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Flammability & Degradation of Fuel-contaminated Fluorine Free Foams



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Fuel contamination is a serious issue with Class B firefighting foams. Also known as the fuel-pickup problem, fuel contamination is unavoidable because the foam comes in direct contact with the fuel.

Direct and forceful application of foam into the burning fuel creates more severe fuel contamination than gentle or indirect application. The fuel contamination problem can destabilise the foam and degrade it prematurely. More seriously, fuel contamination can make certain contaminated foams flammable thereby causing premature destruction of the foam blanket due to sustained burning, persistent edge flicker fires, flashovers and candle effects. These problems can seriously compromise the extinguishment and burn-back performance, resulting in an overall poorer firefighting performance of the foam.

Recognising this issue, international foam standards and specifications, such as Underwriters Laboratories UL 162 and European Norm EN 1568, have provisions, in qualifying foams, for both gentle and forceful applications. Gentle application requires a back-board to allow indirect discharge of foam onto the fuel. However, forceful foam application is more realistic of most fire situations, involving direct plunging and mixing of the foam into hydrocarbon fuel layers.

EN 1568-3 has an elaborate fire performance test to determine a class rating with a grid primarily based on the distinction between the forceful and gentle modes of application. EN 1568-3 even provides guidelines for bracketing foam concentrates. Only fluorosurfactant-containing foams such as AFFF, FFFP, AR-AFFF, AR-FFFP and FP are recommended for testing under the forceful application on hydrocarbon fuels, because the fluorosurfactants protect the foam and minimise this fuel pickup problem.

The International Civil Aviation Organization's (ICAO) standard Level B fire test and US Military specification (MIL-F-24385F), both of which only cover hydrocarbon fuels, require direct and forceful foam discharge onto the burning fuel in recognition of modern aircraft rescue and fire fighting (ARFF) techniques. Some manufacturers of F3 (Fluorine Free Foam) agents only recommend their products for fires that can be fought with gentle modes of application to minimise these fuel contamination issues. Because of the additional foam-destroying effects of polar solvent fuels, multi-purpose foam agents such as AR-AFFF and AR-FFFP are always tested and preferentially used with indirect (gentle) applications on polar solvents, but are widely used forcefully on hydrocarbon fuels.

Laboratory Foam Flammability and Foam Degradation Test – Dynax Method

Dynax research has developed a laboratory method for determining the effects of fuel contamination on the flammability and foam degradation of fuel-contaminated foams.

This test was used to evaluate several fire-fighting foams currently available on the market. Both F3 and fluorosurfactant-based, film-forming foams were tested and compared using this test procedure.

• Test Procedure

Test Fuels: Four test fuels were used: gasoline (unleaded 87 Octane from Shell), n-heptane (from Cole Palmer), cyclohexane (from Spectrum Chemicals) and Jet A (obtained from Westchester County, New York Airport Fuel Depot). The fuel was coloured with an oil soluble red dye (0.05% Lockwood Concentrated Red Oil Stain Powder #6331) to aid detection of fuel particle distribution in the foam. In separate testing the dyestuff was found not to have any effects on the test results.

Foam Flammability: Foam was generated in a blender (Hamilton Beach 7 Speed Blendmaster) using an appropriate premix solution (1%, 3% or 6%) in Poland Spring water. Eighty millilitres (mL) of the foam was added to a graduated cylinder containing 20 millilitres of the test fuel, and they were mixed by turning the cylinder upside down ten times by hand with a quarter turn rotation each time. Approximately 12 millilitres of the foam and fuel mixture was transferred to a glass Petri dish using a three-millilitre transfer pipet, and a gentle flame from a hand-held burner (Professional Cooking Torch by Bonjour) was passed over the foam without touching it to test its flammability.

Foam Degradation: In a separate set of tests, 80 millilitres of foam and 20 millilitres of fuel were mixed in a graduated cylinder the same way as in the flammability test. As soon as the foam and the fuel get mixed, a timer is turned on to measure the time taken for half of the initial volume of the fuel-contaminated foam to collapse (50% Foam Collapse Time). This foam



Table 1 – Comparison of Flammability of Fuel-contaminated Fluorine-free Foams and AFFF/AR-AFFF

Test Foam Agent	Flammability Of Fuel-contaminated Foam		
	Gasoline	N-heptane	Cyclohexane
Fluorine-free Foam Agents			
Product A-F3-6%	All flashed and burned away	All flashed and burned away	All flashed and burned away
Product B-F3-3%/6%			
Product C-F3-3%			
Product D-F3-3%/3%			
Product E-F3-3%/6%			
AFFF / AR-AFFF Agents			
Product 1-AFFF-3%	None flashed or burned	None flashed or burned	None flashed or burned
Product 2-AR-AFFF-3%/3%			
Product 3-AR-AFFF-3%/3%			
Product 4-AR-AFFF-1%/3%			

collapse time is a quantitative measure of the impact of fuel contamination on the stability of fuel-contaminated foam. For this test, only gasoline was used.

F3 Test Samples: The following products were purchased in the open market:

- Product A-F3-6%.
- Product B-F3-3%/6%.
- Product C-F3-3%.
- Product D-F3-3%/3%.
- Product E-F3-3%/6%.

AFFF/AR-AFFF Samples: These commercial film-forming foam agents were obtained directly from the manufacturers:

- Product 1-AFFF-3%.
- Product 2-AR-AFFF-3%/3%.
- Product 3-AR-AFFF-3%/3%.
- Product 4-AR-AFFF-1%/3%.

● **Results**

Foam Flammability: As the test results show in Table 1, all five F3 foams tested showed instant flash and sustained burning until the foam was completely destroyed. However, in stark contrast, none of the film-forming foams tested caught fire, so no burning at all was observed. This critical difference in the foam flammability between the fluorine-free and film-forming foams was observed with all the test fuels, except Jet A. The Jet A-contaminated foams did not catch fire with either F3 or film-forming foams simply because of its high flash point (>38°C) and relative resistance to ignition.

Foam Degradation: All five F3 foams tested showed rapid degradation in the presence of gasoline. As shown in Table 2, the 50% Foam

Collapse Times for F3 foams ranged from 4.5 minutes to 9.5 minutes, whereas none of the film-forming foams showed any indication of foam volume decrease at ten minutes time when the test was terminated. Other fuels were not tested, but they are expected to have the similar foam-degrading effects.

Why Do Fluorine-Free Foams Become Flammable & Degraded When Contaminated With Fuel Whereas Film-Forming Foams Do Not?

1. Hydrocarbon surfactants attract fuel.

All firefighting foams including F3 foams contain fluorine-free surfactants used mainly as foaming agents: some are derived from natural products such as protein hydrolyzates, while many others are synthetic hydrocarbon surfactants. F3 foams generally contain very high levels of fluorine-free surfactants, especially hydrocarbon surfactants, to compensate for other missing ingredients.

Synthetic hydrocarbon surfactants contain hydrocarbon chains with varying lengths in their molecules. These hydrocarbon chains have inherent affinity to oil, a fundamental property known as oleophilicity or lipophilicity, literally meaning oil or fat loving. These hydrocarbon chains which constitute a major portion of the hydrocarbon surfactant molecules attract oil and therefore oil-based fuels, such as hydrocarbons. For example, n-octyl sulfate, a hydrocarbon surfactant commonly used in firefighting foam agents, contains a fuel-loving hydrocarbon chain, CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂-(C8), and heptane, a test hydrocarbon fuel commonly representing Class B fires in many foam standards, contains the same, but different length hydrocarbon

Table 2 – Stability Test Results of Gasoline-contaminated Foams

Test Foam Agent	50% Foam Collapse Time (Min.)
Fluorine-free Foam Agents	
Product A-F3-6%	4.6
Product B-F3-3%/6%	9.5
Product C-F3-3%	4.5
Product D-F3-3%/3%	5.5
Product E-F3-3%/6%	6.7
AFFF / AR-AFFF Agents	
Product 1-AFFF-3%	No collapse*
Product 2-AR-AFFF-3%/3%	No collapse
Product 3-AR-AFFF-3%/3%	No collapse
Product 4-AR-AFFF-1%/3%	No collapse

*Test for all AFFF/AR-AFFF samples were terminated at 10 minutes.

chain, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (C7). The longer the length of the hydrocarbon chains, the more oil-loving they get.

F3 foams with very high levels of hydrocarbon surfactants thus have the inherent problem of attracting hydrocarbon fuels more strongly than fluorine-containing foams, especially film-forming ones. Natural protein foam (P), one of the oldest and most effective fluorine-free foams, despite its well-known, superior foam stability, still cannot be used in subsurface applications because of this fuel pick-up problem. For these applications, a small amount of fluorosurfactants is used most effectively in FP foams to prevent this fuel contamination problem.

2. Fluorosurfactants repel fuel.

Unlike the oleophilic (oil loving) hydrocarbon surfactants that attract fuel, fluorosurfactants contained in the film-forming foams are inherently oleophobic/lipophobic (oil/fat hating) and they repel fuel. Fluorosurfactants used in fire-fighting foams, such as AFFF, FP and FFFP, contain in their molecules a common chemical functionality that is responsible for the fuel repellency, a perfluorinated chain, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2$ -(C6), which is a common backbone of C6-telomer-based fluorosurfactants currently used in film-forming foams.

These perfluorinated chains are also responsible for the fluorosurfactants' low surface tension and heat stability. These C6-telomer-based fluorosurfactants are recognised as safe for continued use, because they are not bioaccumulative and have very low toxicity profile. They are very different from the PFOS (C8)-based fluorosurfactants, which have been shown to be a PBT (Persistent, Bioaccumulative and Toxic) chemical, and are consequently now banned from use in fire-fighting foams in many countries.

When foam bubbles are generated from a firefighting foam solution containing both hydrocarbon surfactants and fluorosurfactants, both surfactants adsorb onto the foam bubble surface and help stabilise the foam. The fluorosurfactants, however, preferentially adsorb and align themselves on the bubble surface with the oleophobic fluorinated chains sticking out into the air due to their higher surface activity, a measure of their lower surface tension. This provides varying levels of fuel repellency and hence protection against fuel pickup into the foam blanket. In contrast, F3 foams without any such fluorosurfactant protection will pick up substantial amounts of hydrocarbon fuel, leading to significant problems of flashback, edge flicker fires and re-ignition during firefighting applications.

3. Hydrocarbon fuel can spread over the F3 foams, but cannot spread over the film-forming foams.

The development of AFFF in the early 60s was based on the discovery that the fluorosurfactants impart not only very low surface tensions to their aqueous foam solutions, but also fuel repellency and thermal stability against heat breakdown of the foam bubbles. It was also discovered that the low surface tension provided by the fluorosurfactants, when coupled with the low interfacial tension provided mainly by the hydrocarbon surfactants, makes it possible for the aqueous foam solutions to spread spontaneously and form an aqueous film on the fuel surface (the spreadability of foam solution over the fuel).

This aqueous film formation and its role in the firefighting effectiveness of AFFF foams for Class B fires is well known and generally understood: it provides a fuel vapour barrier that helps achieve rapid extinguishment and improved burn-back per-

formance. However, the reverse case, in other words, the spreadability of fuel over the foam and its role is not well understood despite its direct, detrimental effects on the flammability of F3 foams when contaminated with fuel.

4. Spreadability of fuel over the F3 foams is causing their flammability and degradation when contaminated with fuel.

We found that the relative spreading tendencies (spreadabilities) of the fuel over the surface of the foam solution, or vice versa, was a key factor that determined the distinctive difference between the flammability of fuel contaminated F3 and film-forming foams.

Spreadability of one liquid over the surface of another liquid is a measure of mutual repellency between the two liquids. For example, all the premix solutions of film-forming foam agents tested showed spontaneous spreading tendencies on all the test fuels, whereas none of the premix solutions of F3 agents showed spreading on any of the test fuels. More importantly, all test fuels showed spontaneous spreading on all of the F3 premix solutions, but none of them showed spreading on any of the premix solutions of film-forming foam agents.

This spontaneous spreading of the fuel over the F3 premix solutions was found to be a direct cause of the flammability and degradation of the fuel-contaminated F3 foams. In the case of the fuel-contaminated film-forming foams, the fuel particles remain literally trapped and wrapped around by the foam solution contained in the foam bubbles, much akin to the oil drops in an oil-in-water emulsion, and therefore the fuel particles are not exposed to air for burning in the presence of an ignition source.

The detrimental effect of fuel contamination on the stability of the contaminated F3 foams is due to the spreadability of the fuel over the foam bubbles. The spreading fuel over the bubble surface destabilises the foam bubbles, which leads to their collapse.

In this paper, only the foam flammability and degradation data are presented and discussed. A follow-up paper containing more detailed analyses of the aforementioned relative spreadability data in relation to the flammability and degradation of fuel-contaminated foams will be presented in a science/technical journal.

Conclusions

The reproducible fuel-contamination simulation tests carried out in these laboratory experiments represent an extreme case of a fuel pick-up or contamination situation. However, it is clearly demonstrated that the flammability and degradation of fuel-contaminated F3 foams are both fundamental problems. These problems are caused by the presence of large amounts of the inherently fuel-attractive hydrocarbon surfactants and the absence of fuel-repellent fluorosurfactants in the F3 foam and their high surface tensions relative to those of the hydrocarbon fuels.

When compared with the film-forming foams, this fundamental foam flammability problem with F3 foams can be more detrimental to their overall performance than their lack of film formation in fighting hydrocarbon fires. This foam flammability issue can severely limit the range of applications for F3 foams, suggesting only gentle applications of an aspirated foam are appropriate to avoid the foam-destroying and flammability-causing effects of these fuel contamination problems, when more forceful application is usually desirable.

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