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WHAT PROPERTIES MATTER IN FIRE-FIGHTING FOAMS?

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WHAT PROPERTIES MATTER IN FIRE-FIGHTING FOAMS?

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SUMMARY

The perfluoroalkyl sulphonate surfactants used in film-forming fire-fighting foams and a range of other applications have been classified as so-called persistent organic pollutants (POPs). The US EPA has recently introduced restrictions which effectively stop further production of perfluoroalkyl sulphonate-based surfactants, such as perfluorooctyl sulphonate (PFOS) and its salts, in the USA. The US EPA has also commissioned a hazard assessment study of perfluorooctanoic acid (PFOA) and its salts, in which the initial findings appear to identify issues that could lead to the potential phase-out of the PFOA surfactants. Thus it seems inevitable that in the foreseeable future the use of fluorinated surfactants will be substantially regulated for all but a small number of critical applications. As a consequence of their highly dispersive use, it is likely that fluorinated surfactants included in fire-fighting foam formulations will be scrutinised closely by environmental authorities around the world.

This paper reviews the existing protocols for testing the extinguishment of liquid-fuel fires with aqueous foams. The requirements and objectives of the testing protocols are critically appraised. Subsequently, the paper explains the fire suppression behaviour of foams in terms of the fundamental properties of these materials including their bulk viscosity, yield stress, drainage rate and interbubble gas diffusion (coarsening). The limitation of the spreading coefficient, as presently defined, is also explored, and the need for dynamic measurements of surface tension and surface viscosity is stressed, together with a need to gain a better understanding of the interfacial forces between a hydrocarbon fuel and a spreading foam. The paper also argues that replacements for presently used film-forming chemicals that would be environmentally acceptable are unlikely to be developed. From this perspective, new research needs to focus on developing new foam formulations that produce low bulk viscosity and very low yield stress foams, which are also characterised by better stability including slower drainage and reduced coarsening rates.

1. INTRODUCTION

Fluorinated surfactants [Kissa, 2001] have become one of the critical components of high performance film-forming fire-fighting foams, applied against fires of liquid fuels (Class B combustible). For this reason, all foams used on liquid-fuel fires came to be denoted as Class B foams, as opposed to Class A foams that are routinely employed for fighting fires of carbonaceous materials (Class A combustibles). From this perspective, the present paper focuses on Class B foams.

An example of a common fluorinated surfactant is the sodium or potassium salt of perfluorooctanysulfonate derivative, $C_8F_{17}SO_2-R-COONa$ or $C_8F_{17}SO_2-R-COOK$, consisting of a perfluorinated tail, link section $-SO_2-$, hydrocarbon chain that can contain amine function and a hydrophilic (water attracting) head group $-COO^-$. The head group of a fluorinated surfactant is either ionic or highly polar giving it the hydrophilic properties, with the most common being *anionic* groups such as in $-COO^-$, as in $C_8F_{17}SO_2N(C_2H_5)CH_2COOK$. It is the perfluorocarbon chain, however, that gives fluorinated surfactants their unique and highly-desirable property, namely the chain is simultaneously water repellent (that is, it is hydrophobic) and has no attraction for fat (that is, it is lipophobic). No other common surfactant exhibits this property. In a three-phase air-water-hydrocarbon

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system that exists at the base of a fire of a hydrocarbon liquid mitigated with aqueous foam, a fluorinated surfactant positions itself at the foam solution-air interface, with the head group in the aqueous solution and the perfluorocarbon chain sticking in air, as is pictorially illustrated in Figure 1. This leads to the formation and spreading of thin aqueous foam-solution films on surfaces of hydrocarbon liquids. Such films limit the evaporation of fuel by imposing a barrier to mass transfer and decrease the heat flux from the flame to the fuel.

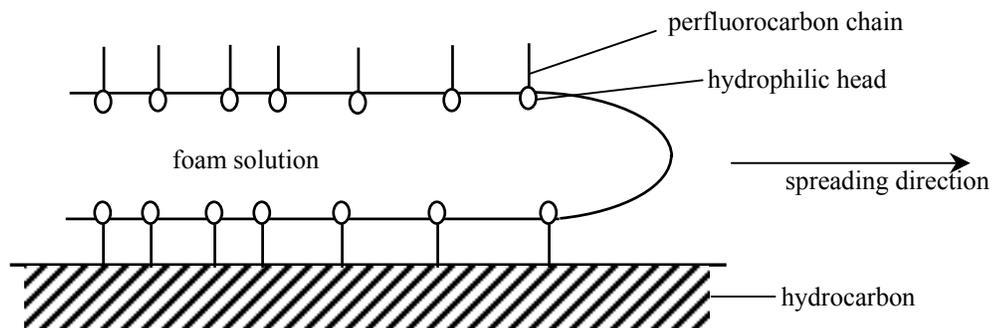


Figure 1: Schematic diagram of a thin film spreading on the hydrocarbon surface. The size of the surfactant molecules, which is miniscule in comparison to the thickness of the thin film, has been greatly exaggerated. For simplicity, the location of molecules of hydrocarbon surfactants (as oppose to fluorocarbon surfactants) is not shown.

There are three groups of fluorinated surfactants associated with uses in film-forming foam concentrates: (i) perfluoroalkyl sulphonates (PFAS) and their derivatives (including PFOS, perfluorooctyl sulphonates); (ii) perfluoroalkyl fatty acids (PFFA) such as perfluorooctanoic acid (PFOA) and its derivatives and (iii) fluorinated telomers such as $C_6F_{13}C_2H_4OH$ or $C_8F_{17}C_2H_4OH$ and its derivatives. PFAS and PFFA are manufactured by electrochemical fluorination, a process that involves passing an electric current through solution containing hydrogenated reactants (such as $C_8H_{17}SO_2H$ or $C_7H_{17}COOH$) and dissolved hydrogen fluoride. The process yields a mixture of straight and branched fluorinated chemicals requiring further separation. The telomer synthesis involves the reaction of tetrafluoroethylene with other fluorinated chemicals, yielding a mixture of straight-chain chemicals, which may still necessitate some separation steps. The telemerisation process resulting in perfluorinated-chain products can be used for production of PFFA as well.

The perfluorinated alkyl chain in surfactant molecules is remarkably stable and chemically inert, both properties also characteristic of other perfluoroalkyl-type chemicals, such as CFCs. From this perspective, concerns have been raised that all PFAS and their derivatives released to the environment eventually degrade to perfluorooctanesulphonic acid (PFOSH) or similar molecules which do not decay further by photolytic, hydrolytic or biological means, and tend to be highly persistent in the environment. The compound is also bioaccumulative and toxic. Recent animal studies indicated potential developmental, reproductive and systematic toxicity of PFOSH [Renner, 2001]. Apparently, PFOSH binds to blood protein and is then circulated in the human body accumulating in the liver and gall bladder. It has been proposed that the body mistakes PFOSH for bile acids and cycles it as it would have done with genuine bile acids. The discovery of low levels of PFOSH and its precursors in the human population and in the wildlife prompted the 3M Company to voluntarily phase out 90 PFAS chemicals by 2003. It should be stressed that this was a pre-emptive measure, as no adverse effects of these chemicals have been reported, either in humans or wildlife.

Following the announcement by the 3M Company on the phase-out of PFAS chemicals, the US EPA has introduced regulations, including the significant “new use” rule (SNUR) effective March 2002. The SNUR impacts 13 PFAS chemicals, which were commonly used in carpet, fabric, leather, textile and paper-coating applications. A new proposed rule, whose comment period concluded at the beginning of July 2002, covers an additional 75 PFAS, including chemicals previously included in the film-forming foams, based on the derivatives of heptadecafluorooctanesulphonyl fluoride $C_8F_{17}SO_2F$ [Robin, 2001]. In response to the call for comments on the original PFAS rule issued by the US EPA in 2001, no submissions were received by the agency in support of the continuous use of PFAS in film-forming foams. The only submission received praised the agency for terminating the use of these chemicals. Hence both the advanced stage of the regulatory process and the public awareness of the environmental issues point to an impending formal phase-out of the FPAS-based surfactants in fire-fighting applications in the USA, a development that is likely to be followed by other OECD countries.

The regulatory situation is different with PFFA and fluorinated telomers-based surfactants, as no regulatory controls have yet been imposed. The most likely environmental fate of PFFA derivatives and fluorinated telomers is the ultimate degradation to PFOA, including PFOA. This transformation involves biodegradation of the nonfluorinated part of fluorinated telomers [Moody and Field, 2000].

As is the case for PFAS, PFFA persist in the environment. With respect to bioaccumulation and toxicity characteristics, the initial studies on PFOA and its ammonium salt published in the open literature were enough of a concern that the US EPA commissioned a fully-fledged review [US EPA, 2002]. Based on the available data, the report concluded that PFOA, and more specifically its ammonium salt, bioaccumulates in various tissues in the body including the liver and kidney, is weakly carcinogenic, though it is not mutagenic. The results from acute-toxicity studies are difficult to interpret, and display considerable scatter, varying from low to high toxicity depending on the animal or plant species. The review showed developmental toxicity in rats, with two-generation reproductive toxicity study still under way. Thus it seems inevitable that the future use of fluorinated surfactants will be substantially regulated, for all but a small number of critical applications.

PFFA, especially PFOA, are manufactured in large quantities by 3M Company for the ultimate production of fluorinated rubbers, where perfluorinated chains are immobilised in place by the complex structure of the rubber. 3M Company has terminated the use of PFFA chemicals in dispersive applications, including FC and FX surfactant lines [US EPA, 2002]. However, other manufacturers still provide PFFA and telomer derivatives for film-forming foam formulations that are presently available in the market place.

In general, there are two approaches to replacing film-forming foams: (i) The first is to identify and synthesise new surfactant molecules that do not contain perfluorinated chains but display the desired film-forming properties. This approach was taken by Robin [2001] who proposed to establish a structure-property relationship database in order to find suitable replacement molecules. Based on previous experience, this line of inquiry may not immediately lead to positive outcomes, as fluorinated surfactants appear to possess unique properties. (ii) An alternative approach is to examine all the properties of fire-fighting foams in order to identify the characteristics that need to be optimised in order to provide the overall suppression performance equivalent to AFFF or FFFP⁴ foams, in the absence of the film-forming surfactants. It is this second approach that will be examined and discussed in the present paper. Initially, we summarise and critically examine the existing standards for testing fire suppression properties of foams and surfactant solutions. We then link these properties with the fundamental behaviour of foam and surfactant solutions, including dynamic surface tension and dynamic surface viscosity of surfactant solutions, foam drainage and foam coarsening, as well as foam bulk viscosity and foam yield stress. The major findings of this investigation are summarised in the conclusion.

2. REVIEW OF THE EXISTING STANDARDS

Table 1 provides a brief summary of the testing protocols for evaluating the performance of low expansion foam systems (that is, of expansion of less than 20), foam concentrates and foams themselves, as described in the most commonly used international standards. Except for the US MIL specifications (MIL-F-24385F), national military standards such the Australian Defence Standard [DEF(AUST) 5603D, 1992] are not included in the review. The table gives the scope of each standard together with areas of most frequent applications.

Table 1: Overview of major international standards relating to low-expansion fire-fighting foams. The terms which are underlined indicate performance criteria embodied by a given standard.

Standard	Scope	Application
ICAO ⁵	Foam concentrate: <u>physical properties</u> (pH, v , sedimentation) Foam: <u>extinguishment and burnback performance</u>	Airport safety, can be specified where rapid fire extinguishment is desired
IMO, MSC/Circ. 582	Foam: <u>extinguishment and burnback performance</u> , expansion, drainage Foam concentrate: <u>storage issues</u> (freezing and	Fixed applications on chemical tankers

⁴ AFFF: aqueous film-forming foam; FFFP: film-forming fluoroprotein

⁵ ICAO: International Civil Aviation Organization; IMO: International Maritime Organization; ISO: International Organization for Standardization; EN: European Norm; NFPA: National Fire Protection Association; UL: Underwriters Laboratories

	thawing, heat stability), <u>use of sea water</u> , physical properties (<u>pH</u> , ν , <u>sedimentation</u> , σ , S)	
ISO 7203-1 & EN 1568-3	Foam: <u>extinguishment and burnback performance</u> , expansion, drainage Foam concentrate: <u>storage issues</u> , <u>use of sea water</u> , <u>aging and heat stability</u> , physical properties (<u>pH</u> , ν , <u>sedimentation</u> , σ , S)	General and light industry, petroleum industry, can be specified for military applications
LASTFIRE	Foam: <u>extinguishment, torch-reignition and burnback performance</u> , expansion, drainage	Large diameter fuel tanks, used by petroleum companies
NFPA 11	Suppression systems: system components and system types, system design, installation requirement and acceptance Foam: expansion, drainage Foam concentrate: concentration determination	System design for flammable liquid hazards within buildings, for storage tanks and processing areas; methods for measuring foam expansion and drainage are often referenced in other standards. Testing of in-service foam concentrates.
MIL-F-24385F	Foam: <u>extinguishment and burnback performance</u> , <u>expansion</u> , <u>drainage</u> Foam concentrate: <u>storage issues</u> (compatibility, precipitation), <u>physical properties</u> (refractive index, ν , S), <u>corrosion issues</u> (pH, general and localised corrosion, total halides), <u>environmental impact</u> (LC ₅₀ , COD, BOD), <u>fluorine content</u>	Military (standard designed specifically for AFFF), aviation [Scheffey et al., 1995]
UL 162	Suppression systems: <u>foam producing equipment</u> (sprinklers and spray nozzles, topside discharge, subsurface injection), <u>material compability</u> (e.g. corrosion, aging) and <u>performance</u> (e.g. drop test) Foam: <u>extinguishment and burnback performance</u> , expansion, drainage Foam concentrate: <u>storage issues</u> , physical properties (S), <u>concentration</u>	Petroleum industry, heavy industry, fixed applications, warehouses, aviation [Scheffey et al., 1995], etc

Footnote to Table 1:

ISO 7203-1 and EN 1568-3 appear to be technically equivalent. EN 1568-3 contains, in Annex H, a description of a small scale fire test which could be applied for quality control.

Commercial fire-fighting foams are used in a variety of fire-mitigation systems, including systems designed for protection of weapons, chemical tankers, large petroleum tanks, unit operations in the processing industry, machinery spaces and crash rescue of occupants in civilian and military aviation accidents. The performance criteria of the foams outlined in Table 2 reflect the objective and scope of each standard. These criteria are specified in terms of extinguishment and reinvolvement following torch reignition and burnback, as a function of preburn time, application density, pan size and its construction.

The standards also impose requirements on storage of foam concentrates (heat stability, freezing and thawing, sedimentation), flow properties (viscosity) and corrosivity (pH); Table 3. In addition, foam solutions are tested for film formation (spreading coefficient requiring measurements of surface and interfacial tension) and compatibility with simulated sea-water and powder extinguishants; Tables 2 and 3.

Details of the test protocols and the most pertinent measures of foam and foam concentrate are reviewed below together with relevant discussion. With the exception of LASTFIRE, the standards do not discuss the reasoning behind their methodologies and the selection of the pass/fail criteria. However, for the MIL specifications, these considerations together with the summary of the evolution of the standard from its introduction in 1963 to present, can be found in a paper by Tatem et al. [2001].

Table 2: Summary of extinguishment and reignition tests described in the major international standards for low expansion foams.

Standard	Air temp, wind vel	Nozzle type	Nozzle pressure kPa	Application density L/(min m ²)	Discharge rate L/min; Duration	Pan size and its features m ²	Fuel type; preburn s	Exting time s	Torch test; footnote	Burnback test; start time after exting test	Sea water or powder compatibility
ICAO	Not given	UNI86	700	4.1 or 2.5	11.4; 120 s	2.8 or 4.5, circular, on ground, backboard	Kerosene (Avtur, Jet A); 60	≤60	No	Yes (record 25%); 120 s	See footnote
IMO	15±5°C <3 m/s	UNI86	630±30	2.53	11.4; 300±2 s	4.5, square, on ground, with backboard	Aliphatic hydroc 84-105°C; 60±5	<300	No	Yes (25% in 900 s); 300±10 s	Sea water
ISO 7203-1 EN 1568-3	15±5°C <3 m/s	UNI86	630±30	2.52	11.4; 300±2 s	4.52, circular, on ground, with backboard	Aliphatic hydroc 84-105°C, 60±5	Depends on class	No	Yes (depends on level); 300±10 s	Sea water, if compatible
LASTFIRE	5-20°C <3 m/s	UNI86	600-1000	3.2 or 2.5	14.4 or 11.3; 420 s	4.5, circular, with baffles, no backboard, above ground	Heptane, 180	<420	Yes; 120, & 780 s	Yes (25% in 240 s); 900 s	No
MIL-F-24385F	<4.5 m/s	NFS footnote	680	1.65 or 2.91	7.57; 90 s	2.6 or 4.65, circular, on ground, no backboard	Unleaded petrol; 10	Depends on pan <30 or <50	No	Yes (25% in 360 s); 60 s	Sea water, powder
UL 162, see footnote	Not given	Hose nozzles, monitors	Not given	4 (2.4 for alcohol resistant foams), footnote	18.6 (or 11.16); 180 s	4.65, square, no backboard, on or above ground footnote	Heptane or polar solvent; 60	<180	Yes	Yes (20% in 300 s); 540 s	Sea water

Footnotes to Table 2:

If the torch test is used, the numbers indicate the timing of the test after completion of the extinguishment test. In case of the MIL-F-24385F, a film formation and sealability test is required that involves passing a pilot flame over a foam-free film-covered fuel surface.

ICAO discusses compatibility of protein and AFFF foams with dry powders, but without providing a test protocol.

LASTFIRE specifies two application rates: 3.2 L/(min m²) for foam stream thrown directly onto the fuel surface, and 2.4 L/(min m²) for gentle (topside pourer) addition.

MIL-F-24385F: NFS stands for National Foam System Inc, one of the manufacturers of the type of nozzle stipulated by the standard. The extinguishment (for small and large pans, respectively) and burnback given in the table apply to the design concentration of foam surfactants in the foam solution. The standard also necessitates extinguishment testing of diluted (2x) and concentrated (5x) foam solutions.

NFPA 11 does cover extinguishment and reignition.

UL 162: This standards covers extinguishment tests with sprinklers, spray nozzles, topside (such as hose stream nozzles and monitors) and subsurface discharge devices. The table summarises the details of the testing protocol only for hose stream nozzles and monitors discharging AFFF and FFFP foams. If the pan is located above the ground (max 305 mm) skirting must be provided on at least three sides of the pan.

2.1 Air Temperature and Wind Velocity

Low ambient temperatures promote cooling of the fuel, decreasing its vapour pressure and resulting in less challenging and easier to suppress fires, which are more difficult to ignite and reignite. Precipitation destroys foams on contact making fires harder to suppress. Wind can assist or inhibit fire-fighting efforts, depending on the particular situation. Although these conditions are directly relevant in actual fire scenarios in which foams are expected to operate, for comparison purposes, tests require an element of reproducibility. For this reason, most standards specify the acceptable ambient temperature range, the maximum wind velocity in the vicinity of the pan and no precipitation (UL 162), if experiments are performed in open space.

2.2 Nozzle Type

It appears that a small UNI-86 type nozzle is widely accepted in all standards reviewed in the present paper, except for the US military specification and UL 162. The latter standard is designed to test a foam concentrate in conjunction with a specific discharge device. The UNI-86 is a long device, approximately 42 cm in extension, whereas the NFS nozzle used in MIL specification is much shorter. The NFS nozzle can be equipped with a fanning tip to allow foam to emerge in a sheet-like fashion rather than as a stream. The nozzle flow rates are listed in column 6 of Table 2.

2.3 Application Density, Discharge Rate and Its Duration

These parameters vary between tests, depending on the objective of each testing protocol. MIL-F-24385F and ICAO (performance level B with 4.5 m² pan fire and the application density of 2.5 L/(min m²)) demand extremely rapid knockdown (90 s for MIL and 120 s for ICAO) at very low application densities of 1.65 and 2.5 L/(min m²), respectively. In the case of ICAO protocol, these requirements follow from the survivability conditions within an aircraft, some distance away from a fire, which are around 1-2 min in duration [Scheffey et al., 2001]. For MIL standard, the objectives are to minimise thermal damage to high-value weapons systems and provide maximum opportunities for occupant rescue, especially within the context of rapid extinguishment of pool fires on the flight deck of an aircraft carrier.

The LASTFIRE protocol allows a relatively long suppression time of 420 s. However, this protocol is designed to gauge the foam performance for extinguishment of a large tank fire, for which the foam's spreading ability and its thermal resistance are more relevant. For these reasons, LASTFIRE introduces a long preburn time of 180 s and stipulates baffles in the pan design.

2.4 Pan Size and Its Features

Both circular and square steel pan sizes have been used in fire extinguishment testing, with the most common size being 4.5 m². This pan size allows fires of about 5 MW in magnitude, capturing the fundamental behaviour of radiation-controlled liquid-fuel fires. For longer preburn times, corners in square pans and circular pans with baffles are more difficult to penetrate by the flowing foam, thus creating more challenging suppression scenarios. In the case of the US MIL standard, the very short preburn times results in fires over circular pans, which are apparently more demanding to suppress than fires over square pans.

Fires on the top of pans buried (this geometry is sometimes used to test fire extinguishers) in the ground and flashed with the soil surface are usually the easiest to extinguish. When a pan is placed in the ground or positioned on short legs, as is the case with LASTFIRE, the extinguishment impediment increases. This is because the rate of heat transfer from the fuel to the soil is fastest for pans buried in the ground.

The pan's side walls (lips or shell) are usually specified as 200 mm in height (ICAO, IMO, ISO), though both UL 162 and LASTFIRE necessitate taller shells. This adds to the difficulty of extinguishment, owing to larger surfaces of hot metals present during the extinguishment.

All testing protocols call for placing a water layer below the fuel. This is done to reduce the consumption of fuel in a test and to limit damage to the pan. The horizontal surface produced by the underlying water ensures combustion over the entire pan surface throughout the test. The thickness of a layer of fuel floating on water, as prescribed by the standards, is sufficient to prevent mixing of the foam with the underlying water in forceful applications, as this would destroy the foam.

2.5 Fuel Type and Preburn Time

Fires of low flash-point liquids (e.g. heptane or petrol) are more arduous to extinguish than fires of high-flash point fuels (such as diesel oil). Low flash-point fuels are characterised by higher vapour pressures, which makes these fuels easier to ignite and reignite and more difficult to seal when they are hot. This is important both during fire mitigation and immediately after the extinguishment, which could be followed by a rapid reignition. From the existing standards, only the ICAO protocol which is designed to test foams on pool fires due to aviation accidents stipulates kerosene (aviation turbine jet fuel), a high-flash point fuel containing hydrocarbons that distil between 190 and 250°C from crude oil. MIL specifications require unleaded petrol that normally would contain hydrocarbons boiling between 30 and 75°C, ensuring a very rigorous testing scenario for the sealing properties of AFFF formulations. This requirement follows the argument that petrol may be present in fires involving military hardware. Other standards use heptane that has a boiling point of 98°C, or a mixture of aliphatic hydrocarbons characterised by a range of boiling points between 84 and 105°C.

Alcohol resistant foams (AR or ATC – alcohol type concentrate in the 3M terminology) are tested on fires of polar liquids such as isopropyl alcohol or dimethyl ketone, which have boiling points of 82 and 56°C, respectively (UL 162). The AR-AFFFs contain polymeric additives that form a water impermeable membrane at the interface between foam and a polar liquid, which prevents water from leaving the foam after an initial delay time [Woodworth and Frank, 1994].

It can be seen in Table 2 that most standards require 60 s preburn times. The two exceptions are LASTFIRE (180 s) and MIL (10 s). The longer preburn time in LASTFIRE was chosen to provide a more demanding test for ranking various foam formulations, under conditions corresponding to large tank fires. The text of the MIL standard provides no reasoning on the 10 s preburn time. Shorter residence times would favour fire mitigation by spreading films rather than by flowing foams, which is in agreement with the objectives of the standard, that is to test the rapid knockdown of the fire at low discharge rates.

Longer preburn times make extinguishment of open-space hydrocarbon fires more challenging with aqueous foams. This occurs for two reasons: (i) The walls of the fuel pan heat up, providing hot metal surfaces for reignition and contributing to foam attrition. In addition, in the case of LASTFIRE, the baffles establish obstacles for spreading foam creating artificial corners which are difficult, for the foam, to penetrate and seal. (ii) Longer preburn times allow more heating of the fuel. Although the surface temperature of the fuel does not change with the duration of preburn (except for multicomponent fuels for which fractional distillation takes place), the temperature profile below the surface becomes flatter as the average fuel temperature increases. This means that the fuel is less amenable to cool down by the foam blanket and the foam itself is subjected to additional attrition. In support of this argument, it has been observed that the first foam flakes landing on hot fuel surface are destroyed and a continuous foam blanket forms only after some delay time [Persson et al., 2001]. It should be noted that foam viscosity decreases with foam temperature. Thus a foam heated by the radiation given off by a fire tends to flow faster than a cold foam [Persson et al., 2001].

2.6 Extinguishment

The US military and the international civil aviation standards impose the most stringent criteria on the extinguishment time of 30 (or 50, depending on pan size) and 120 s for MIL and ICAO standards respectively. This is understandable considering that the present design of aircraft for survivability allows about 90-180 s

[Scheffey et al., 1995, 2005] before critical impact occurs. Within this very short time frame, the airport fire brigade must arrive at the accident site, initiate fire suppression and extinguish a fire. Similar design criteria apply to protecting weapons systems against thermal damage.

As far as we know, only fluorosurfactants-based foams have passed the MIL-F-24385F standard. It appears that the rapid control of pool fires with non film-forming foams can only be achieved if the application density stipulated in MIL specifications is increased to approximately 2.5 L/(min m²). Higher discharge densities in military applications, especially on aircraft carriers would require major reengineering of the existing systems at substantial cost [Scheffey et al., 2001]. Such costs will be the major obstacle for any national armed forces to phase out its use of film-forming foams.

Longer extinguishment times specified by LASTFIRE and IMO standards reflect a different set of requirements in suppressing large tank and ship fires. For these applications, the spreading ability of foams (rather than thin films), its thermal resistance, the propensity to withstand burnback and sealability are much more important.

2.7 Torch Test

This test is designed to determine the diffusion of the fuel through the foam blanket and the extent of fuel pickup by the forceful deposition of foam on the fuel surface. AFFF and FFFP foams usually display good fuel shedding properties as opposed to unmodified protein foam which tend to retain the fuel as a consequence of a forceful application (Woodworth and Frank, 1994). The test is performed by passing a lighted torch above the entire foam blanket at a distance of 25 mm in case of UL 162 and 75 mm in case of LASTFIRE. Small flaming followed by self-extinguishment is acceptable according to UL 162 and for a level 2 pass according to LASTFIRE. The amount of fuel picked up by the foam depends on the interfacial tension between the fuel and foam solution. In general, the smaller the interfacial tension (which is desirable for film forming) the more mixing takes place.

2.8 Burnback

The burnback test starts with removing a portion of the foam coverage. The uncovered fuel is then ignited and the time for the fire to spread to cover 25% of the pan size, or 20% in the case of UL 162, is recorded. The test is performed after a delay time, which varies between specifications, as shown in Table 2. The test commences after the cessation of foam application. The delay time is very important, and has to be considered an integral part of the testing protocol. Longer delay times allow more drainage and therefore make the foam more susceptible to burnback.

In the past, AFFF formulations displayed relatively rapid drainage and low solution holdup in comparison to fluoroprotein based foams. This translated into somewhat reduced burnback performance of AFFFs in comparison to FFFP and FP⁶ foams [Woodworth and Frank, 1994]. This is not the case anymore as the MIL specifications provide a rigorous test procedure, and those foam formulations that pass the MIL test (360 s burnback that follows 60 s delay time) possess relatively good burnback resistance. The MIL performance criteria are unlike the specifications of ICAO that only require recording the 25% burnback time, after 120 s delay time.

Other standards that are not as focused on military and aviation applications, as MIL or ICAO, are driven by different objectives, and necessitate substantially longer burnback times or delay times or both. For example, LASTFIRE demands 900 s delay time and 240 s burnback time (1140 s in total) and IMO necessitates 300 s delay time and 900 s burnback time (1200 s in total).

2.9 Sea Water and Powder Compatibility

In some applications, the availability of sea water and the limited supply of fresh water (chemical tankers, aircraft carriers) makes sea water a convenient choice for diluting the foam concentrate. Accordingly, IMO, MIL and UL standards require suppression testing with sea water, whereas ISO specifies the test only for foam concentrates marked compatible with sea water.

⁶ FP: fluoroprotein

The performance requirements for compatibility with dry powders are embedded only in the MIL specifications. In general, the compatibility with dry powder increases from protein foam (not compatible) to FP and FFFP (reasonably compatible) and AFFF (compatible) [Woodworth and Frank, 1994].

2.10 Drainage and Expansion

The majority of the standards necessitate measurements of foam drainage and foam expansion, which is usually done by methods described in NFPA 11. Foam drainage is quantified by reporting the time when 25% of surfactant solution, initially present in the foam, drains. Except for the MIL specification, the 25% drainage time and foam expansion are not applied for gauging the performance values. Rather, the measurements are used to ensure that these foam parameters do not vary, outside a prescribed range, between the foam tested according to the standard against a benchmark fire and the characteristic values associated with the actual fire-mitigation system. The drainage and expansion measurements also serve as yardstick parameters for comparison of the effects of sea water and temperature conditioning on foam concentrates.

The MIL-F-24385F specifies a minimum 25% drainage time of 2.5 min and the minimum expansion of 5. As opposed to protein-based foams, surfactants present in AFFF formulations form mobile interfaces between air in the foam bubbles and liquid present in lamellae and channels (plateau borders) [Magrabi et al., 2002]. This results in very fast draining rates for AFFF solutions in comparison to protein solutions, as the latter form stationary interfaces characterised by much higher surface viscosity – a parameter that governs the flow in channels between bubbles. This will be described in more detail in the next section.

Table 3: Summary of specifications for foam concentrates and foam solutions.

Standard	pH	Kinematic viscosity mm ² /s	Spreading coefficient mN/m	Sedimentation vol %	Freezing and thawing	Temp dependence/ heat stability
ICAO	6-8.5	<200	Not required	<0.5	Not given	Not given
IMO	6-9.5	<200	>0	<0.25	Yes	Yes
ISO 7203 & EN 1568	6-9.5	<200	>0 (if film forming)	<0.25	Yes	Yes
MIL-F- 24385F	7-8.5	<20	>3	<0.05	Not given	Yes
UL 162	Not given No test if raining	Not given	>0 (if film forming)	Not given	Not given	Yes

Footnotes to Table 3:

The kinematic viscosity for the ISO standard is measured between 1 and 3°C above the lowest temperature for use. Presumably, the same applies for ICAO and IMO standards, but it is not clearly stated. In the case of MIL, the value given applies at 5°C.

Mil-F-24385F provides the most comprehensive list of performance requirements for foam concentrates and foam solutions. In addition to what is listed in Table 3 and in the last column of Table 2, the standard imposes criteria on corrosivity (corrosion rate and total halides concentration), biological and chemical oxygen demand, toxicity and chemical composition (fluorine content, refractive index).

2.11 Spreading Coefficient

The performance criterion on the spreading coefficient (>0 or >3 mN/m in case of MIL specifications; see Table 3) was introduced to test the film-forming capability of foam solutions. The coefficient is defined as

$$S = \sigma_{\text{cyclohexane-air}} - \sigma_{\text{foam solution-air}} - \sigma_{\text{cyclohexane-foam solution}} \quad (1)$$

and necessitates the measurement of two equilibrium surface tension and one equilibrium interfacial tension values. To obtain a large positive coefficient S , both $\sigma_{\text{foam solution-air}}$ and $\sigma_{\text{cyclohexane-foam solution}}$ need to be small. One

should be mindful to ensure that the interfacial coefficient remains sufficiently above zero to minimise fuel pickup, as a consequence of the mixing between foam solution and fuel.

A spreading coefficient close to zero is usually not a good indicator of the propensity of a foam solution to develop spreading films. Examples of foam solutions with small positive coefficients are known to yield no spreading films. There are three reasons for this: Firstly, the expression for the spreading coefficient follows from the thermodynamic (equilibrium) considerations of the minimum Gibbs free energy. However, the spreading process is a dynamic phenomenon. A new interface is continuously being created at the leading edge of the film. This interface is initially depleted of the surface-active agents. The surfactants do diffuse along the interface due to the gradient in the surface concentration to re-establish the equilibrium concentration, but this takes time. Unfortunately, no measurements of the dynamic surface tension of fire-fighting foam solutions have been reported in the literature

Secondly, all tension coefficients decrease with temperature, with the spreading coefficient usually decreasing with temperature as well. This is important since under fire conditions the spreading coefficient can become negative, as foam solution spreads over a hot fuel surface.

Finally, the value of S is obtained for cyclohexane as a reference fuel; the actual fuel in the field may be different and may contain its own surfactants. This is not a conservative approach as one would expect from fire-safety standards. The surface tension of cyclohexane in air is 25.5 mN/m [Woodworth and Frank, 1994]. From this standpoint, the use of n-hexane ($\sigma = 18.4$ mN/m) or isooctane ($\sigma = 17.6$ mN/m) would perhaps be a more conservative choice for a reference fuel in the definition of the spreading coefficient.

2.12 Future of Class B Foams

New short-chain fluorinated surfactant chemistries are being pursued to develop a new generation of film-forming foams. One such an attempt is an AFFF formulation that incorporates derivatives of perfluoroalkoxycycloalkane carbonyl fluoride with fluorinated pendant 1-4 carbon groups [Hansen et al., 1997]. However, no new foam concentrates based on the new chemistry have been brought to the market place, perhaps as a result of the costs involved in testing the compounds of interest for toxicity, bioaccumulation and degradability.

Other approaches include the development of AFFF alternatives that do not display the traditional film-forming characteristics but have other desirable properties, such as low drainage, high thermal stability, low viscosity and very low yield stress. Aqueous foam with such properties provide a good seal against fuel vapours since it tends to close (heal) a broken foam blanket. (These properties are reviewed in more detail in the next section.) For example, a new non-fluorinated foam formulation developed by 3M Company in Australia has recently passed the demanding ICAO performance level B test (4.5 m² pan fire with the application density of 2.5 L/(min m²). Along a similar line, Chemguard Inc. is introducing a new line of Class B foams that are non film-forming. Chemguard Inc. claims that its new formulations satisfy the UL 162 performance test [Anonymous, 2002]. Thus it appears that new alternative formulations for Class B foam should be able to pass all existing performance specifications, with a possible exception of the suppression test of MIL-F-24385F, which was particularly designed to test the film-forming properties of foam solution.

3. FUNDAMENTAL FOAM PROPERTIES

3.1 Foam Drainage

At gas fractions below 0.64, foam bubbles are always spherical in shape. Even above 0.64, in the case of polydisperse foams, small bubbles may fit well into the space left unoccupied by bigger bubbles, to yield foams with spherical bubbles. In general, however, as the gas fraction increases bubbles start to touch each other forming polyhedral foam structures. Some of the concepts used to describe foam morphology are illustrated in Figure 2. A film between two bubbles is called a lamella, a channel formed between three bubbles is named a plateau border, and a junction of three plateau borders is termed a vertex.

The borders (interfaces) between thin films and bubbles (and between plateau borders and bubbles) may be stationary or mobile, depending on the surfactant solution used to generate the foam. If the interface is mobile, a foam solution drains from the foam quickly, as the drainage is assisted by moving boundaries. For stationary interfaces, the velocity of the flowing solution is zero at the interface, which results in slower drainage. These

phenomena and their implication to foam drainage were first reported by Koczko and Racz [1987]. In the rheological vernacular, the parameter which reflects the interfacial mobility is known as the surface shear viscosity or surface viscosity. As far as we know, no measurements of Newtonian (low shear) and non-Newtonian (shear dependent) surface viscosity have been carried out for solutions of fire-fighting surfactants. This situation reflects the lack of dynamic interfacial-tension data described in the previous section. Not surprisingly, even the most complex models of foam drainage are unable to provide accurate predictions for fire fighting foams for drainage time longer than about 200 s; as illustrated in Figure 3.

Recently, Magrabi et al. [2002] performed a comparative analysis of drainage characteristics of two commonly used film-forming foams, AFFF and FFFP. These researchers demonstrated remarkably different drainage and coarsening behaviour of AFFF and FFFP foams, in spite of similar densities and bulk viscosities of both foam solutions. The explanation lies in the difference in the value of the surface viscosity, which engenders mobile interfaces for AFFFs and stationary interfaces in the case of FFFP.

A concerted research effort is required to collect the dynamic viscosity data for various foam solutions and to gain an understanding of the effect of the dynamic viscosity on foam drainage. This effort should be paralleled by similar studies on the dynamic surface tension, as this parameter also affects drainage of foams and, in addition, their collapse (Section 3.2) and their coarsening (Section 3.3). Knowledge of the dynamic surface tension would further the understanding of the spreading mechanism of thin films on surfaces of liquid fuels (Section 3.6).

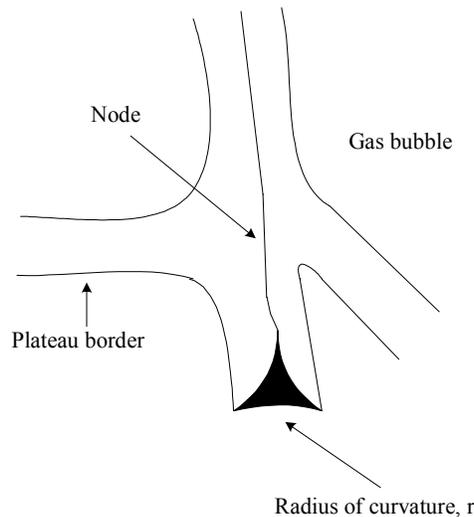


Figure 2: Elements of the idealised polyhedral foam structure.

3.2 Foam Collapse

In a foam blanket spreading over a flammable liquid, the foam at the top of the blanket becomes progressively dry owing to the foam solution undergoing gravitational drainage and evaporation induced by the incident radiative heat flux. Throughout the foam blanket, the thickness of films between adjacent bubbles become thinner as foam solution is piped downwards by a network of plateau borders. Once the film thickness decreases below some critical thickness, the film ruptures and the foam bubbles break, a process that is greatly accelerated in the presence of radiative heat flux. Foam destruction rates as a function of time for thermal radiation in the range of 10 – 35 kW/m² are shown in Figure 4.

Foam collapse proceeds through four well-identified regimes. After an initial exposure to the radiative heat flux, bubbles expand, giving rise to a transient increase in the foam height. The second regime is characterised by rapid drainage forced by expanding bubbles, leading to prompt foam decay. In this regime the foam collapse rates are the fastest. Because of this consideration, delaying the onset of the heat flux-induced drainage would markedly increase foam life. The cessation of the drainage flow gives rise to the third regime, in which the foam collapses by evaporation, at rates substantially below those of the second regime. Heating of the foam sample from below by the hot fuel underlying the foam blanket, gives rise to the boundary effect seen in the fourth

regime. Magrabi et al. [2000] discussed the change in bubble morphology and evolution of the liquid holdup profile after the aging process as a consequence of the imposed heat flux. The aging process involved draining the foam, characterised by the initial expansion of 5, to obtain foams of expansion 20 and 30. Under the imposed heat flux, the aged foams have a comparatively earlier peak drainage rate than the freshly-prepared foams and are less stable than the fresh foams.

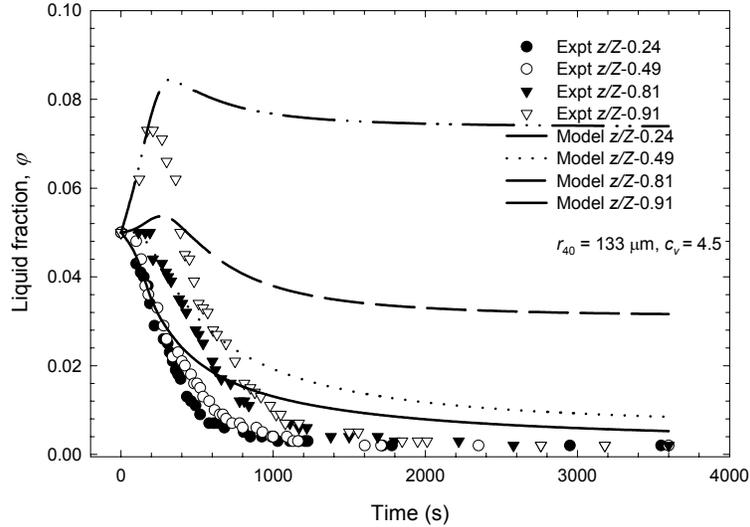


Figure 3: A comparison of the modelled and experimentally measured liquid fraction profiles in a foam column ($\phi_o = 0.05$, $H = 0.2$ m, $c_v = 4.5$, initial bubble size $r_{40} = 133 \mu\text{m}$) at $z/Z = 0.24, 0.49, 0.81$ and 0.91 respectively. The model consists of a partial differential equation of the form:

$$\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial \zeta} \left[\frac{\phi^2}{1-\phi} - \frac{\phi^{1/2}}{(1-\phi)^{3/2}} \frac{\partial \phi}{\partial \zeta} \right] = 0 \quad (2)$$

that needs to be solved with appropriate boundary conditions [Magrabi et al., 2002].

Persson [1992], Magrabi et al. [1997, 2000], Hanauska [2001] and Persson et al. [2001] reported evaporation and drainage rates for foams with and without an imposed external heat flux. These authors also provided empirical correlations for their data. At present, no mathematical description of forced foam decay process is available in the literature and the mechanism remains poorly understood from a quantitative standpoint. Even the additional heat resistance offered by fluorinated surfactants is not well understood theoretically. These are the major obstacles in predicting the interaction between a fire and foam, from first principles.

3.3 Bubble Coarsening

Bubble coarsening arises due to diffusion of gas from small to large bubbles across thin films that separate them. The pressure within bubbles is inversely proportional to the radius of curvature of the bubble surface, which is approximated as the bubble radius. Thus, the mass transfer process in foams is driven by pressure gradient, since pressure in small bubbles exceeds pressure in large bubbles. In practice, bubble coarsening cannot be easily controlled, unless an extra resistance to mass transfer is added at the interface by specifically tailored surfactant molecules. It is also possible to formulate foams with clean gaseous agents (i.e. HFC-227, HCFC-124) that are relatively insoluble in water, which markedly limit the interbubble gas diffusion, and therefore coarsening. However, the large amount of foam that needs to be generated in the course of mitigation of large liquid-fuel fires makes this approach impractical. Thus, the life span of all presently used Class B foams generated with air is eventually limited by coarsening.

The generic mechanism of bubble coarsening is well known [e.g. Magrabi et al., 1999; Gardiner et al. 2000a]. What remains unknown is the effect of the imposed radiative heat on the bubble coarsening and the detailed knowledge of the diffusion coefficients for air through thin films for surfactant-modified interfaces of

importance in fire-fighting foams. Different coarsening regimes of bubbles in a typical film-forming foam are illustrated in Figure 5.

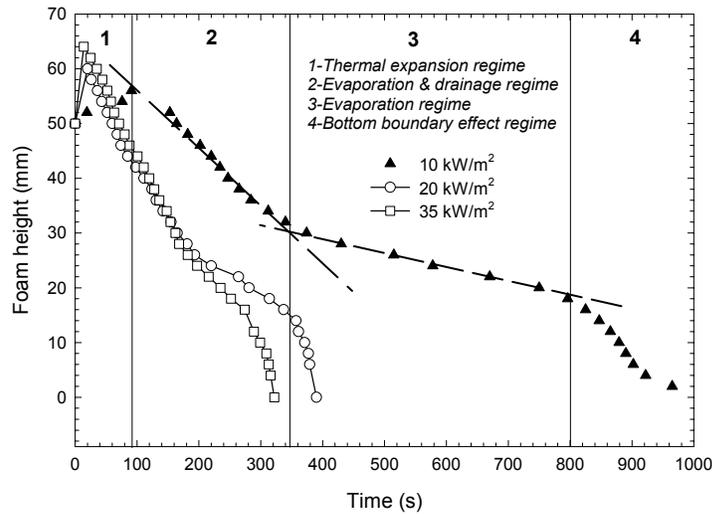


Figure 4: Foam destruction data for compressed-air fire-fighting foam of initial expansion 5. Thermal radiation has considerable effect on the foam decay as observed by comparing the foam collapse plots for 10 and 35 kW/m² [Magrabi et al., 2000].

It should be stressed that foam drainage and bubble coarsening are intimately coupled. Faster drainage leads to more rapid coarsening due to shorter diffusional paths for air transfer between bubbles. On the other hand, coarser foams engender a smaller number of thicker plateau borders with the overall decreased capacity for water holdup. This phenomenon is known as coarsening-induced drainage, as illustrated in Figure 6; compare, for example, the final mass drained for AFFF with the average bubble radii of 133 and 270 μm.

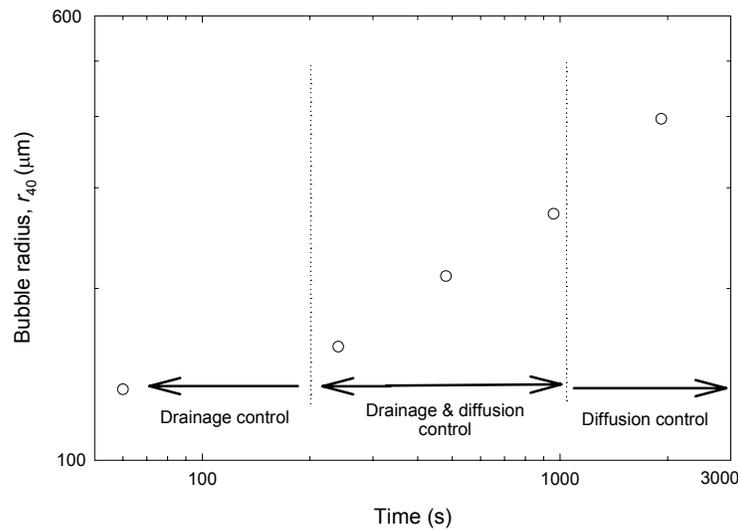


Figure 5: Bubble growth in compressed-air foams ($\phi_0=0.05$) [Magrabi et al., 1999].

3.4 Foam Viscosity

The Herschel-Bulkley model is the most common simple model to describe the steady-state viscosity data of foams and emulsions, including fire-fighting foams. The model has a general form of

$$\tau = \tau_o + k\dot{\gamma}^n \quad (3)$$

where k and n are constants and τ_o is the yield stress. In the special case of $\tau_o = 0$, the Herschel-Bulkley model simplifies to the standard power law model. In another special case of $n = 1$, the model describes the so-called viscoplastic materials, often denoted as Bingham plastics in the rheological literature. Table 4 summarises the parameters of the Herschel-Bulkley model from experimental studies that were conducted over a wide range of gas volume fractions and shear rates. The compilation comes from the doctorate thesis of Gardiner (1999) and includes Gardiner's own data (set no. 7) together with the experimental results of the previous investigators (sets no. 1-6).

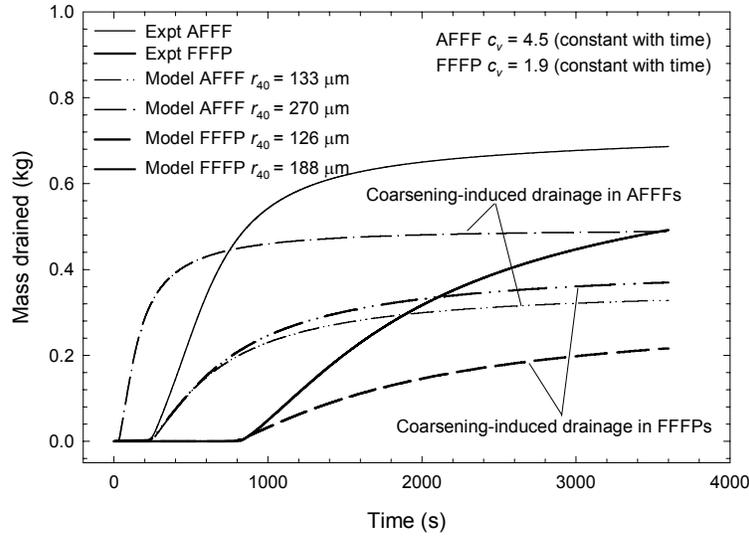


Figure 6: Plot comparing the drainage of foam solution from AFFF and FFFP foam columns ($\phi_o = 0.05$, $Z = 0.2$ m). The graph also shows the modelled drainage profiles in AFFF and FFFP foams using the bubble sizes r_{40} at $t = 0$ and 960 s [Magrabi et al., 2002].

Table 4: Summary of published true foam viscosity data and the models used to fit the data [Gardiner, 1999].

No.	Gas volume fraction	Shear rates s^{-1}	Fitted model	k Pa s ⁿ	n	τ_o Pa
1	0.974-0.996	0.2-18	$\tau = \tau_o + k\dot{\gamma}^n$	1.73-6.8	0.13-0.69	1.32-12.05
2	0.88-0.99	0.2-6.2	$\tau = k\dot{\gamma}^n$	1.43	0.61	
3	0.9-0.94	0.05-500	$\tau = k\dot{\gamma}^n$	18.5	0.5	
4	0.92-0.97	0.01-0.5	$\tau = \tau_o + k\dot{\gamma}$		1	13.5-17.5
5	0.48-0.7	5-1000	$\tau = k\dot{\gamma}^n$	2.5	0.34	
6	0.8-0.83	10-10000	$\tau = k\dot{\gamma}^n$	0.26	0.6	
7	0.81-0.88	2-7000	$\tau = k\dot{\gamma}^n$	2.29	0.29	

There is very little reliable experimental data on fire-fighting foam rheology in the literature. Foams are inherently unstable materials. They evolve by drainage, coarsening, evaporation and, also under fire conditions, bubble break-up, owing to the hot fuel layer and thermal radiation by fire. Thus measurements of foam rheology must be done at time scales which are shorter than the time scales associated with the instability mechanisms. Figure 7 illustrates the experimental results, collected by Gardiner et al. [1998a], which have been carefully corrected for wall slip to yield the actual, rather than instrument-dependent, values of viscosity. At present, it is quite common for fire-safety researchers to collect foam-viscosity data without correcting them for the rheometer-dependent wall slip. Such apparent data can only be useful to compare different foams within a single study and have no fundamental and lasting significance.

As foam moves on the surface of a burning liquid, an expansion gradient develops across its thickness. The foam at the top becomes dry whereas at the bottom of the foam blanket gets wetter. Thus, the foam viscosity

also varies across the foam thickness, and it is important to take this phenomenon into consideration in developing viscosity models. For example, this can be accomplished by the so-called volume-equalisation technique that produces a master-type curve for foams of the same morphology, as it is shown in Figure 8. This figure also illustrates that the viscosity of wetter foams, which are called in Figure 8 as the transitional bubbly-to-cellular foams, is below that of the drier foams normally used in suppression of liquid-pool fires; by definition the viscosity is the ratio of shear stress and shear rate. This means that wetter foam spread more readily on fuel surfaces than dry foam. Wetter foams display lower yield stress, which assists further in their spread. Also note in Figure 8 the difficulty in obtaining reproducible data at low shear rates, that is in the range of interest for extinguishment of pool fires.

The viscosity of fire-fighting foams depends strongly on foam expansion, bubble-size distribution function, liquid phase viscosity, dynamic surface viscosity and the dynamic surface tension. As far as we can see, there are very few investigations of fire-fighting foams in the open literature that include comprehensive foam characterisation. Few experimentalists report the static surface tension, bubble size distributions or liquid phase viscosity. If progress is to be made in gaining a fundamental understanding the spreading mechanism of a foam blanket over hot fuel surface, reliable rheological measurements of well-characterised fire-fighting foams are badly needed.

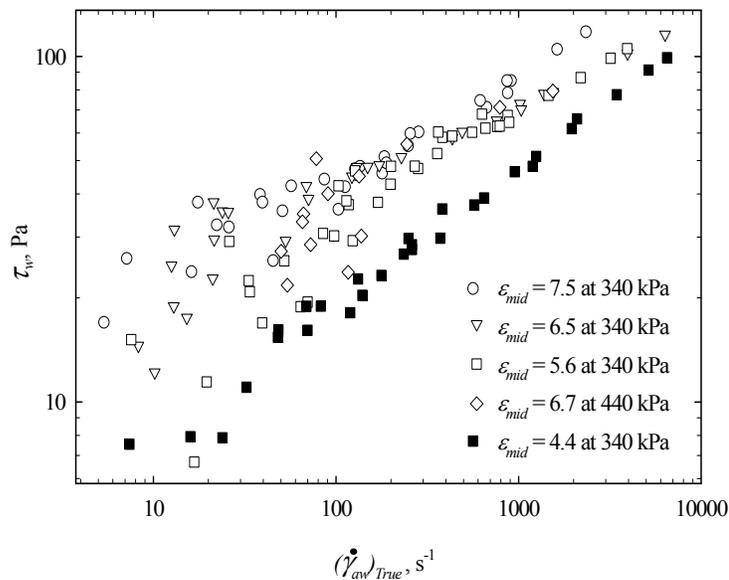


Figure 7: The relationship between yield stress and the corrected stress rate for a series of Class A compressed-air foams studied by Gardiner et al. [1999a].

3.5 Foam Yield Stress

Some apparently fluid materials do not flow unless they are subjected to a shear force. Imagine, for example, compressed-air Class A foam which has the property of sticking to vertical surfaces without flowing down under their own weight. Another realisation of yield stress in fire-fighting foams, this time of Class B foams applied against pool fires, is the inability of some foams to re-heal a broken foam blanket, as a consequence of a hose line dragged across the pool. Foams that display yield stress would not flow back to reseal the broken foam surface. For film-forming foams with yield stress, this is not seen as a problem, as a thin film would rapidly spread on the fuel surface sealing the fuel, providing also some protection against the heat transfer. New foams which are being developed as alternatives for film-forming formulations should exhibit the propensity to re-heal or re-close the broken foam blanket. In other words, they should have low yield stress.

In the rheological literature, the existence of the true yield stress has been the subject of heated debate. Though, it is now appreciated that materials with internal microstructure, such as foams or emulsions, display true yield stress. This is because, at gas fractions above 0.64, bubbles cannot move freely in the foam matrix and can become jammed, unable to move past neighbouring bubbles, unless a force is applied to dislodge them. From this perspective, one can pose a question whether the existence of yield stress is an unavoidable disadvantage of

Class B foams. (Yield stress is an advantage of Class A foams as it allows fire fighters to place these foams on trees and structures in front of an approaching forest fires.)

Figure 9 attempts to address this question by combining a number of experimental results on foams and concentrated emulsions. The figure has been borrowed from a paper by Gardiner et al. [1998b]. All data are scaled by $\sigma/\langle R \rangle$, that is by the ratio of the static surface tension and the average bubble size. From a cursory examination of this figure, it appears that yield stress depends *only* on the gas volume fraction, in addition to surface tension and the average bubble size. This is further corroborated by the data included in the last column of Table 4. The data sets 1 and 4 show that yield stress is important at low shear rates, that is in the range of interest for foam spreading on fuel surfaces. Furthermore, Figure 9 and Table 4 indicate that low-expansion foams display lower yield stress and lower viscosity. Both properties are desired for foam applied against pool fires. It follows that slowly draining foams flow faster than those that dry rapidly, as higher gas fraction imply higher viscosity and elevated yield stress.

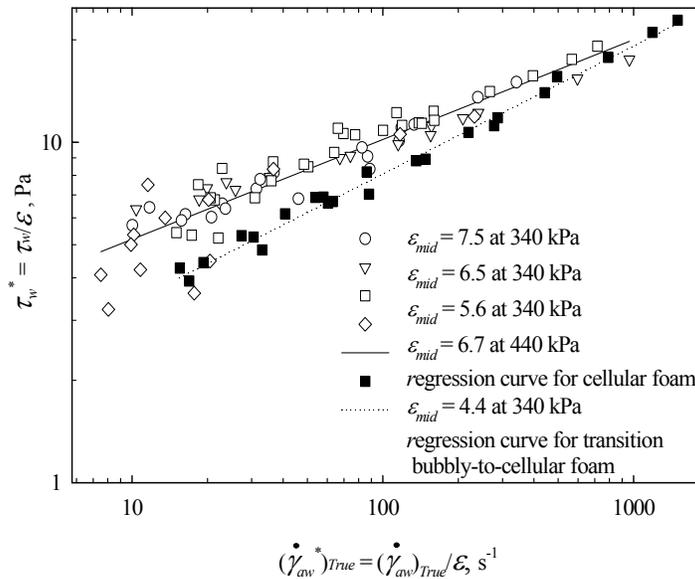


Figure 8: Master curves drawing together shear stress-shear data of foams characterised by different expansion Gardiner et al. [1999a].

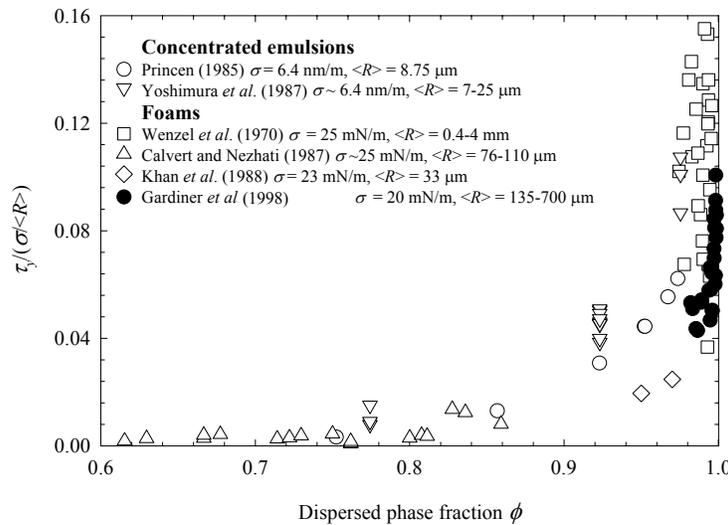


Figure 9: Compilation of yield stress data for foams and concentrated emulsions. References cited in the legend are those listed in the paper by Gardiner et al. [1998b].

However, a closer scrutiny of Figure 9 reveals substantial scatter caused by parameters which were not included in the nondimensionalisation of the yield stress (as defined in the label of the ordinate). The most important of

these are polydispersity of bubble sizes and mobility of the interfaces. The effect of mobility of interfaces on yield stress is yet to be studied but the effect of polydispersity is better known. Foams with monodisperse bubble-size distribution tend to produce packed microstructure that easily blocks the motion. On the other hand, polydisperse foams incorporating a range of bubble sizes can accommodate more readily the microstructural rearrangements during foam flow. The effect of bubble polydispersity on yield stress was studied theoretically by Gardiner et al. [2000b], who examined numerically the yield stress produced by two bubble distributions, as illustrated in Figure 10. Distribution 1 approximates bubble sizes produce by aspirating nozzles, whereas distribution 2 is more akin to compressed-air foams. Figure 11 illustrates the buildup of stress (τ_{xy}) in the foam matrix for the narrow distribution after the imposition of strain (γ). For distribution 1, the stress increases until a critical yield value. This means that foams composed of similar in-size bubbles have a natural tendency to resist flow. In practical terms, foams used for mitigating fires of liquid fuels should contain a wide range of bubble sizes.

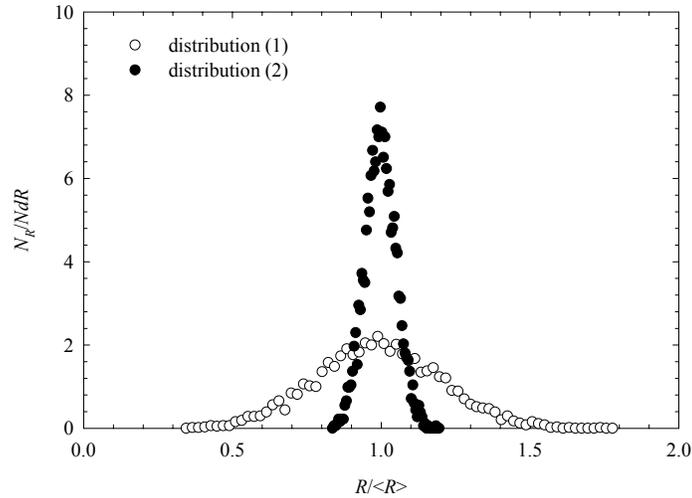


Figure 10: Illustration of two normal bubble size distributions considered in a study on the effect of polydispersity on yield stress [Gardiner et al., 2000b]. SD in the legend stands for one standard deviation.

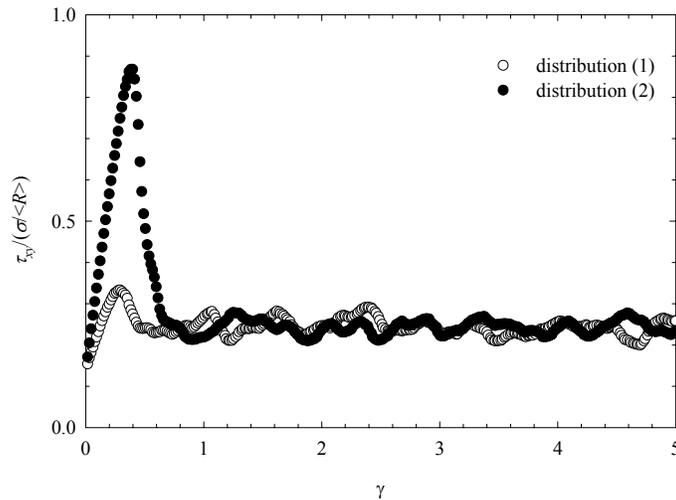


Figure 11: The initial response of τ_{xy} to the imposed shear for the two bubble size distributions shown in Fig. 1; (a) $N = 256$, $\phi = 0.95$, $\dot{\gamma}\tau_d = 0.1$ [Gardiner et al., 2000b].

3.6 Foam Spreading Mechanism

The present mechanistic understanding of foams spreading on surfaces of liquid fuels is based on a momentum balance which includes terms due to inertia, hydrostatic (gravity) forces caused by foam thickness, and resistance to flow at the foam-fuel interphase [Persson and Dahlberg, 1994]. The resistance to flow is expressed via the empirical friction coefficient, which is shown to depend on the density and viscosity of liquid fuel [Persson et

al., 2001]. However, very little is known from a fundamental perspective about the nature of forces acting on the spreading foam blanket by the underlying fuel. Even the simple question of the existence of slip between the fuel and the foam blanket has not yet been addressed, and models with a more realistic representation of foam viscosity are yet to be developed.

4. CONCLUSIONS

The major conclusions of this paper can be summarised in the following points:

- It seems inevitable, that in the foreseeable future, the use of all existing surfactants containing perfluorochains will be regulated, especially in applications associated with the dispersive use of the chemicals such as in fire fighting.
- Two approaches have been suggested in the literature and in this paper to develop replacement formulations for Class B foams: (i) to identify and synthesise new surfactant molecules, using the so-called structure-property relationship, for example surfactants based on short fluorinated 1-4 carbon groups; (ii) to identify and optimise the desirable properties of foams produced from non film-forming surfactant formulations. In this article, we argued that the second approach offers more chances for success in the short term.
- In the text, we also described the desirable properties of non film-forming foams and identified gaps in knowledge that need to be filled in the process of developing new Class B foam replacements. The essential properties of new Class B foams include slow drainage, high heat resistance, slow coarsening, low shear viscosity and low yield stress.
- The most important gaps in knowledge comprise (i) the lack of data on the dynamic surface tension and dynamic surface viscosity, (ii) limited knowledge of foam collapse and drainage induced by the radiative heat flux, (iii) lack of data on diffusion of air across layers of surfactants used in fire-fighting foams, (iv) effect of bubble polydispersity on yield stress, (v) limited amount of true viscosity data collected for well-characterised foams and (vi) limited understanding on the friction mechanism of foams spreading over liquid fuels.

5. ACKNOWLEDGEMENTS

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6. NOMENCLATURE

c_v	velocity coefficient, function of the dimensionless surface viscosity; -
k, n	constants in the Herschel-Bulkley model
N	total number of bubbles in the simulation; -
N_R	number of bubbles of radius R ; -
R	bubble radius; m
$\langle R \rangle$	average bubble radius; m
r_{40}	mean radius defined by the fourth moment; m
S	spreading coefficient; mN/m
Z	height of the foam column; m
φ_o	initial uniform liquid fraction; -
γ	strain; -
ν	kinematic viscosity; m ² /s
σ	surface or interfacial tension; mN/m
τ	shear stress; Pa
τ_d	bubble rearrangement time-scale; s
τ_o	yield stress; Pa

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