d.
31	Gasoline	Buckeye Type-3	27	90	575
32	Gasoline	Buckeye Type-3	27	90	572
33	Gasoline	Buckeye Type-3	24	N/A	n.d.
34	Heptane	Buckeye Type-3	*36*	90	662
35	Heptane	Buckeye Type-3	30	90	646
36	Heptane	Buckeye Type-3	30	N/A	n.d.

n.d.: test not performed; N/A: not applicable

3.3 Tests for AFFF Extinguishment at Half Strength, Mixed with Artificial Sea Water in a 28 ft^2 Fire Pan

Fire extinguishment and burnback times for the AFFF solutions tested at half strength, mixed with artificial sea water are provided in Table 7.

Table 7 – Extinguishment and 25% Burnback Times for 28 ft^2, Half Strength with artificial Sea Water Tests

Test #	Fuel Type	COTS MILSPEC AFFF Concentrate	Fire Out Time (s)	Foam Application Time (s)	25% Burnback Time (s)
MIL-F-24385F Requirement			**≤ 45**	**90**	**≥ 300**
37	Gasoline	National Type 3	42	90	522
38	Gasoline	National Type 3	43	90	461
39	Gasoline	National Type 3	35	N/A	n.d.
40	Heptane	National Type 3	41	90	681
41	Heptane	National Type 3	*47*	90	664
42	Heptane	National Type 3	45	N/A	n.d.
43	Gasoline	Chemguard Type 3	*48*	90	453
44	Gasoline	Chemguard Type 3	36	90	455
45	Gasoline	Chemguard Type 3	37	N/A	n.d.
46	Heptane	Chemguard Type 3	*48*	90	655
47	Heptane	Chemguard Type 3	40	90	508
48	Heptane	Chemguard Type 3	36	N/A	n.d.
49	Gasoline	Buckeye Type 3	38	90	422
50	Gasoline	Buckeye Type 3	31	90	637
51	Gasoline	Buckeye Type 3	31	N/A	n.d.
52	Heptane	Buckeye Type 3	30	90	559
53	Heptane	Buckeye Type 3	45	90	590
54	Heptane	Buckeye Type 3	28	N/A	n.d.

n.d.: test not performed; N/A: not applicable

4.0 PHASE TWO TEST RESULTS

Phase two fire extinguishment and burnback tests were conducted for the following conditions:

- AFFF one-half nominal strength using aged concentrate, mixed with artificial sea water in a 28 ft^2 fire pan.
- AFFF one-half nominal strength, mixed with fresh water in a 28 ft^2 fire pan.
- AFFF at nominal strength, mixed with artificial sea water in a 50 ft^2 fire pan.

4.1 Tests for AFFF Extinguishment at Half Strength using Aged Concentrate Mixed with Artificial Sea Water in a 28 ft^2 Fire Pan

Extinguishment and burnback times for the tested AFFF solutions at half strength with aged concentrate in artificial sea water are provided in Table 8.

Table 8 – Extinguishment and 25% Burnback Times for 28 ft^2, Aged Concentrate, Half Strength, Artificial Sea Water Tests

Test #	Fuel Type	COTS MILSPEC AFFF Concentrate	Fire Out Time (s)	Foam Application Time (s)	25% Burnback Time (s)
MIL-F-24385F Requirement			**≤ 45**	**90**	**≥ 300**
01	Gasoline	National Type 3	33	90	610
02	Gasoline	National Type 3	30	N/A	n.d.
03	Gasoline	National Type 3	28	N/A	n.d.
04	Heptane	National Type 3	*50*	90	720
05	Heptane	National Type 3	*47*	N/A	n.d.
06	Heptane	National Type 3	*48*	N/A	n.d.
07	Gasoline	Chemguard Type 3	34	90	545
08	Gasoline	Chemguard Type 3	*48*	N/A	n.d.
09	Gasoline	Chemguard Type 3	*55*	N/A	n.d.
10	Heptane	Chemguard Type 3	*59*	90	714
11	Heptane	Chemguard Type 3	*52*	N/A	n.d.
12	Heptane	Chemguard Type 3	*62*	N/A	n.d.
13	Gasoline	Buckeye Type 3	28	90	360
14	Gasoline	Buckeye Type 3	25	N/A	n.d.
15	Gasoline	Buckeye Type 3	27	N/A	n.d.
16	Heptane	Buckeye Type 3	34	90	519
17	Heptane	Buckeye Type 3	29	N/A	n.d.
18	Heptane	Buckeye Type 3	31	N/A	n.d.

n.d.: test not performed; N/A: not applicable

4.2 Tests for AFFF Extinguishment at Half Strength, Mixed with Fresh Water in a 28 ft^2 Fire Pan

Fire extinguishment and burnback times for AFFF solutions tested at half strength, mixed with fresh water are provided in Table 9.

Table 9 – Extinguishment and 25% Burnback Times for 28 ft^2, Half Strength, Fresh Water Tests

Test #	Fuel Type	COTS MILSPEC AFFF Concentrate	Fire Out Time (s)	Foam Application Time (s)	25% Burnback Time (s)
MIL-F-24385F Requirement			**≤ 45**	**90**	**≥ 300**
19	Gasoline	National Type 3	28	90	412
20	Gasoline	National Type 3	28	N/A	n.d.
21	Gasoline	National Type 3	30	N/A	n.d.
22	Heptane	National Type 3	31	90	739
23	Heptane	National Type 3	31	N/A	n.d.
24	Heptane	National Type 3	28	N/A	n.d.
25	Gasoline	Chemguard Type 3	*50*	90	482
26	Gasoline	Chemguard Type 3	43	N/A	n.d.
27	Gasoline	Chemguard Type 3	*57*	N/A	n.d.
28	Heptane	Chemguard Type 3	*62*	90	553
29	Heptane	Chemguard Type 3	*60*	N/A	n.d.
30	Heptane	Chemguard Type 3	*65*	N/A	n.d.
31	Gasoline	Buckeye Type 3	35	90	481
32	Gasoline	Buckeye Type 3	35	N/A	n.d.
33	Gasoline	Buckeye Type 3	*61*	N/A	n.d.
34	Heptane	Buckeye Type 3	31	90	726
35	Heptane	Buckeye Type 3	37	N/A	n.d.
36	Heptane	Buckeye Type 3	38	N/A	n.d.

n.d.: test not performed; N/A: not applicable

4.3 Tests for AFFF Extinguishment at full Strength, Mixed with Artificial Sea Water in a 50 ft^2 Fire Pan

Fire extinguishment and summation times for AFFF solutions tested at full strength, mixed with artificial sea water are provided in Table 10.

Table 10 – Extinguishment and Summation Times for 50 ft^2, Full Strength, Artificial Sea Water Tests

Test #	Fuel Type	COTS MILSPEC AFFF Concentrate	Fire Out Time (s)	40 Second Summation Application
MIL-F-24385F requirement			≤ 50	320 (Sec)
37	Gasoline	National Type 3	36	365
38	Heptane	National Type 3	50	363
39	Gasoline	Chemguard Type 3	50	354
40	Heptane	Chemguard Type 3	39	359
41	Gasoline	Buckeye Type 3	38	364
42	Heptane	Buckeye Type 3	40	359

5.0 ANALYSIS & DISCUSSION OF TEST RESULTS

5.1 Extinguishment Performance

There does not appear to be a clear trend in extinguishment time between gasoline and heptane fuels that holds for all AFFFs and all test conditions. In general, the extinguishment times were slightly longer for heptane (particularly in the half strength tests), but exceptions to this trend are observed. Heptane does have a lower surface tension in comparison to gasoline and therefore film formation is more difficult on heptane [5]. Because of this trend it may be appropriate to extend the required fire out time for the half strength tests to 50 seconds instead of the 45 seconds currently required for gasoline fuel. In the full strength tests, all of the AFFFs tested were able to extinguish the fire within 30 seconds in at least two out of three replicates using both fresh water and artificial seawater, on both gasoline and heptane fires. Therefore, there does not appear to be a reason to alter the 30 second extinguishment requirement for a change to heptane test fuel. In the 50 ft^2 tests, all three AFFFs tested passed the fire out time and the summation requirements on both fuels, with no clear trends observed between heptane and gasoline. It does not appear necessary to change the requirements for the 50 ft^2 test from their current values.

5.2 Burnback Performance

As noted previously in preliminary testing on heptane conducted in 2010, heptane fuel tends to produce far longer burnback times than gasoline [6]. As an example, in Table 9 the burnback times for the three AFFFs averaged over three minutes longer on heptane than on gasoline. Because the burnback test is much easier to pass on heptane, an AFFF would still be able to pass the test while providing burnback protection that is not as good. In Reference 6 it was found that reduction of the total foam application time to 60 seconds from the current 90 seconds produces burnback times on heptane comparable to the current values using gasoline, resulting in a comparably challenging test.

6.0 RECOMMENDATIONS

6.1 Changes to Fire Test Protocol

We recommend changing the test fuel for AFFF MILSPEC qualification to commercial grade heptane of the boiling point range used in the present test series (87-105 °C specification, 93 - 99

°C typical). The present test series demonstrates that heptane presents a comparable challenge to AFFF performance as gasoline, and use of heptane avoids the difficulty in obtaining ethanol-free gasoline, as well as seasonal and location-dependent variations in fuel properties.

The recommended changes listed below for fire out time and burnback procedure are intended to make a qualification test on heptane as comparable as possible to the current MIL-F-24385F on gasoline.

We recommend increasing the allowable fire out time for the half strength tests to 50 seconds from the current 45 seconds. We do not recommend changing the allowable fire out time for the full strength 28 ft^2 tests (currently 30 seconds), nor for the 50 ft^2 tests (currently 50 seconds).

For the burnback tests, we recommend reducing the total foam application time from the current 90 seconds to 75 seconds. We do not recommend changing the 25% burnback times from their current values.

6.2 Other Changes to MIL-F-24385F

In addition to the change of the test fuel and other modifications above, we suggest the following changes to other aspects of the qualification test for consideration.

6.2.1 Fish Toxicity Testing

MIL-F-24385F specifies AFFF concentrate fish toxicity testing on *Fundulus heteroclitus*, commonly known as the killifish or mummichog. This species is found in streams and estuaries on the east coast of the U.S. and Canada, and can live in both salt and fresh water. Significantly, it is known to be an extremely hardy species which can survive in wide ranges of temperature, salinity, turbidity, and oxygen concentration, as well as in environments with high levels of pollution [7]. Of special relevance to AFFF toxicity testing is the ability of this fish to survive low oxygen levels, as one of the toxicity mechanisms of AFFF concentrate is thought to be adherence of the surfactants in AFFF to the fishes' gills, causing suffocation.

Because of the ability of *Fundulus heteroclitus* to survive in harsh conditions, it appears not to be an appropriate indicator species, as other fish species in a given environment may have significantly lower LC50 concentrations for AFFF concentrate. Furthermore, *Fundulus heteroclitus* is not commonly used in toxicity testing; for toxicity testing of non-MILSPEC AFFF concentrates; most data are recorded using either rainbow trout (*Oncorhynchus mykiss*) or fathead minnow (*Pimephales promelas*). An EPA guideline on fish toxicity testing [8] recommends rainbow trout and bluegill sunfish (*Lepomis macrochirus*) as indicator species, respectively, for cold and warm freshwater environments "since they are sensitive indicator species and a large data base which characterizes the response to environmental contaminants is available." For species which can live in saltwater environments, Reference [9] recommends the Atlantic silverside (*Menidia menidia*) or the sheepshead minnow (*Cyprinodon variegatus*); however the latter species is also known to be able to survive oxygen depletion, so may not be an appropriate species for AFFF testing.

Tyndall AFB has conducted toxicity testing on alternative fire suppressant agents on the fathead minnow (*Pimephales promelas*), using Type 3 MILSPEC AFFF as a baseline compound [10]. In different series of tests Chemguard and Ansul AFFFs have been used as baseline compounds. In both cases, the LC50 for these AFFFs on *Pimephales promelas* was greater than the 500 ppm requirement of MIL-F-24385F. In the case of the Ansul AFFF, the measured LC50 of 522 ppm was only slightly greater than 500 ppm.

We recommend that the fathead minnow (*Pimephales promelas*) be used as the test species for AFFF fish toxicity, with minimum LC50 concentrations of 400 ppm and 800 ppm for Type 3 and Type 6 concentrate, respectively.

6.2.2 Halide Concentrations Test

MIL-F-24385F currently includes a test for halide concentration following the procedure of ATSM D-1821. We recommend removing this test for the following reasons:

1. The test is not general for all halides; in particular, it does not include fluorides
2. The D-1821 standard is obsolete, and
3. The rationale for determining halide concentration in the AFFF concentrate is presumably to ensure the concentrate is not too corrosive to metal surfaces; however, MIL-F-24385F already includes pitting and corrosion tests on various metals of construction used in shipboard AFFF systems.

Therefore, any AFFF which produced excessive corrosion would be identified in the corrosion tests, rendering the halide test redundant.

6.2.3 COD/BOD

We recommend leaving the Chemical Oxygen Demand test unchanged, as this measured the amount of organic material present in AFFF, which may cause oxygen depletion in case of spillage into a body of water.

We recommend deleting the Biological Oxygen Demand test. This test tends to give poor reproducibility of results between analytical laboratories, and sometimes an impossible BOD/COD ratio greater than one is found. Most of the organic material in AFFF consists of glycol ether solvents, and the biological consumption rate of these compounds, which are not typical food sources in the environment, depends on the biota added to the solution for the test. Furthermore, although the BOD/COD ratio is intended to assess biodegradability of the material, the components of AFFF which are not biodegradable are the fluorosurfactants, which are a small proportion of the material, but extremely persistent in the environment.

6.2.4 Refractometry

Because the purpose of the index of refraction requirement is to allow shipboard determination of proportioning accuracy via refractometry, we propose changing the requirement from a fixed refractive index value to following the procedure specified on the Shipboard Maintenance Requirement Card (MRC), which specifies a field procedure for shipboard determination of AFFF proportioning by refractometry [10]. In accordance with Table 2 of reference 10, the proportion of AFFF concentrate in an AFFF solution is calculated by the following formula, which assumes a linear interpolation of refractive index between pure water and pure concentrate:

$$A = R_s \text{ (index of AFFF solution)} - R_w \text{ (index of artificial seawater)}$$

$$B = R_t \text{ (index of AFFF concentrate)} - R_w \text{ (index of artificial seawater)}$$

$$\%\text{ foam concentration} = 100 \times A \div B$$

The acceptable range for shipboard and/or field foam concentration analysis specified in reference 11 is 5% to 8% for Type 6 AFFF solutions and 2.5% to 4% for Type 3 AFFF solutions. This recommendation is also consistent with a previous finding noted in reference 11.

6.2.5 Repeatability of Passing Fire Extinguishment and Burnback Times

Currently, the MILSPEC requires specified fire extinguishment times for various test conditions. However, there is no guidance for the number of tests allowed to achieve a passing time. In testing, outlier values for fire out time are obtained, due to factors in the test conditions other than the foam itself. However, an AFFF should not be given a passing grade due to a fortuitous value obtained on a single test which is not repeatable. Therefore, we recommend that the requisite fire extinguishment and burnback times must be obtained on two consecutive tests for the result to be considered a "pass".

6.3 Other AFFF Issues

The following topics are not formally related to the proposed change in AFFF test fuel or other modifications to the MILSPEC test. They are, however, important for assuring adequate AFFF fire protection in DoD which have come to our attention during recent AFFF testing.

6.3.1 Packaging

It was noted that the specified color scheme for AFFF packaging (white letters on a green background for Type 3, white letters on a blue background for Type 6) was not followed for any of the Type 3 AFFFs tested. All containers were white, and the different brands used three different colors of lettering: Buckeye and Chemguard used green lettering, National used blue lettering, and Ansul used red lettering. While these samples were purchased commercially rather than being obtained through the DoD supply, commercially-obtained samples can find their way onto Navy ships through shipyards or other contractors.

6.3.2 Shelf Life

Based on previous AFFF testing conducted at NRL, in which AFFF remaining from the original qualification tests and subsequently stored for a long period (typically 20 years or more) failed to perform well, we recommend instituting a maximum shelf life requirement for AFFF concentrate of fifteen years.

7.0 REFERENCES

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