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# Characterization of the Dynamic Surface Tension of Aqueous Film-Forming Foam

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# CHARACTERIZATION OF THE DYNAMIC SURFACE TENSION OF AQUEOUS FILM-FORMING FOAM

## 1.0 INTRODUCTION

Aqueous film-forming foam (AFFF) was first developed at the Naval Research Laboratory in the 1960s [1] and since that time has been an important component of fire protection against liquid fuels. AFFF has also gained wide acceptance in other service branches and among civilian users. Military Specification AFFF used in specified Defense Department applications must conform to the provisions of Mil-F-24385 [2] (current revision: F), which is under the control of the Naval Sea Systems Command. AFFF is sold as a concentrate (either 3% or 6% for MilSpec materials), where the numerical value is the proportion at which the concentrate should be mixed with water. In other words, a 3% concentrate (referred to as "Type 3" AFFF) is intended to be used as a mixture of 3 parts concentrate and 97 parts water; a 6% concentrate (Type 6), 6 parts concentrate and 94 parts water. The concentrate/water mixture is sprayed from a nozzle in either a fixed system (in the flight deck of aircraft carriers, for example) or from a handheld fire hose. The mixture is self-foaming without additional mechanical agitation or aspiration, and forms a coating on a flammable liquid to suppress combustion and inhibit reignition.

A significant distinction of AFFF compared to earlier fire fighting foams is the ability of the concentrate/water mixture to form an aqueous film on top of a hydrocarbon fuel surface, even in the absence of foam [1,3]. Without bubbles to impart buoyancy, the density of the aqueous layer is greater than that of the hydrocarbon. It is by reduction of surface energy that the film is able to spread on the fuel surface. The reduction in surface energy which allows film formation to occur is made possible by use of fluorinated surfactants, which lower the surface tension of the AFFF/water mixture to the range of 15-19 dynes/cm, compared to typical values of approximately 25 dynes/cm for hydrocarbon fuels, and 25-30 for water containing hydrocarbon surfactants.

The condition for film formation to be possible is that the Spreading Coefficient for the aqueous layer  $a$  on the fuel  $f$ , given by

$$S_{af} = \sigma_f - \sigma_a - \gamma_{af} \quad (1)$$

where  $\sigma_f$  and  $\sigma_a$  are the surface tensions of the fuel and aqueous phase, respectively, and  $\gamma_{af}$  is the interfacial tension between the two liquids, must be positive. While a negative value of the spreading coefficient makes film formation energetically impossible, a positive value does not guarantee that film formation will occur. There are cases known (usually with very small positive values of  $S$ ) where spreading is not observed [4,5].

AFFF compositions contain both hydrocarbon and fluorocarbon surfactants, in addition to viscosity enhancers such as diethylene glycol monobutyl ether (butyl carbitol) [6]. Recently, perfluorooctyl sulfonate (PFOS) based surfactants used in AFFF have been found to be environmentally persistent, bioaccumulative, and toxic (PBT), leading the 3M company to cease manufacturing AFFF and replace PFOS with alternative surfactants for other applications [7]. Following 3M's withdrawal, the EPA issued a Significant New Use Rule restricting production of these fluorosurfactants by other manufacturers [8]. While MilSpec AFFF formulations from other suppliers, using other varieties of fluorosurfactants, remain available [9,10], scrutiny is

currently being paid to the possible environmental effects of these surfactants as well, leading to the possibility of future restrictions on the composition, manufacture, or use of AFFF.

## 2.0 DYNAMIC SURFACE TENSION

Surface tension is the energy required to create a unit area of surface. The surface tension is related to the intermolecular attractive forces in a solid or liquid. Molecules on the surface are not completely surrounded by other molecules, thus they experience less attractive forces and are in a higher energy state. In general, the stronger the intermolecular forces in a material, the greater the surface tension will be. Water in particular has strong intermolecular forces due to a permanent dipole moment and intermolecular hydrogen bonding, and thus has a surface tension much higher than most other common liquids. The static surface tension can be measured by gradually applying a force to a metal ring suspended at the liquid until the force is greater than the surface tension and the ring escapes the surface of the solution.

Surfactants added to a liquid reduce the surface tension by preferentially collecting at the surface, and creating a lower energy surface than that of the pure liquid [10]. Most surfactants have a molecular structure with a water soluble moiety at one end of the molecule, and a hydrophobic moiety at the other end. The surfactant molecules orient themselves at the surface with the hydrophobic portion sticking out of the water. Typical hydrophobic moieties in surfactants include alkyl groups, fluoroalkyl groups and methylsiloxo groups. All of the parent compounds (alkanes, fluoroalkanes, and silicones) have surface tensions much lower than that of water, with fluorinated surfactants being able to achieve the lowest surface tension.

The dynamic surface tension (DST) of a surfactant solution is the instantaneous surface tension at a finite surface age. DST is a monotonically decreasing function of surface age, which for very low values of surface age, approaches the value for the pure liquid (water, for instance) in the absence of any surfactants [12]. For very high surface ages, the dynamic surface tension asymptotically approaches the equilibrium value. For a pure liquid, the surface tension will be independent of surface age, as there is no equilibration process to occur.

The dynamic surface tension of a surfactant solution is the result of the time dependent process of the surface tension reaching its equilibrium value. Surfactant molecules cannot instantaneously cover a newly-created surface, but must first reach the surface by diffusion. The time for this to occur depends on the surfactant concentration, and also on the temperature, which influences the diffusion coefficient. Additionally, time is needed for molecules of a solution to orient themselves and form a homogenous monolayer; frequently this process is observed to have an energy barrier, leading to a temperature dependence of its rate [13]. Typical equilibration times for surfactant solutions to achieve equilibrium surface tension are on the order of seconds or even minutes.

AFFF compositions lower the surface tension of water primarily by using a variety of surfactants. The equilibrium surface tension of AFFF is an important parameter due to its role in allowing film formation, and is measured as part of the MilSpec qualification process. Up to the present, however, the dynamic surface tension of AFFF has not been characterized, even though

many of the processes in AFFF use (e.g. the time for the liquid stream to reach the fuel surface, the time in which foam formation occurs) in fire fighting happen on short time scales at which the equilibrium surface tension is unlikely to be achieved. The goal of the present study is to provide the first characterization of the dynamic surface tension of AFFF. The dynamic surface tension of five commercial AFFF concentrates is investigated as a function of dilution, salinity (AFFF can be used with either fresh or salt water) and temperature.

The DST of a material can be measured by a variety of methods, which are capable of interrogating different ranges of surface ages. The method used in these studies, capable of measuring dynamic surface tension on the shortest time scales, is the maximum bubble pressure method [12,14,15]. Air is bubbled through a capillary typically ranging between 0.1 and 1 mm diameter. At a given insertion depth of the capillary into the liquid being studied, the maximum overpressure required to form the next bubble is related to the instantaneous surface tension of the liquid. By varying the bubble rate, surface tensions for a variety of surface ages can be obtained. In each cycle of bubble formation, the pressure reaches a minimum as a bubble breaks free of the capillary, then reaches a maximum as a new bubble begins to form. The time interval between the pressure minimum and maximum is designated the "surface age"; typically plots of dynamic surface tension use either surface age or bubble rate as the x-axis. Surface ages typically achievable using maximum bubble pressure tensiometers range from less than 10 milliseconds to greater than 10 seconds.

### 3.0 MATERIALS AND METHODS

Five commercial AFFF formulations were tested: 3M FC-203CE, 3M FC-206CF, Angus Tridol M 6%, Ansul Ansulite AFC-5, and Chemguard C-601MS. The FC-203CE is a 3% concentrate, the other four concentrates tested were all 6% concentrates. The 3M products, as well as the Ansul and Chemguard formulations, have been qualified against Mil-F-24385F.

The dynamic surface tension of the five AFFF formulations were measured using a maximum bubble pressure tensiometer (Kruss BP2). Nitrogen gas was used to form bubbles at the orifice of a capillary. For all trials, the capillary immersion depth in the solution was 10mm. The data collection recorded the bubble rate, surface age, and dynamic surface tension (derived from the bubble overpressure) for each surface age. The range of surface ages recorded typically ranged from 8 milliseconds to 20 seconds, with 10 surface ages measured within each decade. At the beginning of each day, a comparison run was performed using distilled water, whose surface tension is 72.3 dynes/cm @ 25 °C, to verify proper functioning of the instrument. Dynamic surface tensions measured with water were typically within  $\pm 0.2$  dynes/cm of the nominal value for all surface ages greater than 20 ms. Except as otherwise noted, all measurements were performed at an ambient temperature of  $23 \pm 1$  °C.

Two types of capillaries were used in this study. One was a glass capillary which had an inner tip diameter of 0.209 mm. The surface of the glass capillary was treated with dichlorodimethylsilane to create a hydrophobic surface layer covered with methyl groups on the glass. When using a glass capillary, which is normally hydrophilic, an appropriate coating is important. The analysis used to determine the dynamic surface tension by the capillary bubble

pressure technique is not accurate if the interior surface of the capillary can be wetted by the fluid being studied. A check of the hydrophobic coating by measuring the surface tension of n-heptane, as recommended by the manufacturer, verified that the glass surface was appropriately silanized.

The other capillary type used was made from poly(tetrafluoroethylene) (PTFE). Two PTFE capillaries were used, having inner tip diameters of 0.274 mm and 1.101 mm. Since PTFE is intrinsically a material with a low surface energy, approximately 18 dynes/cm, no surface modification is required to this capillary. A number of fluorinated liquids, as well as aqueous solutions of some fluorinated surfactants, are however capable of wetting PTFE. As noted below, due to the high concentrations of surfactants in AFFF, both glass and PTFE capillaries were wetted by the AFFF mixtures. The PTFE capillaries, however, could only achieve maximum surface ages of a few seconds, whereas the glass capillary could in most tests achieve surface ages of 20 seconds or more. Previous bubble pressure studies of systems containing fluorosurfactants have generally used PTFE capillaries [12]. Our results here demonstrate that PTFE is not superior to silanized glass in exhibiting ideal capillary behavior.

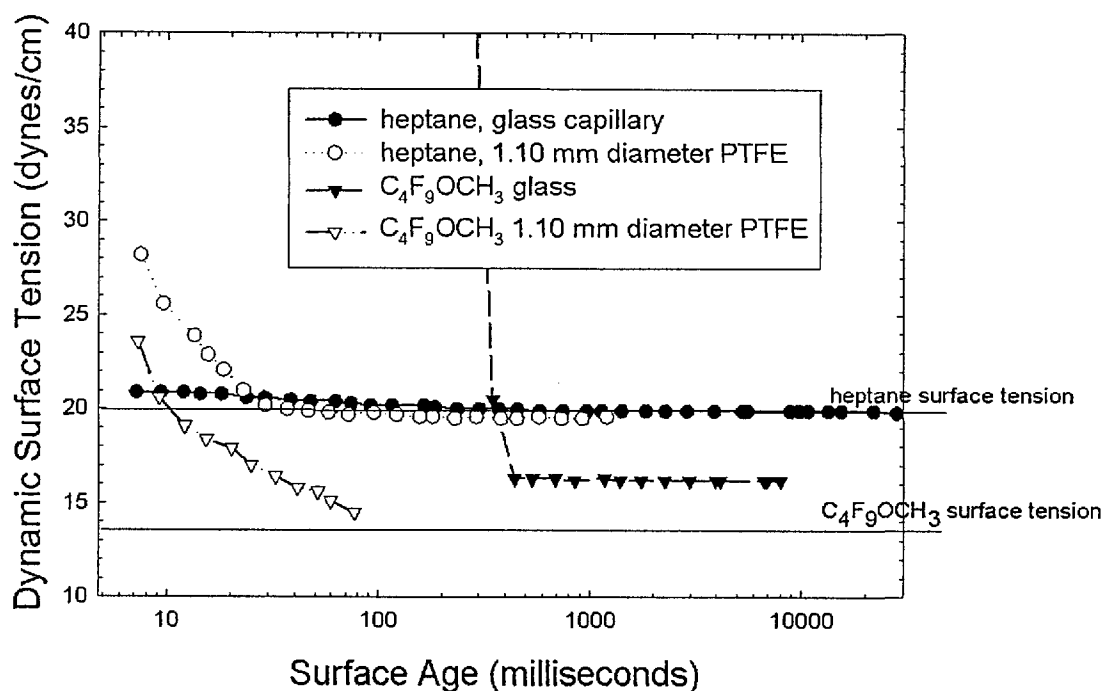
For studies comparing fresh water to salt water, artificial sea water was prepared by mixing 41.2 grams of "Sea Salt" defined in ASTM D-1141-52 and consisting primarily of sodium chloride (58.5%), magnesium chloride (26.5%), and sodium sulfate (9.8%), in 1 liter of distilled water. This creates a salt concentration typical of ocean water. For series of measurements investigating the effect of variations in temperature, a thermostatically controlled water bath was used to control the temperature of the solutions between 25 and 55 °C.

## **4.0 RESULTS AND DISCUSSION**

### **4.1 Comparison of Glass and PTFE Capillaries**

The analysis used to determine the surface tension from the bubble pressure assumes a quasi-static equilibrium between the air pressure tending to expand the bubble and the surface tension tending to minimize the surface area. Under some conditions, particularly wetting of the inside of the capillary, dynamic effects become important, invalidating the analysis and leading to errors in determination of the dynamic surface tension [15]. The presence of dynamic effects can be investigated by measuring the surface tension of pure liquids in the bubble pressure tensiometer. For a pure liquid the surface tension is independent of surface age and so an apparent variation in the surface tension with bubbling rate indicated non-ideal behavior. The tensiometer manufacturer recommends using a hydrocarbon such as hexane or heptane to verify proper silanization of glass capillaries. An inadequately coated capillary showing an apparent increase in surface tension at low surface ages (< 100 milliseconds) of significantly more than 1 dyne/cm (6% of the surface tension of n-hexane) compared to the value at surface ages of 10 seconds or more.



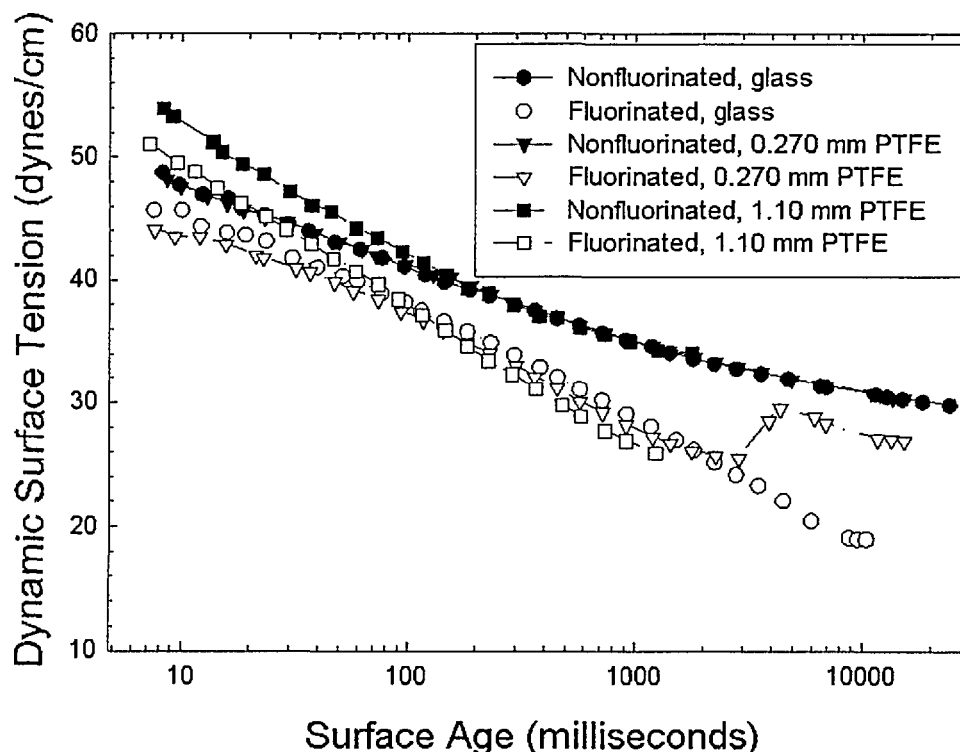


**Figure 1: Use of the bubble pressure tensiometer to measure the surface tensions of n-heptane and perfluorobutyl methyl ether as a function of surface age to assess the effects of capillary wetting and other non-ideal behavior using glass and PTFE capillaries. The horizontal lines indicate the accepted values of surface tension for the two liquids.**

The dynamic surface tensions of two pure liquids, n-heptane and perfluorobutyl methyl ether,  $C_4F_9OCH_3$ , were measured with both the silanized glass and the PTFE capillaries. The fluorinated ether is good test of the limitations of the capillary materials, because it has a very low surface tension of 13.6 dynes/cm [16], less than that of either capillary material. Also, it contains both hydrocarbon and fluorocarbon moieties, as does AFFF, which are chemically similar to both the PTFE and the methyl monolayer in the capillary materials. The results of these measurements are shown in Figure 1. The surface tension measurement of heptane using the glass capillary show values for all surface ages very close to the accepted equilibrium value, indicating a good hydrophobic coating on the capillary.

Use of the glass capillary with the fluorinated ether produced unrealistically large values of the apparent surface tension for low surface ages. At surface ages greater than 500 milliseconds, consistent values of surface tension were measured; they were, however, about 3 dynes/cm higher than the accepted surface tension for this compound. A systematically high number is consistent with a greater bubble pressure required to counteract the tendency of the liquid to wet the inside of the capillary. This suggests that wetting is influencing the measured value of the DST.

Using the 1.1 mm diameter PTFE capillary, measurements for both heptane and the fluorinated ether show dynamic surface tensions which are systematically high for surface ages less than 100 milliseconds. For higher values of surface age, data for heptane using both capillaries agree closely. For the fluorinated ether, the PTFE capillary's determination approaches the accepted



**Figure 2. Comparison of the dynamic surface tension of 3M 203CE AFFF (fluorinated) and a nonfluorinated foam concentrate, using capillaries made of silanized glass (0.209 mm) and of PTFE in two sizes (0.270 mm diameter and 1.10 mm diameter).**

value for a surface age near 100 milliseconds, but the instrument was unable to obtain valid measurements for slower bubbling rates.

Figure 2 shows measurements of dynamic surface tension using the glass capillary, and the PTFE capillaries of both diameters, for the 3M 203CE AFFF formulation, and a non film-forming foam which does not contain any fluorinated surfactants. The non-fluorinated composition has an equilibrium surface tension of approximately 27 dynes/cm, higher than that of n-heptane, so it is not expected to be able to wet either capillary material. Indeed, the measured dynamic surface tensions for the glass capillary and the smaller diameter PTFE capillary are nearly identical, indicating that the different capillary compositions do not influence the measurement for this material.

For the fluorosurfactant-containing AFFF, there is a slight difference between these two capillaries. More significantly, the small diameter PTFE capillary gave nominal values of surface tension which varied erratically at high surface ages, jumping abruptly at a surface age of approximately 3 seconds. This behavior is reproducible on successive instrument runs, but is nonphysical for a dynamic surface tension, indicating non-ideal behavior of the instrument. Slope discontinuities in the plot of surface tension as a function of surface age in the region for surface ages in the 1-5 second interval are also sometimes seen with fluorosurfactant containing liquids when the glass capillary is used (for example, in some of the data for AFFF shown in the following figures). For the glass capillary, the discontinuities are much smaller in magnitude than for the PTFE capillary.

The large diameter PTFE capillary gave readings for the foam solutions which were systematically greater than those obtained with the other two capillaries, for surface ages less than 100 milliseconds. The large diameter PTFE capillary, rather than the two smaller diameter capillaries, is probably giving inaccurate readings, since it also did so for pure liquids. The large diameter capillary was unable to determine dynamic surface tensions at surface ages greater than 2000 ms for any materials studied.

These studies indicate that no ideal capillary material exists for fluorocarbon liquids or aqueous solutions containing high concentrations of fluorosurfactants. The silanization process of the glass capillary does not serve to make the material non-wettable by fluorocarbons. Also, a number of fluorosurfactants are claimed by their manufacturers to facilitate wetting of PTFE, meaning that PTFE cannot always prevent inadvertent wetting by solutions containing high levels of fluorosurfactants. Of the available materials, the silanized glass allows the greatest range of surface ages to be studied, and except for pure fluorocarbon liquids, is not more sensitive to wetting than PTFE. Thus the silanized glass capillary was used in subsequent testing.

#### 4.2 Survey of Dynamic Surface Tensions of AFFF Formulations

Figure 3 shows the results of measurements of the dynamic surface tensions of the five AFFF formulations, using the bubble pressure tensiometer. All data were recorded at ambient temperature with the AFFF concentrates mixed with water at their recommended concentrations, using the silanized glass capillary.

Table 1 summarizes the quasistatic values, the maximum achievable surface ages, and measurements of the equilibrium surface tension, taken by the Du Nouy ring method in a static tensiometer (Fisher Autotensiomat). The static tensiometer was calibrated against several hydrocarbon liquids having known surface tensions similar to that of the AFFF formulations, to determine corrections to the measured values. The systematic uncertainty in the determination of the equilibrium surface tension was estimated to be  $\pm 0.5$  dynes/cm.

**Table 1: Quasiequilibrium and Equilibrium Surface Tensions for AFFF Products Studied**

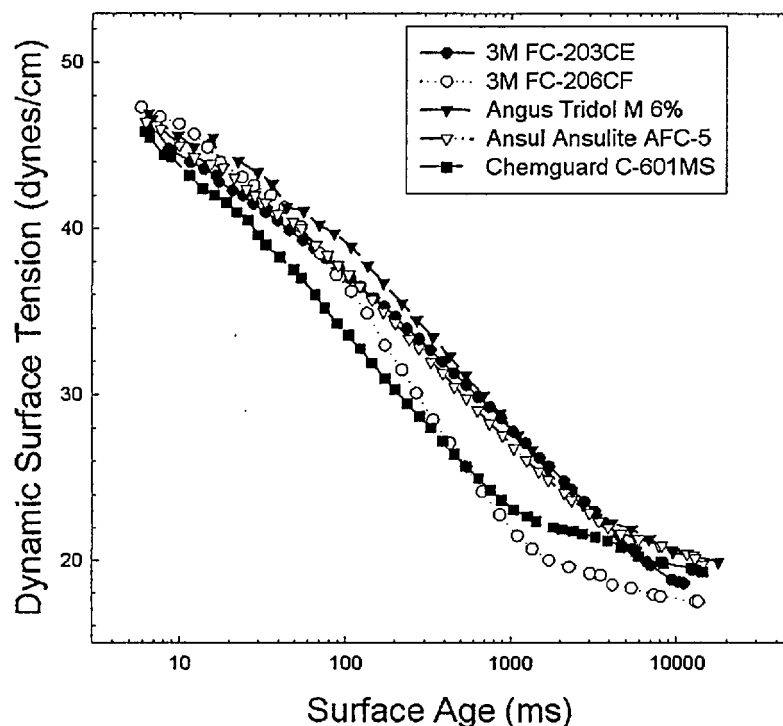
| <b>Product</b>       | <b>Minimum Dynamic Surface Tension @ Maximum Surface Age</b> | <b>Equilibrium Surface Tension (Du Nuoy Ring)</b> |
|----------------------|--------------------------------------------------------------|---------------------------------------------------|
| 3M FC-203CE          | 18.6@11.1s                                                   | 17.0                                              |
| 3M FC-206CF          | 17.5 @13.5s                                                  | 16.2                                              |
| Angus Tridol M 6%    | 19.9@17.9 s                                                  | 18.1                                              |
| Ansul Ansulite AFC-5 | 19.7@14.4s                                                   | 18.7                                              |
| Chemguard C-601MS    | 19.3@14.4s                                                   | 18.5                                              |

For all the AFFF formulations tested, the quasistatic surface tension from the bubble pressure tensiometer was 1-1.5 dynes/cm greater than the equilibrium value. This behavior is consistent with the expected asymptotic approach of dynamic surface tension to equilibrium. The fact that

the surface tension is still significantly above the equilibrium value even for surface ages between 10-20 seconds indicates the importance of surface tension on shorter time scales. For most of the AFFF MilSpec qualification tests, the test fire must be extinguished within 30 seconds.

For surface ages less than 10 milliseconds, the AFFF formulations have values of surface tension between 45 and 50 dynes/cm, compared to 72 dynes/cm for water. The high levels of surfactant contained in AFFF suggest that some reduction of surface tension due to the surfactant occurs almost immediately. Furthermore, the components present in AFFF influence the surface tension. For instance, a mixture of 1% diethylene glycol monobutyl ether in water (the approximately concentration when an AFFF/water mixture is applied to a fire) has a dynamic surface tension ranging from 60 dynes/cm to 55 dynes/cm over the range of surface ages measurable in our instrument, with slight dependence on surface age (data not shown).

The different formulations of AFFF vary slightly in the shape of the surface tension curves. In spite of differences in their surface tensions at high surface ages, all the products are very similar in surface tension at the lowest surface ages. This result suggests that the surface tension at low surface ages is important to foaming and other dynamic properties critical to rapid suppression of fires, since the qualified products have all met the same fire suppression standard. A dynamic surface tension of less than about 24 dynes/cm is needed to permit film formation on cyclohexane (the liquid for which the spreading coefficient is determined and the film forming ability is tested in Mil-F 24385F) assuming an interfacial tension of at least 1 dyne/cm [4]. It is noteworthy that this value of surface tension is not reached until the surface ages are greater than approximately 1000 ms.



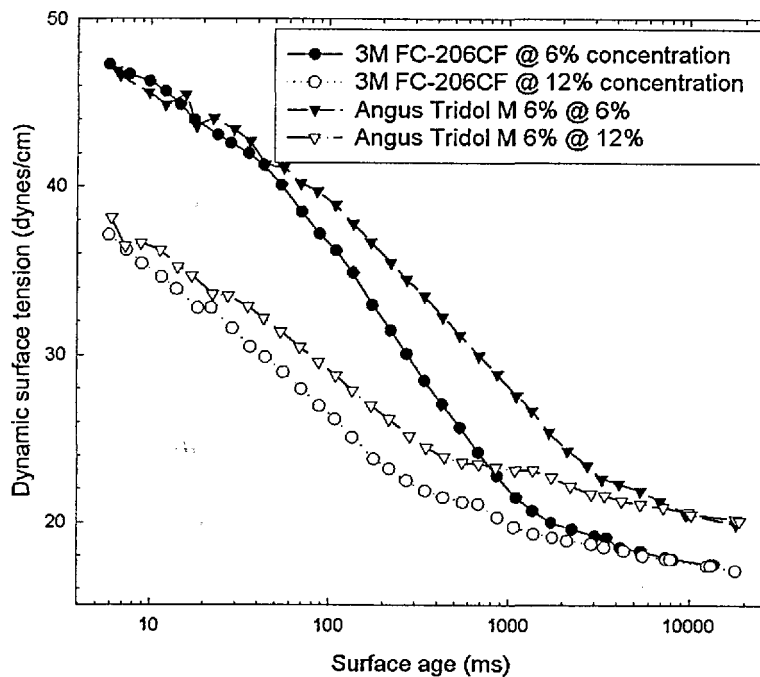
**Figure 3: Dynamic surface tension measurements for the five AFFF formulations tested, with the concentrates diluted as recommended in distilled water, using the glass capillary in the bubble pressure tensiometer.**

### 4.3 Effect of Variations in Concentration

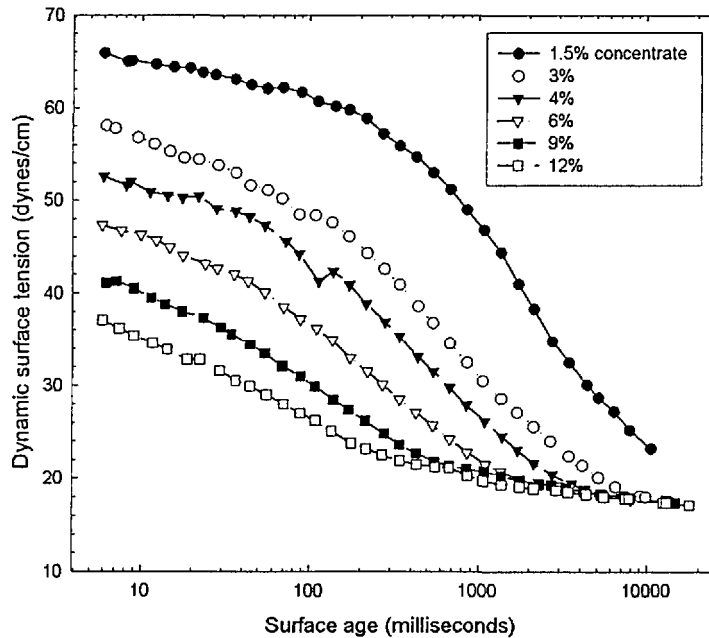
The qualification testing for MilSpec AFFF involves a series of fire suppression tests in which the concentrate is mixed with water at its design concentration (3% or 6%) before use. Additional tests are conducted with the concentrate mixed with water at one-half the design concentration and at five times the design concentration. At these concentrations, the product must still extinguish the test fire, although a longer time is allowed for extinguishment. The effect of changing the mixing ratio of the AFFF concentrate with water is to change the surfactant concentration. This has a large effect on the dynamic surface tension by changing the time required for the surface tension to reach its equilibrium value. A higher concentration reduces the equilibration time, but this is undesirable in AFFF as the surfactants can cause environmental problems.

The effects of varying dilutions of the AFFF concentrate on the dynamic surface tension were tested for a range of mixtures, with the amount of concentrate varying from one-quarter to twice the design value. Figure 4 shows the surface tension curves for the 3M 206CF and Angus Tridol M formulations, mixed with distilled water at their design concentration of 6%, and at 12%. For both products, the surface tension at low surface ages decreases as more concentrate is mixed with the water. At very high surface ages, on the other hand, the 6% and 12% curves for each product converge.

The coincidence of the 6% and 12% curves is due to the high concentrations of surfactants present in AFFF. If the surfactant concentration is above the critical micelle concentration, further increases in surfactant concentration do not affect the equilibrium surface tension. This is



**Figure 4: Dynamic surface tension curves for two AFFF formulations, with the amount of concentrate mixed in water at the nominal value (6%) and at twice the nominal value (12%).**



**Figure 5: Dynamic Surface Tension of 3M 206CF 6% AFFF as a function of surface age for concentrate mixes with distilled water from 1.5% to 12% (0.25 to 2 times the nominal mixture ratio).**

typically the case for AFFF. Thus the quasi-static surface tension is not expected to vary appreciably with dilution of the concentrate, as the measurements confirm. At low surface ages the dynamic surface tension depends on the concentration of the AFFF concentrate in the water, but not substantially on which concentrate is used. This is because, as seen in Figure 3 all concentrates have very similar surface tensions at short time scales when mixed at their nominal concentrations). At high surface ages, the surface tension depends on which formulation is used, but not on the concentration.

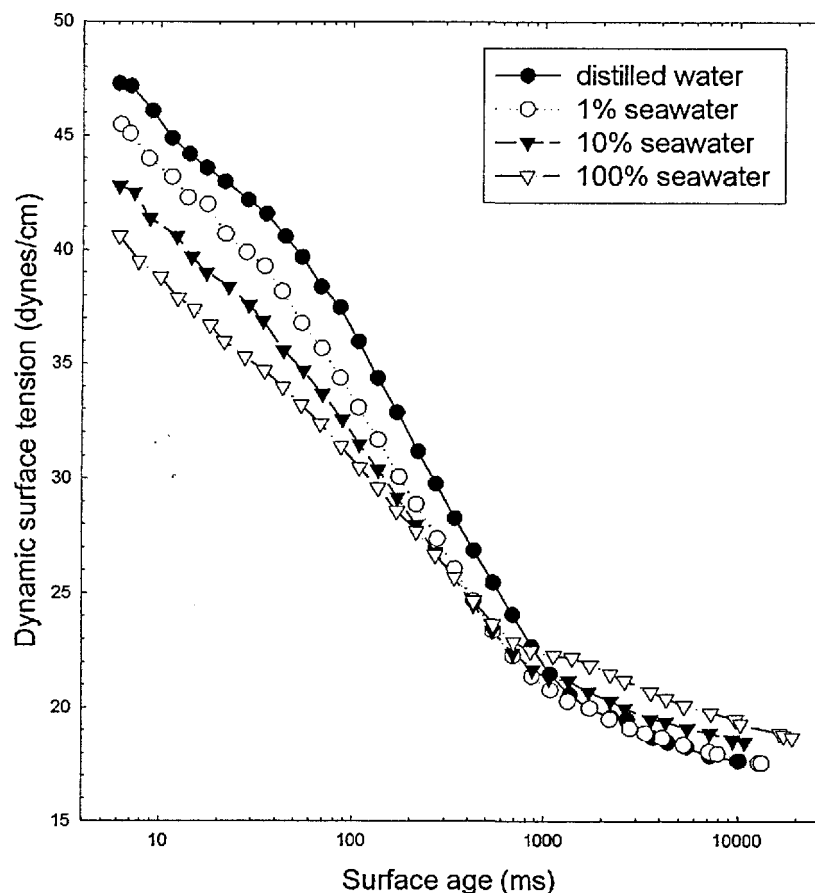
Data for a wider range of mixtures of the 3M 206CF concentrate in water are shown in Figure 5. As in Figure 4, at low surface ages, surface tension continues to decrease as the amount of concentrate present in the mixture increases. At high surface ages, the surface tension curves fall onto a common line; for a given value of surface age there is a critical mixture above which adding more concentrate does not affect the surface tension. The coalescence occurs at values of surface tension well above equilibrium, or even quasi-equilibrium. This behavior indicates that for sufficiently concentrate-rich mixtures, other factors besides surfactant transport to the surface (for instance an energy barrier [13]) must be the rate-limiting step in achieving equilibrium surface tension for these materials.

#### 4.4 Effect of Salinity

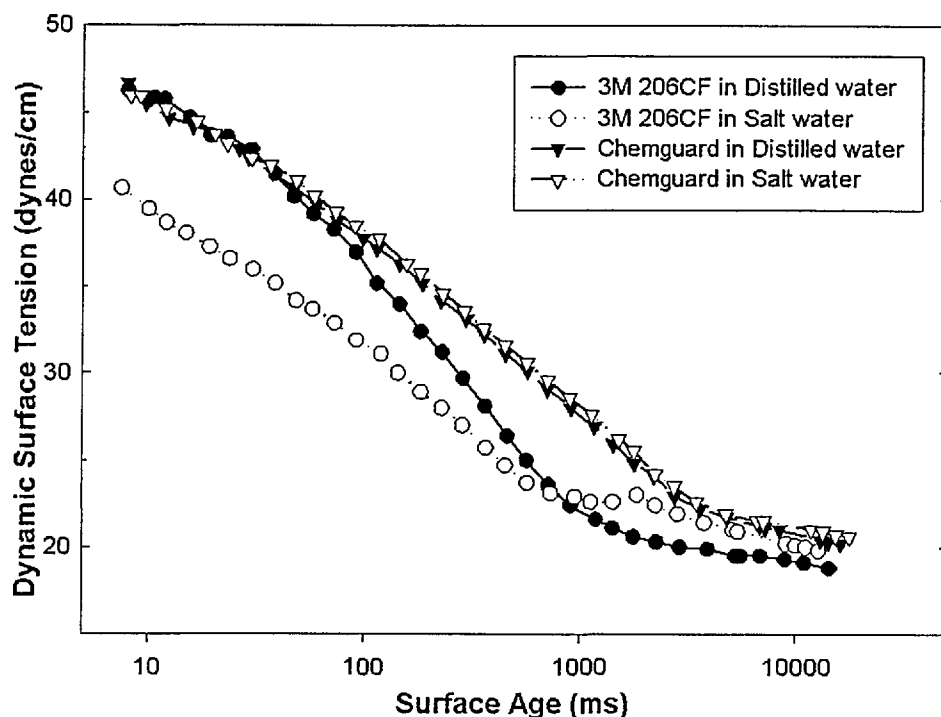
Since AFFF is intended for shipboard as well as land use, it must be effective when mixed with either fresh water or sea water. For this reason the qualification testing of MilSpec AFFF is both

salt water and fresh water. The five AFFF formulations were tested for various mixtures of artificial sea water and distilled water. Data for the 3M 206CF concentrate in water mixtures ranging from pure distilled water to pure artificial sea water is shown in Figure 6. The dynamic surface tension of this formulation varies significantly with salt content. The effect of increased salinity is to decrease the surface tension on short time scales, and to increase it on long time scales. For comparison, data was collected using municipal tap water, which in terms of its effect on the dynamic surface tension of the 206CF formulation, was similar to a mixture of 1% sea water in distilled water.

Among the different AFFF formulations tested, substantial differences were noted in the effect of salinity. The 3M 203CE formulation and the Chemguard and Angus products had a smaller but qualitatively similar effect of salinity (decreased surface tension at low surface ages, increased at high surface ages) to that of the 3M 206CF. For the Ansulite product, there was no significant difference in the dynamic surface tension between distilled water and sea water, as shown in Figure 7. Surfactants are known to vary greatly in their sensitivity to ionic content, so the differences probably result from differences in the particular surfactant mixtures used in each formulation. The effect of salt content can be significant for some AFFF formulations, but not others. There is not a general or simple relationship governing this behavior. Figure 8 compares



**Figure 6: Dependence of dynamic surface tension on salinity for 206CF. The concentrate was mixed at its nominal value (6%) in a variety of mixtures of distilled water and artificial sea water. Data was recorded at room temperature using the silanized glass capillary.**



**Figure 7: Comparison of the effect of artificial sea water vs. distilled water on the dynamic surface tension of the 3M 206CF and Chemguard C 601MS AFFF formulations.**

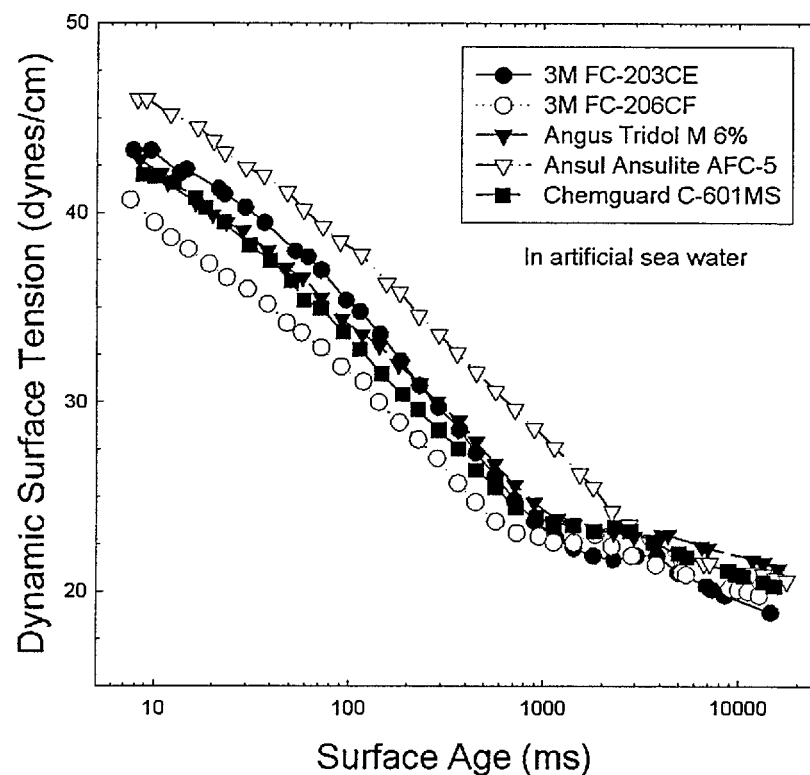
the DST of all the products tested in artificial sea water. Due to the differing sensitivities to salinity of the AFFF formulations, a greater variation in the dynamic surface tension curves is seen between the products when sea water is used, compared to fresh water. This is particularly evident at low surface ages.

#### 4.5 Effect of Temperature Variation

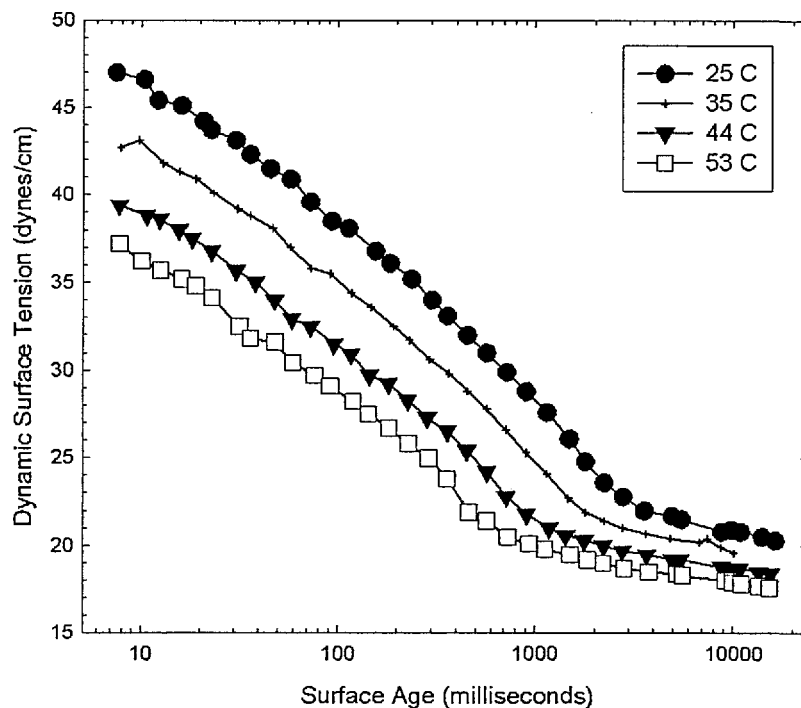
In the normal course of use, AFFF encounters wide variations in temperatures, depending on the ambient temperature and instantaneous heat release and geometry of the fire. Both the fire suppression and burn back resistance will suffer if the foam's properties are adversely impacted by the high temperature environment near the fire. Thus, the temperature dependence of the surface tension is important.

The Angus Tridol M 6% formulation was tested at temperatures from 25° C to 55° C in both salt and fresh water solutions with the PTFE capillary, and with fresh water using the glass capillary. The three sets of data all exhibited similar trends: at a fixed surface age, the dynamic surface tension decreased as a function of temperature. Data for the trial using the glass capillary with fresh water is shown in Figure 9.





**Figure 8: Dynamic surface tensions of the five AFFF concentrates in artificial sea water, recorded at ambient temperature.**



**Figure 9: Dependence of dynamic surface tension of Angus Tridol M 6% AFFF formulation, mixed at the nominal concentration in distilled water, on temperature.**

The equilibrium surface tension of common liquids decreases as a function of temperature, due to thermal motions reducing the intermolecular binding energy as the temperature increases. The data shown in Figure 9 are consistent with this expectation. At low surface ages, however, the reduction in surface tension is much larger than under quasistatic conditions of high surface ages. Thus the effect of temperature on dynamic surface tension is more greater than on equilibrium surface tension.

The decrease in dynamic surface tension with increasing temperature is thought to result from two factors [13]. First, the diffusion coefficient of the surfactant in water increases with temperature, decreasing the time needed for enough surfactant to form a monolayer to reach the surface. Second, in cases where there is an energy barrier to monolayer formation, a higher temperature will minimize its effect.

## 5.0 CONCLUSIONS

We have characterized the dynamic surface tension of five formulations of aqueous film-forming foam, and investigated the effects of dilution, salinity, and temperature on this property. Knowledge of the dynamic character of the physical properties of AFFF will enable more complete understanding of the behavior of AFFF, since properties such as film spreading rate and foam formation are known to depend on the dynamic surface tension [17]. Subsequent steps in understanding the role of dynamic surface tension on the performance of AFFF will include investigation of the dynamic surface tension of other, non film-forming, fire suppression foams, and of simplified model formulations intended to clarify the roles of different components of AFFF on DST. Correlation of the dynamic surface tension of different commercial and model foam formulations with properties such as foam characteristics and fire performance will elucidate the relationship between physical properties and effectiveness. For investigation of the dynamic surface tension of aqueous solutions of fluorosurfactants, we have found that PTFE is not superior to silanized glass as a capillary material.

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## 7.0 REFERENCES

1. R. L. Tuve, H. B. Peterson, E. J. Jablonski, and R. R. Neill, *A New Vapor-Securing Agent for Flammable Liquid Fire Extinguishment*, NRL Report # 6057, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, March 13, 1964.

2. U. S. Military Specification Mil-F 24385F, 7 January 1992: *Fire Extinguishing Agent, Aqueous Film-Forming Foam (AFFF) Liquid Concentrate, for Fresh and Sea Water*, Naval Sea Systems Command, Sea 05Q, 1333 Isaac Hull Ave. SE, Stop 5160, Washington DC 20376-5160.
3. J. T. Leonard and J. C. Burnett, *Suppression of Evaporation of Hydrocarbon Liquids and Fuels by Films Containing Aqueous Film Forming Foam (AFFF) Concentrate FC-196*, NRL Report # 7842, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, Dec. 31, 1974.
4. H. E. Moran, J. C. Burnett, and J. T. Leonard, *Suppression of Fuel Evaporation by Aqueous Films of Fluorochemical Surfactant Solutions*, NRL Report # 7247, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, April 1, 1971.
5. Svitova, T., Hoffmann, H., and Hill, R. M., "Trisiloxane Surfactants: Surface/Interface Tension Dynamics and Spreading on Hydrophobic Surfaces," *Langmuir* 12:1712-1721 (1996).
6. C. A. Moody and J. A. Field, "Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams" *Environ. Sci. Technol.* 34: 3864-3870 (2000).
7. United States Environmental Protection Agency, "EPA and 3M Announce Phase Out of PFOS," Headquarters Press Release, May 16, 2000.
8. "Perfluoroalkyl Sulfonates; Proposed Significant New Use Rule" *Federal Register*, Vol. 67, No. 47, pp. 11014-11030, March 11, 2002.
9. Qualified Products List QPL-24385-31, *Products Qualified Under Military Specification Mil-F-24385*, 30 October 1998, Naval Sea Systems Command, SEA 05Q, 1333 Isaac Hull Ave. SE, Stop 5160, Washington DC 20376-5160.
10. Qualified Products List QPL-24385-32, *Products Qualified Under Military Specification Mil-F-24385*, 24 April 2002, Naval Sea Systems Command, SEA 05Q, 1333 Isaac Hull Ave. SE, Stop 5160, Washington DC 20376-5160.
11. E. Kissa, *Fluorinated Surfactants and Repellents*, 2<sup>nd</sup> edition (Marcel Dekker, New York, 2001)
12. D. E. Hirt, R. K. Prud'homme, B. Miller, and L. Rebenfeld, "Dynamic Surface Tension of Hydrocarbon and Fluorocarbon Surfactant Solutions using the Maximum Bubble Pressure Method," *Colloid. Surf.* 44:101-117 (1990).
13. J. Eastoe, J. S. Dalton, P. G. A. Rogueda, and P. C. Griffiths, "Evidence for Activation-Diffusion Controlled Dynamic Surface Tension with a Nonionic Surfactant," *Langmuir* 14: 979-981 (1998).

14. P. Spanoghe, J. Cocquyt, and P. Van der Meeren, "A Low-Cost Dynamic Surface Tension Meter with a LabVIEW Interface and Its Usefulness in Understanding Foam Formation," *J. Chem. Ed.* 78:338-342 (2001).
15. S.V. Lylyk, A. V. Makievski, V.I. Koval'chuk, K. H. Schano, V. B. Fainerman, and R. Miller, "The effect of capillary characteristics on the results of dynamic surface tension measurements using the maximum bubble pressure method" *Colloid. Surf. A* 135 (1-3): 27-40 (1998).
16. *HFE-7100 Product Information Sheet*, 3M Special Materials Company, St. Paul, MN.
17. D. Benventi, B. Carre, and A. Gandini, "Role of Surfactant Structure on Surface and Foaming Properties," *Colloid. Surf. A* 189:65-73 (2001).