AFFF AND ITS ONGOING USAGE IN FIRE FIGHTING WITHIN THE ROYAL AUSTRALIAN NAVY

PURPOSE

1 The purpose of this document is to highlight the likelihood that the AFFF fire fighting foam which is currently used widely within the RAN, and other Australian Defence services, is expected to become unavailable in its current form in the next 1-5 years.

2 There is a current push by the US EPA to remove the chemicals PFOA and PFOS from all products. AFFF contains trace levels of PFOA, these are a by product of the process which fluorinates the foams. Fluorinating foam gives it desirable properties for fire fighting such as heat resistance and spreadability.

3 The removal of PFOA from AFFF will require new foams to be retested against DEF(AUST)5000 Vol 7. Pt 2.

4 As a replacement to the current AFFF, the options will be reformatted AFFF or Fluorine Free Foam. The RAN / ADF needs to investigate these replacement options and identify an acceptable new foam and foam system to replace the current fire fighting foam.

INTRODUCTION

5 The Royal Australian Navy (RAN) currently uses Ansul's Aqueous Film Forming Foam (AFFF) as its main fire fighting foam, this foam is fluorinated and therefore is likely to contain PFOA. This foam comes in two options, one that conforms to US MIL-F-24385F, the other to DEF(AUST)5706, regarding desired qualities, such as burn back, drainage time and expansion ratio. The main advantage of AFFF is the ability to create a thin film over a burning hydrocarbon surface that effectively starves the fire of oxygen. AFFF has been found to be toxic to the environment and is on the list of materials that must be actively contained following its release [1].

6 AFFF is used widely throughout the RAN fleet, as well as within the Australian Army and RAAF for fire fighting applications. It is used predominately in situations where its fire fighting qualities far exceed other foam types, such as aircraft fires and fuel spill fires. Fire fighting foam has many advantages over water when fighting class B fires. Whilst normal water would sink below burning liquid fuel due to the difference in density, the foam does not. It remains on the surface of the liquid fuel and prevents further burning by excluding oxygen, cooling the surrounding area and suppressing further vaporisation [1].

7 Older AFFF concentrates contain perfluro octyl sulphoate (PFOS), while current and some older AFFFs contain perfluorooctanoic acid (PFOA) which can have a

detrimental effect on the environment. For this reason a reduction in PFOA has been pursued within the US and other countries where large quantities of AFFF are produced.

8 US EPA regulations do not currently restrict the use of existing stocks of PFOS based (3M) AFFF. European Union regulations require existing stocks of PFOS based foam to be removed from service by June 27, 2011. Proposed regulations in Canada require existing stocks of PFOS based AFFF to be removed from service 5 years after regulation is final (2013) [5].

9 In 2000 foam manufacturer 3M ceased working with PFOS which it used as a building block for its fire fighting foam. 3M stated that they discontinued the manufacture of PFOS based foams due to environmental persistence of the foam [2].

10 All other fluorosurfacant manufacturers were asked by the US EPA to scientifically prove that their PFOS based foams were different from 3M's by the end of 2002 [2].

PFOA Stewardship Program

11 The formation of the PFOA Stewardship Program by the US EPA in January 2006 had a number of goals. Primarily [3][4]:

- *Commit to achieve, no later than 2010, 95% reduction in both facility emissions to all media and product content of perluorooctanoic acid (PFOA), PFOA precursor chemicals, and related higher homologue chemicals, measured from a year 2000 baseline, and*
- *Commit to working toward elimination of PFOA, PFOA precursors, and related higher homologue chemicals from emissions and products by 2015.*

12 The companies who are participating in the program are:

- Arkema
- Asahi
- Ciba
- Clariant
- Daikin
- DuPont
- 3M/Dyneon and
- Solvay Solexis

These companies have facilities across China, France, Germany, Netherlands, Italy, Japan, United Kingdom, and United States [3].

13 The US are strongly encouraging other nations to support the participating companies, and are also urging other countries to follow a similar course of action.

14 With the US strongly pushing towards the removal of PFOA and higher order fluorocarbon chains, it appears that these chemicals will be removed from all products by 2015. There has also been claims that PFOA will be placed on the Toxics Release Inventory as a persistent, bioaccumulative, and toxic chemical [15]. When this eventuates it will leave the RAN in a position where it is using a foam which it can no longer source. Existing stocks will not last a substantial amount of time due to usage and shelf life, and therefore alternatives will need to be sort. To avoid being put into this position, an investigation into PFOS and PFOA and a review of the current direction within the industry is required immediately.

15 There is currently no legislations within Australia that will limit the usage of foams containing PFOAs, however if the manufacturers stop making them within the US and Europe then the RAN will no longer be able to obtain new stock. The Department of the Environment has been contacted and they are unaware of any upcoming restrictions within Australia on the usage of PFOAs. It does mean that the RAN will be able to use the stock which it has been able to procure before manufacture of foams containing PFOAs ceases.

PFOS AND PFOA

16 Studies have shown very low levels of PFOA and other perfluorinated compounds (PFC's) in the environment and in the blood of the general population [6].

17 Though there has been extensive research on whether PFOA has an adverse effect on humans due to the fact that it is a persistent chemical, it is not desirable to be manufacturing it [7].

18 In 2005 the EPA stated that some studies have linked PFOA to liver, pancreatic, and testicular cancer, reduced birth weight, birth defects, and immune suppression [11]. As a result of this and other testing, the EPA stated that low levels of exposure to PFOA could pose a "potential risk of developmental and other adverse effects" in humans [11].

19 Researchers from the UCLA School of Public Health recently found that women with higher blood levels of PFOA and PFOS took longer to become pregnant. It was the first known study linking perfluorinated chemicals to infertility [12].

20 While companies, such as Du Pont, claim that evidence indicates that PFOA exposure does not pose a health risk to the general public, a growing body of scientific evidence suggests the chemical has toxic effects [12]. A 1961 internal document indicated that Du Pont scientists had already warned company executives to avoid human contact with PFOA [11].

21 PFOA, also known as C8 (see Fig 1) or Ammonium Perfluorooctanoate (APFO), is used in the manufacturing process of fluoropolymers. Fluoropolymers impart desirable properties, including fire resistance and oil, stain, grease, and water repellency [8].

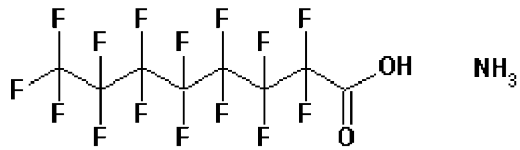

Fig 1. PFOA (C8) structure [9]

22 In fluorotelomer products, such as those used in firefighting foams and repellants, PFOA is not used in the manufacturing process but occurs at trace levels as an unintended by-product [6]. 'Traditional' fluorotelomer based products enclose carbon chains ranging in length from C6 to C16. It is the carbon chains which are longer than or equal to C8 which are of concern, due to their ability to break down into C8 (PFOA).

23 Traditionally the choice between the environmental impact of fire fighting foams, and their fire fighting performance has been the deciding factor when choosing between fluorinated and non-fluorinated foams [14]. Fluorinated foams (such as the AFFF which the RAN currently uses) provide a greater level of fire fighting ability than their non-fluorinated counterparts. Fluorosurfacants are capable of reducing the water surface tension from 60mN/m to near 16mN/m. This characteristic allows the formation of a thin aqueous film on top of solvents, promoting the spreading of the foam, and therefore the suppression of the solvent vapour [2]. The fluorinated end also adds a heat resistant film at the fire front and reduces solvent solubilisation in the foam [2]. It can be seen that the properties which using a fluorinated foam provides is exactly what the RAN and all defence forces are looking for in a fire fighting foam. When using a non-fluoronated foam the loss of the solutions natural 'desire' to spread over the burning hydrocarbon and lower heat resistance results in a fire fighting foam which is much less robust, and is harder to use. Due to the loss of spreading, the fire fighting crew will have to control the hose nozzle in a much more dynamic fashion.

24 By the end of 2008 over 100 alternatives had been presented for review to the EPA. Many of these are perfluoronated with C4 or C6 perfluoroalkyl constituents [10], rather than C8. Data on C4 and C6 have shown a shorter half-life and lower toxicity than PFOA and PFOS [10].

Alternatives to Foams containing PFOAs

25 Currently there is a limited number for foams available which will not be affected by the expected ban on PFOA. These include:

- Reformulated AFFF
- Fluorine Free Foam

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26 **Reformulated AFFF:** is already a solution which is progressing, however modifying these fire fighting agents to only contain carbon chains of C6 and below may well affect the actual fire fighting performance of the foams which they produce. These foams would need to be recertified to US MIL SPEC plus additional large scale testing (such as the F-100 nacelle test and a $1000ft^2$ pool test) to ensure they could effectively and safely be used by the RAN. Currently there is no information available on any reformulated AFFFs which have passed US MIL SPEC testing. If short carbon chain products can be readily used in the creation of AFFF Foams then a situation may arise where very little must be done to convert to a different foam. However relying on this as an option would not be prudent at this stage, as there are currently no reformulated AFFF products on the market. Relying on these products to be created, when there is no guarantee that they would be successful does not appear to be a sound option due to the relatively short time frames in which this issue will come to a head, AFFF is expected to be unavailable from 2015. The Fire Fighting Foam Coalition expects that these new reformulated products will retain all of the same fire suppression capabilities as existing AFFF agents [21], however there is no OQE to support this claim at this time.

27 DuPont have created a product which they call 'Capstone' [13] which is claimed to replace existing flourotelomers. DuPonts 'Capstone' products are sold as fluorinated compounds for use in surfactants utilised to manufacture existing brands of fire fighting foams [14].

28 DuPont have been quoted as saying [14]"Our products are surfactants that are added to products like aqueous film forming foam (AFFF) to provide the film forming capabilities such as properties of extinguishment and that prevent burnback". While this statement may be correct, sufficient testing would need to occur before the RANcould accept these reformulated foams into service.

29 Capstone utilises short carbon chain technology (C6 or less, as opposed to C8 or greater which the US EPA is currently progressing to ban) which should make it an environmentally safe alternative to what is currently used in the AFFF industry. Foams that are created using short chain technologies are referred to as reformulated or telomer-based AFFF.

30 As DuPont intends to adapt its entire range of fluorotelomers to utilise this short chain technology by the end of 2010, foam manufacturers who purchase these products from DuPont will have no choice but to adapt and retest their foams using this new technology.

31 These new reformulated AFFFs may contain trace levels of perfluorohexanoic acid (PFHxA), which are not being addressed by the stewardship program [21]. There is no evidence to show that these products (telomer-based AFFF) will break down into PFHxA, though it is speculated that this may be so. There has been extensive testing within the EPA which was presented at the Reebok conference in September 2007, which provided a very favourable toxicology profile for PFHxA.

32 Studies have shown that it is likely that the primary breakdown product of C6 fluorosurfactants is the 6:2 fluorotelomer sulfonate (6:2 FtS) [21]. Recent studies show the following outcomes when analysing 6:2 FtS:

- Low in acute and sub-chronic toxicity
- Low in Aquatic toxicity
- Negative for genetic and developmental toxicity
- Not bioaccumulative according to regulatory criteria
- Significantly lower than PFOS in biopersistence

33 There is currently no moves by the US EPA to limit the usage of short carbon chain products. As these products cannot break down into PFOA it seems unlikely that short carbon chain products will be targeted by the US EPA.

34 **Fluorine Free Foam:** another possible replacement for the current AFFF would be Fluorine Free Foam.

35 There has been some testing on Fluorine-Free Foams, comparing their performance to Fluorine based fire fighting foams. The testing consistently shows a reduction in performance in Fluorine free foams. Included below are the findings from Ref [18]:

- *Under laboratory conditions, with a foam blanket 1-2 cm deep, best-performing FfreeF formulation (RF6) provides about 30% of the durability of an AFFF for protection against evaporation of low-flashpoint flammable liquids. Increase in the foam thickness for either RF6 or AFFF indicates significant improvement in foam performance. The present measurements, including the ranking of concentrates, are very consistent with those of the flux-chamber apparatus of reference 4;*

- *On the basis of the present study and the success in applying RF foam technology to large surface spills (e.g., by Idemitsu Kosan Co. Ltd., Japan), we propose that RF6 and similar FfreeF formulations could provide satisfactory performance in practical situations. Large-scale experiments are required to verify this suggestion and to provide measurements of thicknesses of recommended foam layers and application frequencies, similar to those developed by Pignato [1] for AFFF. Future legislation may limit the use of fluorosurfactant-based foams in some countries, with RF6 or other RF6-like FfreeF providing an environmentally-acceptable alternative;*

- *The current measurements indicate that two other FfreeF formulations available in Australia in 2004 offer little or no performance for suppression of flammable vapours. The good performance of RF6 is a consequence of the presence of xanthan gum in its formulation. Marketing of two FfreeF (Formulations A and B) in Australia in 2004 was not supported by results of standardised suppression* *tests. The present results affirm a view that one must require approvals and listings of all foams considered during the selection and purchasing processes; and*

- *Under laboratory conditions, inorganic salts present in the foam owing to the use of sea water tend to deteriorate the performance of AFFF and RF6 foams by between 14 and 30%.*

36 Some concerns about the vapour suppression of Fluorine Free foams have also been presented in papers such as Ref [20]. Experiments which showed that AFFF can suppress N-heptane vapour for approximately 140 mins before allowing vapour to break through, also showed that RF6 under the same conditions held for approximately 50 mins [20]. This reduction in vapour suppression capabilities is of concern for the RAN as it would allow the fire to flash back and over power the extinguishing foam more readily than it has been able to with the current foams used within the RAN. This same study showed that the doubling in thickness of the RF6 foam layer to 2cm increased the effective vapour suppression time to 125mins. This doubling in thickness of the foam layer would require a doubling of flow rate at the nozzle.

37 Ref [20] notes that: "*essential properties of any new Class B Foam technology, which omits fluorosurfactants, include slow drainage, high heat resistance, slow coarsening, low shear viscosity and low yield stress*".

Comparison of aquatic Toxicity between AFFF and Fluorine-free foam

38 All data contained within this section is from Ref [21]. Tests were performed with:

- Fluorine-free Foam A – 3% concentrate
- Fluorine-free Foam B – 3% concentrate
- Milspec AFFF – 3% concentrate
- AR-AFFF – 3% concentrate
- UL AFFF – 3% concentrate

Agent	**LC50 (mg/L)**
Fluorine-free Foam A	65
Fluorine-free Foam B	71
Milspec AFFF	2176
AR AFFF	3536
UL AFFF	5657

Table 1: 96 hour LC50 test with Rainbow Trout, Lower Number = Higher toxicity

Agent	**LC50 (mg/L)**
Fluorine-free Foam A	171
Fluorine-free Foam B	171
Milspec AFFF	884

AR AFFF	1487
UL AFFF	1726

Table 2: 96 Hour LC50 Test with Fathead Minnows, Lower Number = Higher toxicity

It can be seen by the above data that fluorine free foams seem to have a higher aquatic toxicity than AFFF. This is because they contain higher concentrations of hydrocarbon surfactants and solvents, which are more toxic than fluorosurfactants [21].

A summary of the above data can be put as follows: The removal of Fluorosurfactants from fire fighting foam does not mean that it is less toxic or more 'environmentally friendly'. This brings up an important issue when trying to select a direction for the RAN to move in.

While these tests indicate that Fluorine-free Foam may well be more toxic in the short term, it has a much shorter life than PFOA. It is this environmental persistence which makes PFOA undesirable.

39 Included below is some known Fluorine free foams and some of the available background information:

40 **3M Australia**: released a Fluorosurfacant free Class B fire fighting concentrate that was 100% biodegradable and contained no persistent chemicals (such as PFOA). It met the Civil Aviation Organisation level B fire performance specification [2]. 3M provide a RF series of foams which also have the already mentioned properties. These foams are also compatible with Sea Water [16].

41 3M Australia claimed that their RF series of foams are the first non-fluorinated fire fighting foams to meet ICAO Level B fire performance rating [16]. These foams when used at 1% are also usable against Class A fires [16]. The RF Series comes as RF 3 and RF 6 which is 3% and 6% foam respectively.

42 3Ms most recent foam is RF-ATC which is a fluorine free foam that can be used on hydrocarbon type fuels at 3% proportioning as well as alcohols, polar solvents and water-miscible type fuels at 6% proportioning [16].

43 It should be noted that 3M make no claims that this foam is suitable for Military purposes and it has not passed US MIL SPEC testing.

44 **Solberg:** Solberg also make a range of Fluorine free foams [17]. Called RF6 Re-healing foam it is designed to be utilised at 6% against Class B fires and at 1% against class A fires. As with the 3M foams these contain none of the PFOAs and PFOSs that some current fire fighting foams contain.

45 Solberg RF6 has been designed to meet and exceed ICAO Level B and DEF (AUST) 5706 [17]. Solberg does claim that their foams are ideal for a wide range of customers including defence, however again it needs to be noted that this foam has not passed

US MIL SPEC testing. The testing which Solberg foam underwent to pass the ICAO tests included passing the 60 second extinguishing requirements for the 7m^2 sized fire pan, and the large scale testing of a 500m^2 aviation fire consisting of 3375 litres of aviation fuel. The foam successfully extinguished the large fires in 43, 29, and 51 seconds in three separate tests, which placed it safely under the 60 second extinguishment requirement.

46 This foam is effective at fighting fuels with up to 20% alcohol in them [17].

47 **Chemguard:** Chemguard ECOGUARD is a foam which has been produced to combat class B fires. It is stated in [19] that the foam is to be used on Class B fires only. The foam is a 6% or 3% mix solution.

48 ECOGUARD was designed to UL 162 which is a standard for Synthetic Foams. There is no information to suggest that this concentrate has passed or been tested to US MIL SPEC.

Supporting Technologies

49 There has been work going into technologies which may help counter the higher flow rates which these newer foams will likely require. Technologies such as Ultra High Pressure (UHP) fire fighting systems have been tested by the USAF in Fire Extinguishing Effectiveness Tests (FEET) program and it has been found that there is a reduction of more than 70% in agent usage when extinguishing pool fires [23][24].

50 It has also been proposed that Combined Agent Fire Fighting which incorporates different agents such as Foam and Dry Powder can be utilised to improve fire fighting capabilities [23][24].

51 Using a combination of these technologies could assist these new, and less effective, fire fighting agents achieve the performance requirements of the RAN. However using a UHP system would require the new high pressure system to be installed on RAN platforms.

Way Forward for the RAN

52 It is recommended that the following steps be taken in order to mitigate against the likely removal of foams containing PFOAs from degrading the RAN's fire fighting capabilities.

- Intermediate (2010-2015):
    - Buy additional stock of currently used foam (Ansulite MIL SPEC 6%) in order to have sufficient stores for usage until 2020 (provided shelf life is ok)

  - Platforms retiring by 2020 do not need modification, can be maintained and utilise the purchased stocks. (eg FFG, LPA)
  - DSTO and DNPS to undertake active investigation into reformulated AFFF/FfreeF for navy application. This will require testing of at least 2 of each type of foam in accordance with DEF(AUST) 5000 Vol 7. Pt 2. This work needs to consider the use of high pressure systems and their benefits such as reducing the required agent discharge. This work may be best done in collaboration with a university.

- Long Term (2016→)
  - Modify existing fleet procedures and systems to support a new foam fire fighting solution.

Conclusions

53 The Fire Fighting Foams which are currently within use in the RAN (as well as the RAAF and Australian Army) are likely to be chemically changed within the next 1 to 5 years. No matter which direction that the RAN decides to head, i.e. fluorine free foam or reformulated AFFF, testing and requalifying of foams to DEF(AUST) 5000 Vol7 Pt2 will be required before the RAN can safely adopt any new foam.

54 Air Services Australia is currently testing Solberg RF6 foams, and have agreed to provide RAN with their findings. It is our understanding that this will include environmental performance as well as fire performance.

55 Once foam has been purchased they generally have a shelf life of around 10 years, this will allow the RAN to provide itself a 'buffer' to ease the transition to a different fire fighting foam.

56 When replacing the foam which is currently used, the RAN should take the opportunity to research fire fighting effectiveness against new fuels, such as ethanol based fuels, in order to make sure that the new foam will be effective against these fuels.

57 A transition to a new foam will not have as large an effect if the RAN acts now, further researching the implications that the banning of PFOAs will have on the fire fighting foam industry.

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