# New Additive for Low Viscosity of AFFF/AR Concentrates—Study of the Potential Fire Performance

Marie-Laure Carruette, Bureau Veritas Consulting

Henry Persson, SP Swedish National Testing and Research Institute-Fire Technology, Sweden

Martial Pabon, DuPont de Nemours (France), Chantereine, Mantes le Ville F-78202 Mantes la Jolie, Cedex, France

**Abstract.** The aim of this study was to investigate the potential fire performance of alcohol resistant foams using a new additive developed by DuPont. The main intention of the new additive is to allow a lower amount of polysaccharide in the formulation of AFFF/AR concentrates thereby reducing their viscosity. A comparative study was performed using two similar formulations of AFFF/AR-concentrates, one traditional concentrate (designated F1) and a novel concentrate (designated F2), which contains the new additive and half the traditional amount of polysaccharide. The study, performed at SP Fire Technology, comprised small scale fire tests in combination with a series of additional tests aimed to provide detailed information about expansion and drainage characteristics, foam spread properties, the influence of heat exposure and vapour suppression capability.

The study confirms the desired reduction of the viscosity of an AFFF/AR foam concentrate, using a lower amount of polysaccharide in its formulation, while with the use of the new additive, the fire performance has the potential to be similar or even better than a traditional AFFF/AR foam.

Key words: foam, surfactant, polymer, additive

## **Background and Introduction**

According to the European standard EN 1568 [1], fire-fighting foams are used to control and extinguish class B fires and to inhibit their re-ignition. They have a great advantage over water as their low density allows them to blanket the burning liquids they are used to extinguish. In any discussion of fire fighting using foams, it is important to distinguish between their use on non-water miscible (such as oils, aromatics) and water-miscible, (such as alcohols or ketones) liquids [2], as foams are water-based. Polar liquids (typically watermiscible) destroy classical foams on contact by dehydration. They are consequently the most difficult to extinguish [3].

FFFP/AR (film-forming fluoroprotein foam) and AFFF/AR (aqueous film-forming foam) are two types of "Alcohol Resistant" foams, which can be used on hydrocarbon and polar solvent chemicals. Traditionally, these foams are developed for the use at 3% proportioning rate for petroleum products and 6% for polar solvents, ("3 by 6 versions"). In recent years,

a new generation of these foam concentrates has been developed for use at 3% on both petroleum products and polar solvents, ("3 by 3 versions"). Common for all these foams is that they contain water-soluble polymers of the polysaccharide type [2], which are insoluble in many polar solvents and precipitate to form a polymer layer on the fuel surface, to protect the foam. However, the use of polysaccharides results in a high viscosity in the foam concentrate and their non-Newtonian behaviour often leads to problems when used in conventional foam proportioning equipment [4].

Considering this problem, a new additive has been developed by DuPont, the FORAFAC<sup>®</sup> 1268, to reduce the amount of polysaccharide in the formulation of the foam concentrate and thereby reduce its viscosity while trying to improve the fire performance. To demonstrate the possible improvements of an alcohol resistant foam using this new additive, two AFFF/AR foams were evaluated in a comparative study involving small scale fire tests, expansion and drainage characteristics, foam spreading properties on liquids and the heat resistance and the vapour suppression capability of the generated foams. Those tests, developed at SP Swedish National Testing and Research Institute, Fire Technology in previous research projects [5–8], were applied to the two foam concentrates used in this study.

"The first of the two foams (designed F1) was considered as a basic AFFF/AR "3 by 3 version," with a typical polysaccharide loading (1%). It has to be noticed that a "3 by 3" AFF-AR of the market can contain from 1 to 1.5% polysaccharide [9] or even more. In the formulation of the second foam (designated F2), the new additive was used and the amount of polysaccharide was reduced. Both foams were formulated by DuPont (formearly ATOFINA) specifically for this study. The intention was not to formulate two "commercial foams" but rather to achieve the best AFFF/AR foam composition to facilitate a study of the influence of the new additive.

In this paper, the formulations are first described in order to specify, as clearly as possible, their composition and underline their differences. A summary of the experimental work is given, presenting the various testing conditions and the results obtained followed by a discussion of the overall results.

## **Formulation of the Foams**

As AFFF/AR foams, the main components of the two foam concentrates were:

- hydrocarbon surfactants, which are used to decrease the interfacial tension between the foam solution and the solvent,
- fluorinated surfactants, which produce a low surface tension in the foam solution,
- solvents, which aid solution of the surfactants,
- water-soluble polysaccharide, which create a precipitate to protect the foam from the solvent.

The detailed formulation of the foam concentrates is presented in Table 1, where the mass percentage of each compound is given. The formulation was then completed by the addition of demineralised water. Both foam concentrates were formulated to be used in 3% concentration for water miscible and water immiscible fuels ("3 by 3 versions"). As shown in Table 1, the only difference in the formulation of the two foam concentrates consists

TABLE 1

Products	Role	F1 Foam Concentrate (% by mass)	F2 Foam Concentrate (% by mass)
Dowanol DPM	Co-solvent	10	10
Rewoteric AMVSF	Hydrocarbon surfactant	2.4	2.4
Texapon 842	Hydrocarbon surfactant	8	8
Simulsol SL8	Hydrocarbon surfactant	2	2
Forafac <sup>®</sup> 1157N	Fluorinated surfactant	5	5
Kelzan ASX	Polysaccharide	1	0.5
Forafac <sup>®</sup> 1268	Fluorinated polymer	0	2.53 [0.76% A.A.(*)]
Demineralised water	1 2	71.6	69.57

Formulation of the Two Foam Concentrates. The Composition is Given in Mass Percentage. The Role of Foam Concentrate Components Can be Found Elsewhere [9]

(\*) Active Agent. It has to be noticed that the balance between the active agent and the commercial product consist of water and a co-solvent.

of the presence of the new additive (FORAFAC<sup>®</sup> 1268) in the F2, and the reduction of polysaccharide in its formulation, from 1 to 0.5%.

Viscosity measurements were performed with the two foam concentrates, using a Carri-Med Rheometer–CSL 100 with a cone-plate geometry. Three different temperatures were used: 5, 10, 20°C. "The values presented in Figure 1 correspond to the viscosity of the foam concentrates obtained at the equilibrium for a given shear rate. Four values of the shear rates were used: 0.3, 0.6, 1, 3 s<sup>-1</sup>. Those values are below the one found in the pumping equipment (50 to  $100 \text{ s}^{-1}$ ) [4] but still in the range recommended by the EN standard [1]. It is more representative to use a low shear rate before than to reach the steady state (50 to  $100 \text{ s}^{-1}$ ) the share rate in the tubes and pumps is very low and it is well known that



Figure 1. Viscosity measurements for the two foam concentrates F1 and F2 at three different temperatures: 5, 10, 20°C.

for aqueous solutions containing polysaccharide the lower is the shear rate, the higher is the viscosity. We then have chosen to run the viscosity measurements in the worst case. As shown in Figure 1, the viscosity of the F2 foam concentrate was three times lower than F1 because of its lower content of polysaccharide.

### **Experimental Methods and Results**

For all the tests performed, the foam concentrates were used in 3% concentration with tap water or simulated seawater, according to EN 1568 [1]. The foam was generated using a UNI86-R nozzle with the single stream outlet and a foam solution flow rate of 2.5 l/min. This nozzle is a laboratory scale version of the UNI86, developed by Lancia et al. [10] in the framework of the European (CEC) project FAIRFIRE.

#### Extinguishing Properties of the Fire Fighting Foams

A series of small scale fire tests was performed on acetone, to establish the extinguishing properties of the two fire-fighting foams, using part of the SP method 2580 [11]. This method was developed in the FAIRFIRE project, as a small scale test procedure giving results correlating with Part 3 (foams for water-immiscible fuels) and Part 4 (foams for water-miscible fuels), respectively of the European standard EN 1568 [1]. Due to the reduced scale compared to EN 1568, the requirements in SP method 2580 have been changed in order to reflect similar extinguishing and burn back properties. Based on the findings in the FAIRFIRE project, the requirements shown in Table 2 is used in the small scale procedure for water-miscible liquids (acetone).

The test method prescribes a 0.41 m<sup>2</sup> fire tray to simulate the 1.73 m<sup>2</sup> pool fire prescribed in the EN 1568-4. Acetone was used as fuel (30 litres) and the foam was applied gently using a backboard, as shown in Figure 2. Heat radiation measurements were used as a complement to the visual observations recorded by the operator during the tests. However, it should be noted that some differences may be observed between these two values, especially for the 25% burn back, as they do not represent the same physical measurement. The visual observation of 25% burning surface does not correspond exactly to 25% heat radiation. This is also true for the 90% control, but the time difference is normally less significant as the 90% control is reached relatively quickly.

#### TABLE 2

Requirements Used in the Small Scale Fire Test Procedure on Water Miscible Liquids in Order to Correlate with the EN 1568-4 Standard [1, 11]

	Exting Performa	uishing ince Class	Re	el	
Test Procedure	I	II	Α	В	С
EN 1568-4 [1] SP method 2580 [11]	<3 min <3 min	<5 min <5 min	>15 min >14 min	>10 min >8 min	>5 min >1 min



Figure 2. Small scale fire test set-up according to the procedure used to investigate the extinguishing properties. During the extinguishing phase time to 90% control (left) and extinction (right) was recorded. Heat radiation measurements were used as a complement to visual observations.

The repeatability and reproducibility of the method was investigated in the FAIRFIRE project and proved to be good, the variation of time to control was normally within 5 seconds and extinguishment within 5–10 seconds [5]. In this study, some duplicate tests were conducted with seawater and the repeatability obtained was in the same order, as shown in Table 3. It could be noted that the repeatability is slightly worse for the burn back tests compared to the extinguishing tests. This is typical, as the burn back test depends on the time to control and extinguishment. A more efficient control and extinction results in less foam destruction and a correspondingly larger volume of foam available to protect the fuel against reignition during the burn back test.

A summary of the results obtained for the two foams using tap water and seawater is presented in Table 3. Using tap water, both foams fulfil the Class I extinguishing performance requirement. However, the F2 foam shows both a faster control and extinguishment, compared to the F1 foam, about 20 seconds difference. Comparing the burn back resistance, F1 shows a slightly better result. However, both foams are classified as level B for burn back resistance.

Most synthetic foams are affected by the use of seawater. According to Mulligan [2], an improved salt tolerance is possible with a careful selection of surfactants, so that foams are only slightly sensitive to seawater. As shown in Table 3, F1 was influenced by the use of seawater. The time to extinction was increased and burn back resistance decreased (Limit between Class I/II—Level C). In contrast, F2 had improved extinguishing results and only a slightly decreased burn back resistance.

#### **Foam Properties**

*Expansion Ratio and Drainage Characteristics.* The expansion ratio and the time to 25 and 50% drainage, respectively, are generally considered to provide the fundamental foam characteristics. In this project, they were used to verify the quality of the foams and were measured before each test was performed.

rrepurea vang lap								
	F1 /T2	ıp Water (*)	F2 / T	ap Water (*)	F1 /	Seawater	F2 / Se	awater
lest	Visual (min:s)	By Radiation (min:s)						
Extinction								
90% control	1:09	1:10	0:52	0:58	2:30/2:25	2:21/2:22	1:10/1:00	1:05/0:53
99% control	1:30		1:28		2:51/2:48		1:25/1:07	
Extinguished	1:50		1:30		2:58/3:02		1:30/1:15	
3urn Back								
Sustained flames in the tray	5:55		5:00		1:25/1:15		2:55/3:20	
25% Burnback	12:58	13:53	10:55	11:39	1:30/1:27	2:01/2:16	7:01/9:05	7:56/10:01
100% Burnback	14:45		12:30		1:50/2:25		8:00/10:30	
Class(I/II)	-	Class I	•	Class I	Limit betv	veen Class I/II	Class	I Limit
Level (A/B)	Ι	evel B	Γ	evel B	Le	evel C	between	Level B/C
(*) Only single tests performed.								

TABLE 3 Results of the Fire Tests According to SP Method 2580, Performed with F1 and F2 Foams, Prepared Using Tan Water and Commission



#### Figure 3. Drainage rate (DR) curves for F1 and F2, prepared with tap water and seawater respectively. The full lines represent tests using tap water and the dashed lines those conducted using seawater.

The procedure that was used is based on EN 1568-4 but modified to allow continuous measurements without the interference of an operator. The tap on the outlet of the drainage vessel was replaced by a filter paper inside the vessel to prevent passage of foam. During a test, the vessel was placed on a scale connected to a data logging system, allowing a continuous measurement of the drainage rate, as shown in Figure 3. The correlation of the results with those obtained using the EN-standard has been studied and proven to be good, although the modified method gives a slightly faster drainage. The repeatability has also been investigated and was found to be about the same for the two methods [12].

Table 4 shows average values of the expansion ratio obtained from duplicate tests with tap and sea water. The F1 foam produces a higher expansion ratio than the F2 foam. However, the expansion ratio can be considered as typical for low expansion foams (5–9) measured using the UNI 86R test nozzle for both tap water and seawater. As mentioned in the fire tests, both foams were slightly effected by the use of seawater as are most synthetic foams, decreasing the expansion ratio. Considering the drainage, the repeatability of the method was verified by conducting triplicate tests using tap water. As shown in Table 5, the results are similar.

## TABLE 4 Expansion Ratio for F1 and F2, Prepared with Tap Water and Seawater

Water	<b>F1</b>	F2
Tap water	8.2 (±0.3)	7 ( $\pm 0.2$ )
Seawater	7.1 (±0.1)	5.5 ( $\pm 0.1$ )

D		F1			F2		
with Tap Water	F1-1	F1-2	F1-3	F2-1	F2-2	F2-3	
Time to 25% (min:s)	11:23	11:09	11:04	6:33	6:37	6:20	
Average (% variation)	11	11:12 (±1.6%)		11:12 (±1.6%) 6:30 (=		0 (±2.6%	5)
Time to 50% (min:s)	21:01	21:01	20:24	11:06	11:17	11:04	
Average (% variation)	20	:49 (±0.9	%)	11:0	09 (±1.29	%)	

TABLE 5 Time to 25 and 50% Drainage for F1 and F2

TABLE 6 Times to 25–50% Drainage Measurements for F1 and F2 Prepared with Tap Water and Seawater

	F1-Taj	p Water	F2-Ta	p Water	F1-Seawater		F2-Seawater	
Drainage Time (min:s)	F1-1*	F1-2**	F2-1*	F2-2**	F1-1*	F1-2**	F2-1*	F2-2**
Time to 25% Time to 50%	10:52 18:47	11:33 19:41	6:59 11:57	6:56 11:45	10:23 17:14	09:45 16:09	04:12 08:05	4:18 08:10

\*Immediately after preparation of the premix solution

\*\*Five hours after preparation of same premix solution.

Studying the results, one may notice that F1 drains very slowly and the time to 25% exceeds 11 minutes. This may be due to the higher amount of polysaccharide used in F1 compared to F2 (1% and 0.5%, respectively), which tends to retain the water and slow down the drainage. The F2 foam, which contains half the amount of polysaccharide in its formulation, drains faster but the results remain in the usual range observed for AFFF/AR.

In order to study the ageing properties of the foam solution, the expansion ratio and drainage tests were repeated after 5 hours, using the same premix solution. Both tap water and seawater were used. Premix stability might be a problem and for certain foams the premix time is restricted by the manufacturer. The results are shown in Table 6 and Figure 3, and indicate that F2 seems very stable. Considering the different results for tap water and seawater, the drainage seems slower for F1, with longer drainage times and a lower drainage rate. This is due to the effect of the polysaccharide as explained above, which is present in higher amounts in this foam concentrate. Moreover, the use of seawater also accelerates drainage properties of both foams, as shown in Figure 3.

### **Foam Spreading Properties**

The spreading properties of the two AFFF/AR foams were investigated by conducting foam flow tests on acetone and water, respectively, as shown in Figure 4. The tests were conducted in a tray with a length of 1.3 m and a width of 0.6 m. The foam was applied via two sliders into an overflow cup in order to achieve a gentle foam application, essential for the test



Figure 4. Test set-up for the spreading tests on acetone and water. The foam was applied via two sliders into an overflow cup to achieve a gentle application of the foam and the time for the foam front to pass the 0.6 m distance was measured.



Figure 5. Formation of a polymer layer at the surface of the acetone in the foam spread tests (photo taken about 5 minutes after application).

with acetone. The cup was located at one end of the tray and the foam was forced to spread towards the other end. The speed of the foam front was recorded along a distance of 0.6 m, as shown in Figure 4. A video camera was used to record the foam front passage along the measuring distance. The video was analysed after each test and the foam front velocity calculated.

The tray was filled with 20 litres of liquid  $(17.5 \pm 2.5^{\circ}C)$ , i.e. a depth of around 35 mm. To protect the liquid surface during the initial stages of the test, when the foam spray was being initiated or from drop-out from the foam stream throughout the experiment, a plexiglas board was placed above the tray, as shown in Figure 4.

During the foam spread tests on acetone, the formation of the polymer layer was clearly visible, as shown in the picture in Figure 5.

The spreading rate was evaluated for both foams and the results are shown in Table 7. Let us consider the tests on acetone. The F2 foam, with the new additive, has a higher foam spread rate compared to F1. When tap water was used, the spread rate for F2 was approximately 40% higher than for F1. Using sea water, the foam spread rate was significantly reduced for both foams and the difference between them was less marked. For the tests performed on a layer of water, the foam spreading rate was very similar for both foams and considerably higher compared to the corresponding tests on acetone, especially for F1.

#### TABLE 7 Spreading Rates (m/s) of the Two Foams on Acetone or Water

Те	est performed on:	F1 (m/s)	F2 (m/s)
Acetone	Premix with Tap water	0.04	0.056
	Premix with Seawater	0.033	0.038
Water	Premix with Tap water	0.063	0.062



Figure 6. Test set-up used for the heat resistance tests to study three different parameters; drainage, evaporation and destruction.

# **Heat Resistance**

The ability of the foams to resist heat radiation was been investigated, in order to obtain a better understanding of the extinction mechanisms. A layer of foam ( $H_{\text{foam}} = 50 \text{ mm}$ ), placed on acetone ( $H_{\text{acetone}} = 25 \text{ mm}$ ;  $T_{\text{acetone}} = 20^{\circ}$ C) in a glass vessel was subject to heat, as shown in Figure 6. Three parameters were studied in these tests: the drainage, the evaporation of the foam and the foam destruction.

The study was carried out, based on the methodology described by Isaksson and Persson [7]. However, in the previous study, tests were only performed using heptane in the vessel, while acetone was used in the present set of tests.

The evaporation rate was measured by continuous weight measurements of the foam. The foam destruction was measured using a linear potentiometer connected to a "foam height indicator," which was adjusted manually during the experiment [7]. A different methodology had to be used for the drainage due to the water-miscibility of acetone. Thus, the drainage was recorded by measuring the elevation of the level of acetone in the vessel. A ruler was fixed on the rim of the vessel and a camera recorded the foam/acetone interface throughout the experiment.

The heat radiation onto the foam layer was generated using a cone radiator. It was mounted on a separate stand, giving a distance of 20 mm between the lower rim of the cone and the rim of the vessel. Tests were conducted using three heat flux levels,  $6.1/22.5/42.6 \text{ kW/m}^2$ . These figures are defined as the average "effective" heat of radiation since they were calculated as the weighted average of the radiative flux across the entire surface [7]. The following test procedure was used:



Figure 7. Percentage drainage as a function of time for the two foams at the different heat flux levels: 0, 6.1, 22.5, 42.6  $kW/m^2$ .

- 0:00 min:s, the foam was collected via a slider into a plastic container and the timer and data logging systems started,
- 1:20 min:s, the foam was poured gently onto the acetone surface,
- 2:20 min:s, the cone was turned to a centric position above the vessel and the pilot flame positioned above the foam blanket.

All tests were conducted using tap water. In the first tests series, duplicate tests were conducted to verify the repeatability. As shown in Table 9, the repeatability was very good and most tests were conducted as single tests.

The results are presented in the form of graphs, see Figures 7–9, showing the percentage of drainage and evaporation, and the foam destruction as a function of time.

As shown in Figure 7, there is no significant difference in the drainage properties between the two foams. One important factor is that it is difficult to obtain accurate drainage measurements. As a polymer layer is formed at the foam/acetone interface, it was very difficult to accurately determine the increase of the interface level due to drainage, which also prohibited the calculation of the drainage rate. An improved measurement method is necessary to obtain more accurate results.

In Figure 8, the evaporation of the two foams is shown as a function of time. As expected, the evaporation increased with the radiation level. The evaporation rate was higher for F1 than F2. However, if the evaporation rate constant is calculated, both foams obtain values of 16–19 g/min, kW, see 8, which is in line with previous findings [7, 8].

The change in foam height is plotted in Figure 9 as a function of time. The foam first undergoes an expansion due to the heat, followed by a period of destruction until the foam blanket is consumed. As expected, the foam destruction increases with increasing heat flux. As shown in Figure 9, F2 tends to be destroyed slightly slower than F1, especially during the initial "foam expansion phase" during the tests. This tendency is confirmed by the observed time to ignition of the acetone as shown in Table 9.



Figure 8. Percentage evaporation as a function of time for the two foams at the different heat flux levels: 0, 6.1, 22.5, 42.6  $kW/m^2$ .

# **Vapour Suppression Capability**

The ability of the foam to suppress flammable fuel vapours during and after a successful extinguishment is a very important property and this property is normally evaluated by conducting burn back tests. However, in the burn back test, many factors influence the result, such as the extinguishing time, or the thickness of the foam layer. In order to achieve more quantitative and comparable results, a study of the vapour suppression capability was made using a similar test set-up as previously used by Persson et al. [8]. However, the fuel vapour measurements was improved by using a flame ionisation detector (FID), *J.U.M. VE 5*, connected to a data logging system. This instrument continuously measures the total organic hydrocarbons in a gaseous sample, which in this study was assumed to originate from the acetone fuel vapours.

A 70 mm foam layer, prepared with tap water, was placed on a 50 mm layer of acetone in a standard vessel, immediately after its generation and sampling as shown in Figure 10. The vessel was then sealed and connected to the FID. To ensure a good mixture between

TABLE 8 Evaporation Rate Calculated During a 30 Seconds Time Period When the Foam Layer was Approximately Level with the Rim of the Vessel

		F1 Foam			F2 Foam	
Heat Flux Level (kW/m <sup>2</sup> )	Calculating Period (time ±15 s)	Evaporation Rate (g/min)	Evaporation Rate Constant (g/min, kW)	Calculating Period (time ± 15 s)	Evaporation Rate (g/min)	Evaporation Rate Constant (g/min, kW)
6.1	6:00	4.4	17.4	7:00	4.9	19.3
22.5	4:05	16.9	18.0	5:10	16.9	18.1
42.6	3:55	28.4	16.0	4:30	28.0	15.8

TABLE 9 Observations Recorded During the Tests at the Two Highest Heat Flux Levels, 22.5 and 42.6 kW/m<sup>2</sup> Where Ignition of the Acetone Occurred

	F1 Foa	m	F2 Foam		
Heat Flux	Surface Free	Sustained	Surface Free	Sustained	
Level (kW/m <sup>2</sup> )	of Foam (min:s)	Ignition	of Foam (min:s)	Ignition	
22.5*	5:40/5:33	6:40/6:36	5:55/6:12	7:06/7:10	
42.6	4:50	5:00	5:15	5:25	

\*Duplicate tests were conducted at 22.5 kW/m2.



Figure 9. Change in foam height relative to the fuel level as a function of time for the two foams at the different heat flux levels: 0, 6.1, 22.5, 42.6 kW/m<sup>2</sup>.

the vapours and the air in the vessel, a mixer was used, with a rotation of 400 rpm. Two different temperatures of the acetone were used:  $15^{\circ}$ C and  $35^{\circ}$ C.

The concentration of the acetone vapour above the foam layer is plotted as a function of time, in Figure 11. It should be noted that the values recorded were adjusted by subtracting the "initial noise", due to the possible presence of hydrocarbons in the test room. In addition, the time "zero" corresponds to the connection of the FID to the glass vessel (2 minutes after foam was generated and 1 minute after the foam was poured on the acetone layer). To verify the repeatability of the tests, duplicate experiments were conducted and, as shown in Figure 11, the results are very similar. For F1, using  $T_{acetone} = 35^{\circ}$ C, triplicate tests were conducted as a difference was noticed in the second, very rapid, increase of fuel vapours. The general results obtained indicate that the concentration of vapour increases with time as the foams undergoes destruction, mainly due to drainage and formation of a polymer layer. As expected, a higher fuel temperature, which increases the vapour pressure of the fuel, reduces the vapour suppression capability.



Figure 10. Test set up for the study of the vapour suppression capability. The sealed reaction vessel was connected to the FID, to measure the acetone vapour concentration above the foam layer.



Figure 11. Concentration of acetone vapour as a function of time, above a 70 mm foam layer placed on a 50 mm acetone layer at two different temperatures ( $T_{acetone} = 15^{\circ}C/35^{\circ}C$ ) in a sealed vessel.

Comparing the two foams shows that the formation of vapour above the foam layer was slower for F2 than for F1, especially at the higher fuel temperature. In the tests with  $T_{acctone} = 15^{\circ}$ C, the fuel concentration was similar for both foams during the first 20 minutes. After the first 20 minutes, F2 shows a slightly better vapour suppression capability, exhibiting a lower level of acetone vapours concentration than F1. This test was terminated after 45 minutes, when the concentration above the foam layers was constant. A thin foam layer still remained on the fuel providing a good barrier for the acetone vapours. Using a fuel

temperature of  $35^{\circ}$ C, the difference between the two foams was more significant. After about 15–20 minutes, the fuel vapour above F1 increased by a factor three in a very short time. This may be explained by the final destruction of the foam layer above the acetone with only the polymer layer remaining during the rest of the test. Using the F2 foam, the increase of fuel vapour above the foam blanket was delayed compared to the F1 foam, and during the 25 minute test, no major increase of fuel vapours was seen. At the end of the test with the F2 foam, there was still a thin foam layer on the fuel preventing vapour release. However, if the test time had been extended, it is not clear whether a similar increase of the concentration would have been observed, when the foam layer was totally destroyed.

#### Discussion

The viscosity data in Figure 1 clearly shows the difference between the two foam concentrates. The F2 foam concentrate, which contains the new additive, was less viscous, due to the reduction of the polysaccharide solution in its formulation and thus easier to handle in practical use. The potential of the new additive is, however a function of its extinguishing performance rather than its viscosity. This study has aimed to confirm the fire-fighting properties of such a foam. This was done, not only by conducting fire tests, but also by performing detailed studies of a variety of other important parameters.

The expansion ratio and drainage properties, which are normally considered to give the most fundamental information on foams characteristics, remained in the same range as most existing AFFF/AR foams for the F2 foam. The drainage was faster than the very slow draining F1 foam and its expansion ratio was slightly lower. The reduced amount of polysaccharide in the formulation of the F2 foam explains its faster drainage characteristics since the polysaccharide aided water retention.

The small scale fire tests conducted show that F2 obtains similar or better results than F1, especially when seawater was used. The faster fire control may be partly explained by the better spreading properties of the F2 foam. While the spreading rate on water was similar for both foams, it was significantly higher for the F2 foam on acetone. As shown in the FOAMSPEX project [13], the governing mechanisms of foam spread are essentially due to a driving force caused by hydrostatic pressure differences in the foam and a resisting force due to viscous friction between the foam and the fuel. It was also shown that the friction, and thus the foam spread, depends on the kinematic viscosity of the fuel. Considering the similar viscosities of water and acetone, it seems that the formation of the polymer layer, which does not occur on water, is the factor that slows down the foam spread on acetone, due to increased friction. Consequently, one important reason for the higher foam spread rate for the F2 foam might be the reduced concentration of polysaccharide in its formulation.

Using seawater, significant differences were observed in the fire tests. The extinguishing time was increased and the burn back time decreased for F1 while F2 was relatively insensitive to the use of seawater. This tendency was also noted in the drainage properties. The time to 25 and 50% drainage obtained from repeated measurements with the same premix solution, freshly made and after 5 hours, differ only a few seconds for the F2 foam. This difference between the F1 and F2 foam in term of behavior versus the time of storage after dilution could be explained by the aggregates reorganization dynamic after dilution. An AFFF/AR foam concentrate is a complex dispersion in which polymers (polysaccharide and FORAFAC 1268) are in aggregates also containing surfactants. The equilibrium between

aggregated polymers and free polymers but also agregated surfactants and free surfactants depends partly of the concentration. When the F1 and F2 foam concentrates are diluted, the one containing the lower amount of polysaccharide will reach the new equilibrium state faster because of its lower viscosity and because it contains FORAFAC 1268 which has a low molecular weight. As a consequence, the F2 foam will have a stable behavior as a function of storage time because it reaches quickly its new equilibrium. On the other hand, the F1 foam will require a time long enough to find differences in properties as a function of storage time. However, this topic would require a specific study which is out of the field of this article.

The thermal aspect was investigated in the heat resistance study. There was a general tendency for the F2 foam to be destroyed slightly more slowly than the F1 foam resulting in a longer time to the ignition of the acetone was achieved. At the highest heat flux level, the time difference to ignition was about 20 seconds. However, the reason for this difference has not been determined. The evaporation rate constant was almost the same for the two foams, which confirms results from similar tests with other types of foam [7, 8]. Due to the difficulties to measure the drainage rate during the heat exposure tests, it is not possible to accurately compare the drainage characteristics between the two foams. In relative terms (% of initial weight), the results indicated similar behaviour, however the absolute drainage rate  $(g/m^2 \text{ min})$  may differ significantly during heat exposure as observed in the standard drainage tests. To verify this, an improved test methodology is needed.

A study of the vapour suppression capability also confirms the tendency for an improved performance of F2. The increase of vapour concentration above the foam blanket was delayed compared to F1, especially at an elevated fuel temperature.

## Conclusions

The viscosity of an AFFF/AR foam can be reduced by using a new additive which allowed the reduction of the amount of polysaccharide in the foam formulation. This result is of great interest, especially for those foams used at 3% proportioning rate for both non-water miscible and water miscible fuels, "3 by 3 versions", which are normally rather viscous and difficult to handle and proportion.

This study shows that the fire performance of a foam formulated using this new additive (designated F2) has the potential to be similar or even better than a "classical" AFFF/AR (designated F1). The F2 foam was much less sensitive to seawater, compared to F1 foam. This may be due to the use of a low molecular weight molecule instead of the polysaccharide in the formulation of the F2 foam. The various parametres studied in this project, apart from the fire tests, provide complementary information on the behaviour of the foam generated from this new formulation. The results of expansion and drainage characteristics, foam spread properties, influence of heat exposure and the vapour suppression capability, confirmed the fire test results.

### **Acknowledgments**

We wish to thank DuPont and AtoFina for the financial support of this project. We are also grateful to the technical staff at SP Fire Technology, for their participation in the different tests performed and for useful discussions in preparation of this manuscript.

It has to noticed that the ATOFINA Business of fluorinated surfactants and fluorinated acrylic polymers has been acquired by Du Pont de Nemours the 3rd of September 2002.

## References

- [1] EN1568-3/4, Fire extinguishing media—Foam concentrates- Parts 3/4 : Specification for low expansion foam concentrates for surface application to water immiscible/miscible liquids, *European Standard*, October 2000.
- [2] D.J. Mulligan, "Fire-Fighting Foams—True Specialities," Speciality Chemicals, 1990, pp. 343– 347.
- [3] S. Szönyi, "A4P, The Development of Film-Forming Liquid Foam Compounds," *Fire Journal*, Nov. 1984, pp. 53–58.
- [4] M. Bobert, H. Persson, and B. Persson, "Foam Concentrates: Viscosity and Flow Characteristics," *Fire Technology*, vol. 33, no. 4, 1997, pp. 336–355.
- [5] H. Persson and M. Bobert, "FAIRFIRE—Fire-Fighting Foams: Small Scale Tests Procedure-Small Scale Fire Tests," SP REPORT, 1996: 27, SP Swedish National Testing and Research Institute, 1996.
- [6] B. Persson and M. Dahlberg, "A Simple Model of Foam Spreading on Liquid Surfaces," SP REPORT, 1994:27, SP Swedish National Testing and Research Institute, 1994.
- [7] S. Isaksson and H. Persson, "Fire Extinguishing Foam—Test Method for Heat Exposure Characterisation," SP REPORT 1997:09, SP Swedish National Testing and Research Institute, 1997.
- [8] H. Persson, "Fire Extinguishing Foam—Resistance Against Heat Radiation," SP REPORT, 1992:54. (BRANDFORSK-project 609-90), SP Swedish National Testing and Research Institute, 1992.
- [9] M. Pabon and J.M. Corpart, "Fluorinated Surfactants: Synthesis, Properties, Effluent Treatment," Journal of fluorine chemistry, vol. 114, 2002, pp. 149–156.
- [10] A.N. Lancia, A. Lancia, and B. Tirloni, "FAIRFIRE—Fire Fighting Foams: Small Scale Fire Test Procedure," Technical Report No. 2-UNI-86-R Nozzle Specification and Performance, T.R.I. (Tecsa Ricerca Innovazione), Italy, 1996.
- [11] "Foam Concentrates—Quality Control," SP-Method No. 2580, SP Swedish National Testing and Research Institute, Dec. 2000.
- [12] H. Persson and M. Milovancevic, "FAIRFIRE-Fire-Fighting Foams: Small Scale Tests Procedure—Improvement of Drainage and Expansion Methodology," SP REPORT, 1996:28, SP Swedish National Testing and Research Institute, 1996.
- [13] B. Persson, A. Lönnermark, H. Persson, D. Mulligan, A. Lancia, and M. Demichela, "FOAMSPEX-Large Scale Foam Application-Modelling of Foam Spread and Extinguishment," SP REPORT, 2001:13, SP Swedish National Testing and Research Institute, 2001.