

Suppression of Fuel Evaporation by Aqueous Films of Fluorochemical Surfactant Solutions

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13. ABSTRACT
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Small increments of the surfactant solution were added to the hydrocarbon surface to test the effectiveness of aqueous films in suppressing the evaporation of hydrocarbon liquids. The results demonstrated that film formation proceeded in two stages. In the first stage, the surfactant solution appeared to spread more or less evenly over the hydrocarbon substrate causing a large depression in the evaporation rate. After a certain critical thickness was reached, further increments of solution produced relatively little change in the evaporation rate and appeared to form a lens, or hanging drop, on the underside of the film. The critical point corresponded to a film thickness of about 10μ .

Films of sufficient thickness were found to reduce the rate of evaporation of cyclohexane and JP-4 jet fuel by 90 to 98%. The fuel-air mixtures in the vapor space above the filmed hydrocarbon could not be ignited by an open flame. These results demonstrated that in fire fighting applications the film acts as a vapor barrier to prevent reignition of the fire once it has been extinguished by the cooling and blanketing action of the foam.

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ABSTRACT

Solutions of aqueous fluorochemical surfactants were placed on the surface of liquid hydrocarbons and hydrocarbon fuels to study the film-forming ability of the surfactant solutions. Spreading coefficients were calculated for a number of surfactant solution/hydrocarbon liquid pairs and correlations made with visual observations of film formation. In the majority of cases, film formation could be predicted from the spreading coefficient of the surfactant solution on the hydrocarbon substrate. Both pure fluorochemical surfactants and commercially available fire fighting concentrates were used to prepare the aqueous solutions. The hydrocarbon liquids and fuels included n-heptane, isooctane, cyclohexane, jet fuels JP-4 and JP-5, motor fuel (gasoline), and stove and lighting naphtha.

The effect of temperature on surface and interfacial tension measurements was also studied. In general, the surface tensions of the hydrocarbon liquids and the interfacial tensions between the surfactant and hydrocarbon liquid pairs decreased at a rate of approximately 0.07 to 0.12 dynes per cm per °C temperature rise. The surface tensions of the surfactant solutions were found to decrease approximately 0.05 to 0.06 dynes per cm per °C rise.

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PROBLEM STATUS

This is an interim report; work on the problem is continuing.

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SUPPRESSION OF FUEL EVAPORATION BY AQUEOUS FILMS OF FLUORO-CHEMICAL SURFACTANT SOLUTIONS

INTRODUCTION

Many fluorine-containing compounds have been shown to be very effective surface-active agents in water (1). Typically, the surface tensions of aqueous fluorochemical surfactant solutions are below 20 dynes/cm. When such solutions are placed on the surface of hydrocarbon liquids, the resulting interfacial tensions are approximately 4 to 5 dynes/cm or less. Theoretically, a surfactant solution will spread spontaneously to form a film on the surface of a less dense hydrocarbon liquid if the sum of the surface tension of the aqueous surfactant solution plus the interfacial tension between the two liquids is less than the surface tension of the hydrocarbon liquid itself. This behavior (2) is illustrated by

$$S_{a/b} = \gamma_b - \gamma_a - \gamma_i,$$

where

- $S_{a/b}$ = spreading coefficient,
- γ_b = surface tension of the lower liquid phase,
- γ_a = surface tension of the upper layer of liquid,
- γ_i = interfacial tension between liquids a and b.

Thus, when $S_{a/b}$ is positive, a drop of liquid a, when placed on the surface of liquid b, will immediately spread to form a film over the entire surface of liquid b.

It should be noted, however, that spreading coefficients calculated from the surface tensions of pure liquids or solutions indicate only the initial behavior of one liquid on another. After contact of the two liquids, either liquid may dissolve in the other sufficiently to change the energy balance, possibly resulting in the retraction of the surface film into a lens or other less-than-complete form of coverage.

In addition to their spreading properties, fluorochemical surfactants also have exceptional foam-stabilizing properties. Tuve et al. (3,4) proposed the use of these low-surface-tension solutions, which they called "light water," as fire extinguishing agents. In this application, the cooling and blanketing effect commonly associated with foam-type extinguishants is augmented by the formation of a liquid film on the fuel surface which further depresses the transfer of fuel vapor to the combustion zone above the liquid fuel. However, for film formation the liquid must be placed gently on the surface of the fuel; otherwise, the more dense aqueous solution will be carried through the surface of the hydrocarbon liquid and its vapor-suppressing capability lost. Foam has proved to be a satisfactory means of delivery. However, a foamed solution of surfactant alone does not have optimum properties as a fire extinguishing blanket since water rapidly drains from it, leaving a weak, permeable skeleton. The addition of a viscosity modifier such as polyethylene oxide will reduce the rate of liquid drainage from the foam.

The formation of aqueous fluorochemical surfactant films on hydrocarbon liquids has recently been discussed by Bennett et al. (5). These films were shown to reduce markedly the rate of evaporation of such volatile hydrocarbon liquids as toluene and n-octane.

The films did not spread on the surface of 2,2,4-trimethylpentane; therefore, the evaporation rate of this hydrocarbon was not reduced.

At present, little is known of the relative importance of the liquid film in comparison with the foam layer and the effect of viscosity modifiers and other additives on the effectiveness of aqueous film-forming foams (AFFF). This investigation was undertaken to present quantitative data on the mode of action of the aqueous films and to define the parts played by the various constituents of the film-forming solutions. In this report, the ability of solutions of commercially available AFFF concentrates and of aqueous solutions containing a fluorochemical surfactant alone to form surface films on various hydrocarbon liquids is discussed in terms of the physical and chemical properties of the solutions and the hydrocarbons. Also, the effectiveness of the aqueous films in suppressing fuel evaporation, i.e., the transport of hydrocarbon vapors from a pool of liquid fuel to the vapor-air space above is described. In a subsequent report, the relative effectiveness of foamed aqueous solutions as vapor suppressants will be evaluated.

EXPERIMENTAL PROCEDURE

Materials

The fluorochemical surfactants used in this study are given in Table 1. Solutions of concentrates FC-194 and FC-195 were prepared by dissolving 6 parts of the liquid concentrate in 94 parts of distilled water. Since fluorochemicals FS-2 and FX-177 are solids, solutions of these materials were prepared on a weight-percent basis using 0.1 and 0.2 wt-% of FS-2 and 0.25 wt-% of FX-177.

Table 1
Fluorochemical Surfactant Solutions used in this Study

Fluorochemical Designation	Composition	Surface Tension of Solution at 25°C (dynes/cm)
Concentrate FC-194* (lot 107)	Not available	15.5
Concentrate FC-195* (lot 9)	Not available	15.6
(lot 10)		16.4
FS-2 [†]	Perfluoropropyl diether-perfluoropropylamide-N-alkyltrimethylammonium iodide	15.4
		15.2
FX-177*	Perfluoroalkylsulfonamide-N-alkyltrimethylammonium iodide	16.7

*Supplied by 3M Company

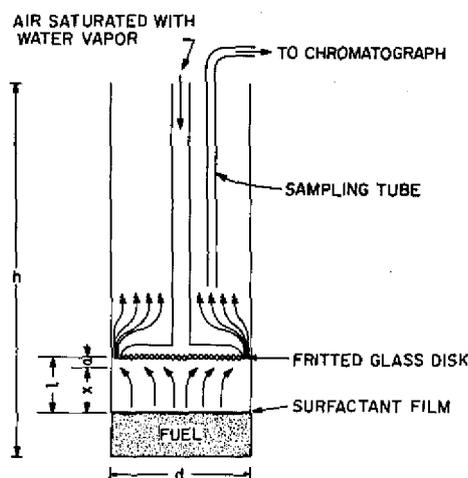
[†]Supplied by E.I. duPont

The hydrocarbon liquids and fuels used in this study are listed in Table 2 along with an indication of the purity of these materials.

Surface and Interfacial Tension Measurements

Surface tensions of the hydrocarbon liquids and of the fluorochemical solutions and the interfacial tensions between various hydrocarbon-surfactant solution pairs were

Fig. 1 - Apparatus for measuring evaporation rates. The dimensions are $h = 25$ cm, $d = 5.1$ cm, $a = 0.70 \pm 0.03$ cm, l is variable, and x is variable. The sample size is 50 ml.



measured by the ring method using a Cenco-du Nouy precision tensiometer and the method described in ASTM Standard D-1331 (6).

To determine if the surface tension of either the surfactant solutions or the hydrocarbon liquids was affected by mutual saturation of the liquid pairs, saturated solutions were prepared by placing equal quantities of each liquid in a stoppered flask and allowing them to remain in contact with occasional gentle mixing for a period of about 24 hours. Samples were withdrawn for surface tension measurements by placing a pipette well below the surface of each liquid.

Testing for Film Formation

In testing for film formation, the surfactant solution was contained in a 1000- μ l syringe and delivered through a Teflon capillary mounted vertically to discharge downward onto a 7-cm-diameter crystallizing dish containing the fuel. The tip of the capillary was positioned so that each droplet of solution just broke free from the capillary before touching the fuel. Fifty microliters (9 drops) of solution was used. An application rate of roughly one drop per second allowed film formation with little danger of the solution breaking through the fuel surface. Visual observations determined whether an aqueous film formed on the hydrocarbon surface. If film coverage was incomplete, the edge of the film could readily be seen due to a difference in the reflection of light. When complete coverage of the hydrocarbon was obtained, usually the edge of the film could be observed advancing to the rim of the fuel pool. The presence of a complete film was confirmed by just touching the covered surface of the fuel with a platinum ring (such as used in the tensiometer) and withdrawing the ring. In this manner, an intact film could be seen clinging to the ring.

Apparatus for Studying Evaporation Rates

To study the effectiveness of aqueous fluorocarbon surfactants in suppressing the evaporation rate of hydrocarbon liquids, a new apparatus, called an "evaporometer," was developed. This apparatus (Fig. 1) uses a fritted glass disk similar to that described by Sebba and Briscoe (7) and employs the adsorption principle of Langmuir (8). The entire assembly was surrounded by a water jacket for temperature control. A sample of hydrocarbon liquid was placed in the evaporometer and the surfactant solution placed on the hydrocarbon surface. Air was then admitted to the chamber through the fritted glass

disk to pick up hydrocarbon and water vapor from the vapor space and transport the vapors through the annular space between the fritted disk and the apparatus wall. A sampling tube, located a few centimeters above the disk, carried the hydrocarbon-water vapor mixture to a Beckman GC-5 chromatograph which was equipped with a hydrogen flame detector. This detector is insensitive to water vapor over the concentration ranges involved; hence, it indicates only the hydrocarbon portion of the mixture.

The chromatograph column absorbent material, SE-30 (methyl silicone rubber gum), produced sharp, narrow peaks with the pure hydrocarbon liquids so the percentage of hydrocarbon vapors in the gas stream could be determined directly from the peak height. When multicomponent fuel mixtures such as JP-4 jet fuel were analyzed, the resulting chromatograms consisted of a series of overlapping peaks followed by an irregular tail. To interpret these chromatograms, the chromatograph was assumed to be equally sensitive to all of the components in the mixture, so that the hydrocarbon concentration could be computed from only those peaks obtained during the first two minutes of the run. By this procedure, 95% or more of the hydrocarbon present was accounted for and the uncertainty due to instrument drift during the tailing period was eliminated. Since in these experiments the chromatograph was used to determine relative concentrations only, the assumption of equal sensitivity and the dropping of part of the curve did not introduce serious errors.

To verify this point, the evaporometer was charged with 50 cc of a multicomponent fuel (JP-4) and allowed to run for 1 hour. Eight vapor-air samples were analyzed during this period. Although peak heights associated with some of the constituents changed drastically, possibly due to the loss of the more volatile components, the total hydrocarbon vapor concentration remained surprisingly constant, as indicated by the area under the curve obtained during the first 2 minutes of each chromatograph run. The largest deviation from the average of the area measured was 0.29%; the average deviation was 0.08%.

Diffusion Theory Applied to the Evaporometer

According to the laws of diffusion, the rate of mass transfer from an area of one concentration to an area of lesser concentration depends on the concentration gradient, i.e.,

$$\frac{dq}{dt} = DA \frac{dc}{dx} \text{ or } q = \frac{DA(C_o - C_x)t}{x},$$

where

q = amount of volatile material transferred,

t = time,

D = diffusion coefficient,

A = area of source = area of receiver,

C_o = concentration at the source (conveniently expressed as the vapor pressure P of a liquid source),

C_x = concentration at the receiver,

x = distance between source and receiver.

When using the evaporometer, the distance x in the diffusion equations above cannot be measured directly, since a gas layer of indeterminate thickness flows under the glass frit. Instead, the term (L - a) can be substituted for x to give

$$q = \frac{DA(C_o - C_x)t}{L - a}.$$

For a given hydrocarbon this equation can be rearranged to

$$C = K \frac{P}{L - a},$$

where

C = concentration of fuel vapor in the effluent gas stream,

K = overall constant including the diffusion coefficient, the area of the fuel surface, and any "edge effects" due to the different diameters of the frit and fuel surfaces,

L = distance from the fuel surface to the underside of the glass frit,

a = thickness of the flowing air layer.

For the preceding equation to be valid, the magnitude of a should be constant regardless of the distance L. To test this point, the evaporometer was charged with cyclohexane and the concentration of its vapor measured at four values of L ranging from 1.68 to 3.69 cm. From these experiments, the value of a was found to be 0.70 ± 0.03 cm. As a check for reproducibility, the evaporometer was charged again with cyclohexane and allowed to run for an hour during which time the effluent air was sampled nine times. The maximum deviation from the average peak millivolts recorded was 0.33%; the average deviation was 0.17%. Thus, the evaporometer can be used to obtain reliable and reproducible data on evaporation rates.

Measurement of Evaporation Rates

To measure evaporation rates, the evaporometer was charged with 50 cc of the hydrocarbon liquid and allowed to equilibrate at 15°C. A stream of purified compressed air, saturated with water vapor, was passed through the apparatus at a rate of 630 cc/min. A portion of the vapor-laden air was drawn continuously through the same line and into the chromatograph sampling valve at 40 cc/min. At least three samples were taken at approximately 2-minute intervals to determine if the evaporation rate was uniform and to provide the initial or reference concentration for comparison with later concentrations. Then, the surfactant solution was placed on the fuel surface by means of a syringe with a long (31-cm), fine-bore, Teflon tube. The syringe was marked in 0.01-ml divisions and had a capacity of 1.0 ml. For measuring quantities of 0.05 ml and larger, the graduations on the syringe were used; for smaller quantities, the volume of surfactant solution was estimated by counting the number of droplets used (average droplet size = 0.0050 ml).

A waiting period of 2 minutes was allowed after adding the last drop of surfactant solution to permit the sampling line to fill with vapor at the new concentration. Then the chromatograph valve was actuated and the vapor concentration determined. The analysis was repeated at 2-minute (minimum) intervals for single hydrocarbons and at 5-minute intervals for mixed hydrocarbons. The peak millivolts (or area) recorded for each sample analyzed after applying the film-forming solution was divided by the corresponding value for the unfiled hydrocarbon and reported as percentage relative to initial vapor concentration. These percentages were then plotted against time to compare the effectiveness of various surfactant solutions in retarding evaporation of the hydrocarbon liquids. As an additional check on the evaporation progress, the fuel level in the evaporometer was measured at regular intervals with a cathetometer.

Table 2
Hydrocarbon Liquids and Fuels used in this Study

Hydrocarbon Liquid	Grade	Supplier	Surface Tension at 25°C (dynes/cm)
Cyclohexane	Certified A.C.S.	Fisher	24.2
n-Heptane	Certified Spectroanalyzed	Fisher	19.8
n-Heptane	Commercial	Phillips	20.9
Isooctane	Certified A.C.S.	Fisher	18.3
Avgas	115/145	1st sample	19.4
		2nd sample	19.5
JP-4	Navy specification	1st sample	22.4
		2nd sample	22.8
JP-5	Navy specification	1st sample	25.6
		2nd sample	25.8
Motor fuel	Regular	1st sample	20.5
		2nd sample	21.5
Naphtha	Stove and lighting		20.6

EXPERIMENTAL RESULTS AND DISCUSSION

Surface and Interfacial Tension Measurements

The results of the surface and interfacial tension measurements are given in Tables 1 to 3. From these data, which represent the averages of several determinations, spreading coefficients were calculated for the various surfactant solution-hydrocarbon liquid pairs. The results of these calculations plus the visual observations on film formation are given in Table 3. In accordance with predictions based on the equation discussed in the Introduction, films did not form when the spreading coefficient $S_{a/b}$ for the surfactant solution-hydrocarbon liquid pair was negative. However, in three cases where the spreading coefficients were slightly positive, film formation was not observed. Due to the low values for the spreading coefficients in these experiments (0.3 - 0.5 dynes/cm), the possibility of experimental error cannot be discounted. In the remaining 27 cases where the spreading coefficients were positive, film formation was observed as predicted.

In those cases where film formation was observed, the first few increments of solution appeared to spread evenly over the hydrocarbon surface. Further addition of solution resulted in the formation and growth of a drop extending downwards into the hydrocarbon layer. When an excess of solution was added, the pendant drop reached a critical size. At that point, a substantial portion of the drop would break off and fall through the hydrocarbon layer while still leaving a residual film on the hydrocarbon surface.

Effect of Mutual Saturation

The results of the surface tension measurements on the mutually saturated surfactant solutions and hydrocarbon liquids are shown in Table 4. In general, the surface

Table 3
Interfacial Tensions, Spreading Coefficients, and Film Formation Observations for
Various Surfactant Solution-Hydrocarbon Liquid Combinations

Surfactant Solution	Hydrocarbon Liquid	Interfacial Tension (dynes/cm)	Spreading Coefficient (dynes/cm)	Film Formed
FC-194 (lot 107)	Cyclohexane	4.3	4.4	Yes
	n-Heptane, cert.	5.5	-1.2	No
	n-Heptane, comm.	4.3	1.1	Yes (very slow spread)
	Avgas (1st sample)	4.6	-0.7	No
	JP-4 (1st sample)	3.6	3.3	Yes
	JP-5 (1st sample)	4.9	5.2	Yes
	Motor fuel (1st sample)	3.7	1.3	Yes
FC-195 (lot 9)	Cyclohexane	3.2	5.4	Yes
	n-Heptane, cert.	4.2	0.0	Yes
	Isooctane	2.5	0.2	Yes (slow spread)
	Avgas (1st sample)	0.5	3.3	Yes (slow spread)
	JP-4 (2nd sample)	3.6	3.6	Yes
	JP-5 (2nd sample)	4.9	5.3	Yes
	Motor fuel (1st sample)	2.6	2.3	Yes
FC-195 (lot 10)	Naphtha	2.8	2.2	Yes
	Cyclohexane	1.5	6.3	Yes
	n-Heptane, cert.	3.2	0.6	Yes
	Isooctane	2.8	-1.3	No
	Avgas (1st sample)	2.1	1.0	Yes
	JP-4 (1st sample)	2.7	3.3	Yes
	JP-5 (1st sample)	4.2	5.0	Yes
0.1% FS-2	Motor fuel (1st sample)	1.2	2.9	Yes
	Naphtha	0.8	3.4	Yes (slow spread)
	Cyclohexane	6.3	2.5	Yes (very slow spread)
	Avgas (2nd sample)	3.7	0.4	No
	JP-4 (2nd sample)	4.8	2.6	Incomplete; irregular outline
0.2% FS-2	JP-5 (2nd sample)	6.3	4.1	Yes (slow spread)
	Motor fuel (1st sample)	3.4	0.5	No
	Cyclohexane	5.6	3.1	Yes
	Avgas (2nd sample)	4.0	0.3	No
	JP-4 (2nd sample)	5.0	2.6	Yes
0.25% FX-177	JP-5 (2nd sample)	6.1	4.5	Yes
	Motor fuel (2nd sample)	2.7	3.6	Yes
0.25% FX-177	Cyclohexane	6.7	0.8	Yes (Moderately slow spread)

Table 4
Surface Tension of Surfactant Solutions Saturated with
Fuels and of Fuels Saturated with Surfactant Solutions
(Contact Time 24 hours)

Liquid	Contaminant	Surface Tension (dynes/cm)	Change in Surface Tension (dynes/cm)
6% FC-195 (lot 10)	Cyclohexane	16.0	-0.4
6% FC-195 (lot 10)	Avgas	15.2	-1.2
6% FC-195 (lot 10)	JP-4	15.9	-0.5
6% FC-195 (lot 10)	JP-5	15.8	-0.6
6% FC-195 (lot 10)	Motor fuel	15.2	-1.2
Cyclohexane	FC-195	24.0	-0.2
Avgas	FC-195	19.1	-0.4
JP-4	FC-195	22.7	-0.1
JP-5	FC-195	25.6	-0.2
Motor fuel	FC-195	21.6	1.4
0.2% FS-2	JP-4	15.0	-0.2
0.2% FS-2	JP-5	15.1	-0.1
JP-4	0.2% FS-2	22.5	0.1
JP-5	0.2% FS-2	25.2	-0.4

tensions of the surfactant solutions decreased slightly on continued contact with the hydrocarbon liquids during the 24-hour period. This effect is particularly noticeable in the case of avgas and motor fuels, both of which contain polar additives which, if extracted by the surfactant solution, would be expected to lower its surface tension. The hydrocarbon liquids showed very little change in surface tension except for motor fuel, which could be expected to show an increase in surface tension if it lost some of its polar material to the surfactant solution. Allowing the liquids to remain in contact for as long as 11 days produced very little change in surface tension readings beyond that indicated in Table 4.

When the surface tension data from Table 4 together with the interfacial tension data presented in Table 3 are used to calculate spreading coefficients of surfactant solutions on fuels, a somewhat different set of values for the spreading coefficients is obtained, as can be seen from a comparison of the data in Tables 3 and 5. However, even after mutual saturation, all coefficients remained positive. Thus, prolonged contact of a film with its fuel substrate should not result in the loss of the film through retraction of the aqueous film into lenses or islands.

Effect of Temperature on the Surface Tension of Aqueous Surfactant Solutions and of Various Hydrocarbons

The variation of surface tension with temperature of several surfactant solutions and hydrocarbon liquids was measured over the range of 10° to 50°C at approximately 5°C intervals. The results of these measurements are shown in Fig. 2 for the hydrocarbon liquids and in Fig. 3 for the surfactant solutions. In general, the surface tensions of the hydrocarbon liquids decreased approximately 0.07 to 0.12 dyne/cm for each 1°C temperature rise, and the surface tensions of the surfactant solutions decreased 0.05 to 0.06 dyne/cm-°C over the same temperature range. FC-195 (lot 10) proved to be the exception in that its surface tension passed through a minimum around 20°C and then began to increase with temperature. Since this minimum was not observed in the surface tension-vs-temperature plot for FC-195 (lot 9), it was concluded that the anomaly was due to some impurity in lot 10 preparation of concentrate.

Table 5
 Spreading Coefficients for Various Fuel-Surfactant
 Solution Combinations Calculated from Surface
 Tensions of Mutually Saturated Liquids

Surfactant Solution	Hydrocarbon Liquid	Spreading Coefficient (dynes/cm)
FC-195 (lot 10)	Cyclohexane	6.5
	Avgas	1.9
	JP-4	4.1
	JP-5	5.6
	Motor fuel (2nd sample)	5.2
0.2% FS-2	Cyclohexane	3.1
	Avgas (2nd sample)	0.3
	JP-4	2.6
	JP-5	4.5
	Motor fuel (2nd sample)	3.6

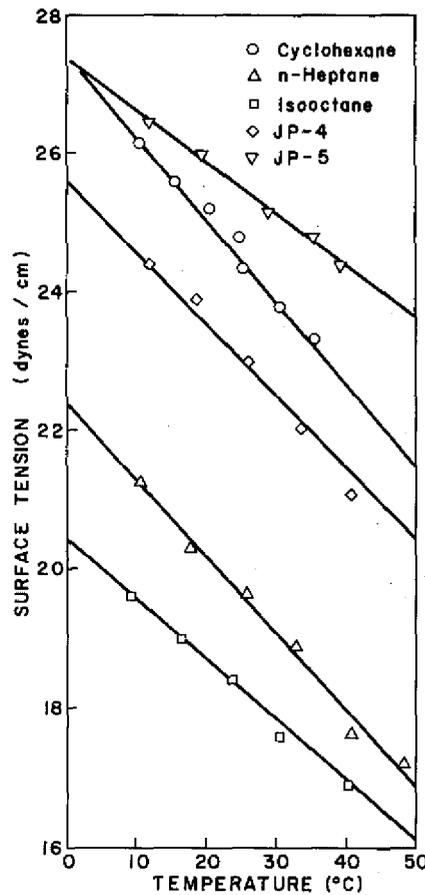


Fig. 2 - Effect of temperature on surface tension of hydrocarbon liquids.

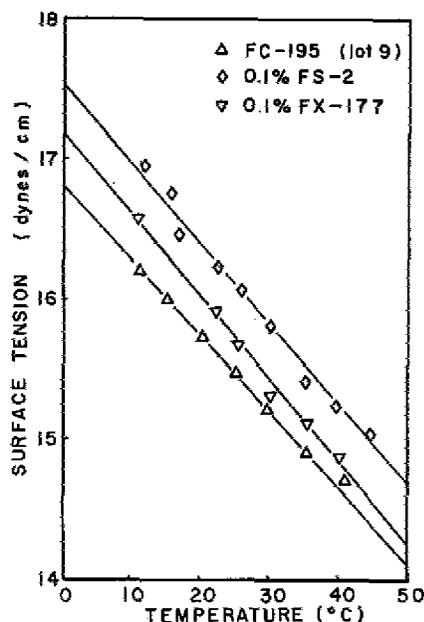


Fig. 3 - Effect of temperature on surface tension of surfactant solutions.

Measurements were also made to show the effect of temperature on the interfacial tension between 6% FC-195 (lot 9) and various hydrocarbon liquids. The results of these tests indicated that the interfacial tension decreased at approximately the same rate as the surface tension of the hydrocarbon liquid. Thus, increasing the temperature should produce only a small change in the value of the spreading coefficient. However, the effect could be significant if a change in sign of the spreading coefficient is involved.

Suppression of Fuel Evaporation by Aqueous Films

As noted earlier in this report, certain aqueous fluorochemical surfactant solutions are capable of spreading spontaneously over the surface of hydrocarbon liquids to form evaporation-retardant films. However, Burnett et al. (5) have demonstrated that monolayers of fluorochemicals by themselves, i.e., in the absence of water, have little, if any, effect on the rate of evaporation of hydrocarbon liquids. Therefore, any significant suppression of evaporation from a hydrocarbon liquid by an aqueous fluorochemical film must be attributed to a relatively thick layer of water in the film. The following work was undertaken to determine the effectiveness of such films as evaporation suppressants and to determine any limitations on the formation of the films. In interpreting this work, it should be kept in mind that the upper or aqueous layer has a greater density than the hydrocarbon substrate. Therefore, at some point in the process of film formation, the interfacial tension may be overcome by the force of gravity resulting in a breakthrough of at least part of the upper layer.

Evaporation suppression tests were made with solutions of both commercial film-forming concentrates and pure fluorochemical surfactants on a surface of cyclohexane. The results of these tests are summarized in Table 6, which gives the minimum vapor concentration in the vapor space above the film and the time required to reach the minimum after application of the surfactant. Since there was a substantial spread in results of replicate determinations, the highest and lowest minima and times are indicated for each group of identical tests. It was noted that after the minimum was reached, the concentration of the vapor became very erratic. In some cases, it rose very slowly with time, and in other cases the vapor concentration increased quite rapidly to a substantial fraction of its original value. Also, fuel vapor bubbles tended to form on the surface of

Table 6
Effectiveness of Various Surfactant Films in
Decreasing Evaporation of Cyclohexane

Surfactant Solution	Volume Used (μ l)	Number of Test Made	Minimum Vapor Concentration* (relative %)	Time Required to Reach Minimum Vapor Concentration (minutes)
6% FC-194 (lot 107)	50	3	6.0 - 9.5	4-6
	100	4	2.0 - 4.6	2-6
	150	2	2.5 - 4.8	2
3% FC-194 (lot 107)	50	4	4.4 - 9.2	4-8
	100	1	4.6	2
6% FC-195 (lot 10)	50	2	2.5 - 3.4	2
	100	5	1.8 - 5.6	2-4
	150	2	2.5 - 2.9	2
6% FC-195 (lot 9)	50	1	4.3	4
	115	1	3.2	4
0.25% FX-177	50	1	9.5	3
	100	2	2.4 - 7.8	3-4
	150	2	1.7 - 2.1	2
0.2% FS-2	45	1	4.3	4
	100	1	3.8	4

*Concentration of cyclohexane vapor in the absence of the surfactant film = 100%.

the film after a few minutes, indicating possibly serious defects in the film structure. Although the data in Table 6 suggest a trend of increasing effectiveness with increasing amounts of solution used and indicate some difference in effectiveness of the various surfactants, the values for the lowest minimum vapor concentration for the individual surfactant solutions fall rather close together. This would imply, as suggested by Bennett et al. (5), that evaporation suppression is due more to the aqueous component of the film rather than to the surfactant. The function of the surfactant is to spread and to maintain the integrity of the film.

It was noted that after application of the film-forming solution, a portion of the solution collected in a drop, or lens, hanging down into the hydrocarbon pool. Since this drop was considered to have some effect on the film stability, it was decided to explore the behavior of films formed from amounts of solution too small to produce a visible hanging drop. For this purpose, a 0.2% solution of FS-2 was used as the surfactant solution and cyclohexane as the hydrocarbon substrate. The FS-2 solution was chosen because it is less viscous than FX-177 and, unlike the commercial AFFF concentrates, does not contain thickeners.

The FS-2 solution was applied to the hydrocarbon surface in quantities ranging from 0.005 ml to 0.100 ml (5 to 100 μ l). The resulting data are presented in Fig. 4, where concentration is expressed in relation to the untreated hydrocarbon (unfilmed cyclohexane = 100%). The data indicate that both the speed and efficiency of vapor suppression is increased by increasing the quantity of surfactant solution. Plots of the minimum vapor concentrations from Fig. 4 vs the volume of surfactant solution are given in Fig. 5. The data produced two intersecting straight lines which are described by

$$\text{Conc (relative \%)} = 100.8 - 4.56 V$$

and

$$\text{Conc (relative \%)} = 5.2 - 0.0141 V,$$

where V is the volume of surfactant in μl . A comparison of the slopes of the two curves indicated that the first increments of the surfactant solution were over 300 times as effective in vapor suppression as the latter increments. Extrapolation of the two lines to their point of intersection gives a critical volume of approximately $21 \mu\text{l}$, which, from the dimensions of the apparatus, corresponds to an average film thickness of 10μ . It seems probable that once this film thickness is achieved, additional surfactant solution results in the formation and growth of a hanging drop which apparently contributes nothing to the vapor suppression qualities of the film. Burnett et al. (5) reported that thinner ($5\text{-}\mu$) films of commercial fluorochemical surfactant solutions reduced the evaporation rates of both toluene and n-octane by 40 to 50%. Their results are in agreement with the data in Fig. 5.

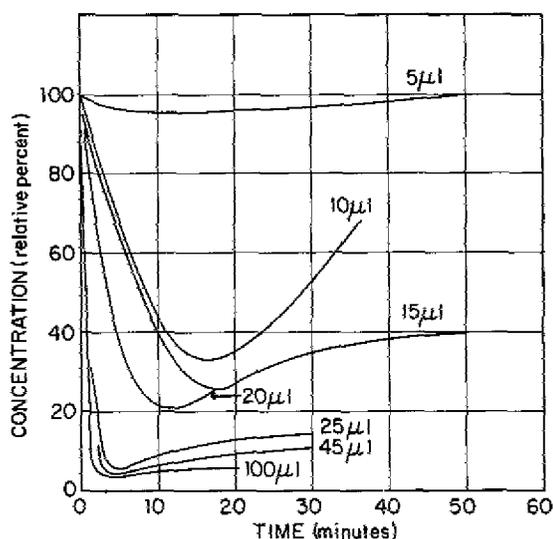


Fig. 4 - Change with time of hydrocarbon vapor concentration over cyclohexane with various amounts of FS-2 film-forming solution. The un-filmed cyclohexane equaled 100%.

As a further check on the estimate of the critical film thickness required to suppress evaporation, a 0.2% FS-2 solution was added dropwise ($5\text{-}\mu\text{l}$ drops) to the surface of cyclohexane liquid contained in glass crystallizing dishes having diameters of 6.6 and 9.7 cm. The underside of the hydrocarbon surface was observed visually so that the addition of the solution could be stopped at the first appearance of a persistent hanging drop or lens. A lens which lasted for at least 15 seconds was considered persistent; prior increments of solution formed transient lenses which spread and disappeared in 2 or 3 seconds. It was found that the maximum amount of FS-2 solution which could be added to the hydrocarbon surface without forming a hanging drop was $43 \mu\text{l}$ in the case of the small dish and $97 \mu\text{l}$ for the large dish. The critical film thickness calculated from these volumes, 13μ , agrees reasonably well with the value of 10μ which, according to the data from Fig. 5, is the critical film thickness for suppression of evaporation from a hydrocarbon surface.

Vapor suppression measurements were also made with various quantities of a film-forming solution containing 6 vol-% of FC-195 concentrate. The results of these tests are given in Fig. 6. As with the FS-2 solution, an initial rapid increase in vapor suppression with small increases in film-forming solution was noted (compare Figs. 5 and 6). The transition to lower effectiveness with increasing quantities of FC-195 solution, however, was not as abrupt as that found for the single-constituent, FS-2 solution. Nevertheless,

Fig. 5 - Minimum hydrocarbon vapor concentration over cyclohexane with various amounts of FS-2 film-forming solution on the surface. The unfiled cyclohexane equaled 100%.

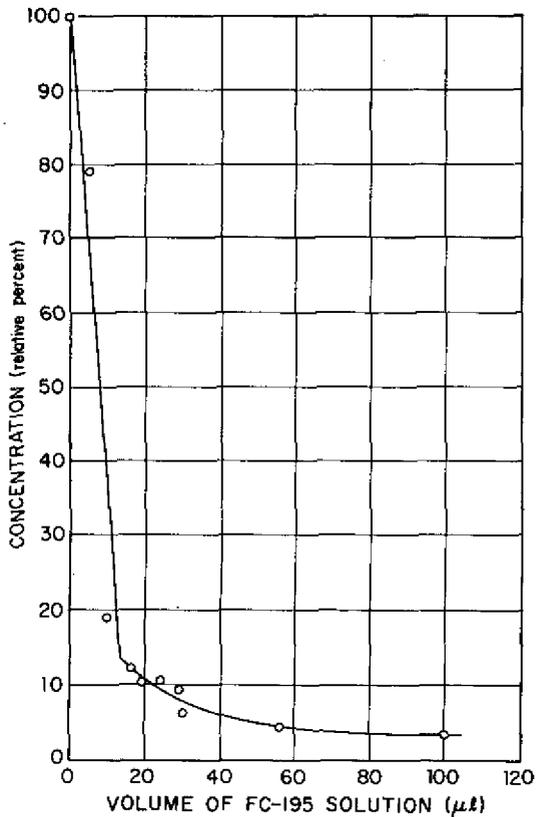
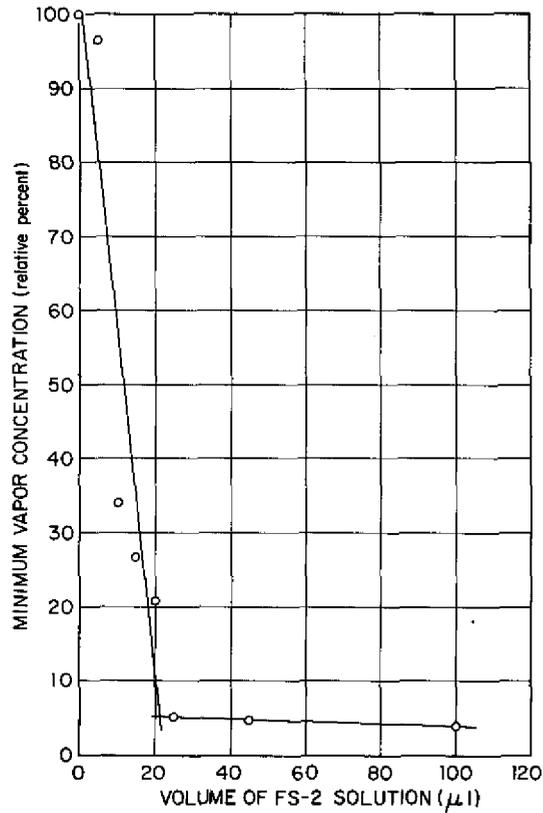


Fig. 6 - Minimum hydrocarbon vapor concentration over cyclohexane with various amounts of FC-195 film-forming solution on the surface. The unfiled cyclohexane equaled 100%.

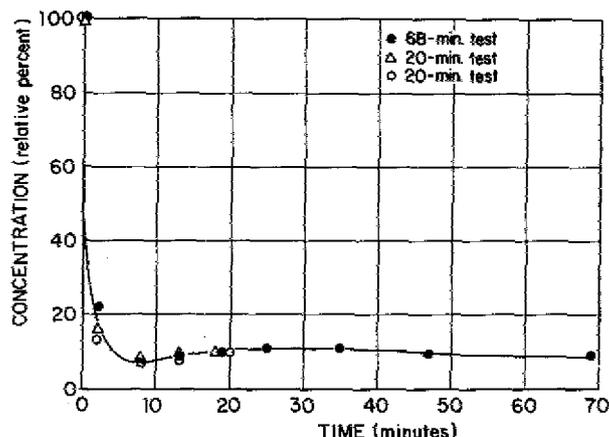


Fig. 7 - Change in hydrocarbon vapor concentration over jet fuel JP-4 with 0.1 ml of 0.2% FS-2 film-forming solution on the surface. (unfilmed JP-4 = 100%)

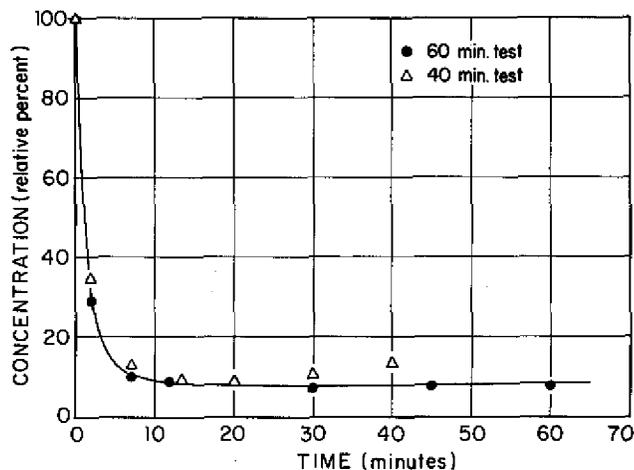
the transition was observed, as indicated in Fig. 6, in the vicinity of $13 \mu\text{l}$, which corresponds to a film thickness of 6.5μ . No particular significance can be attached to the seemingly greater film-forming efficiency of the FC-195 solution as compared with the FS-2 solution, since the quantity of surfactant in the FC-195 solution is not known.

The vapor suppression data presented in Table 6 and in Figs. 4 to 6 are based on the effects of aqueous films on a single, moderately volatile hydrocarbon (cyclohexane). Additional tests were made on jet fuel JP-4 to show the extension of the earlier observations to a common, easily ignitable fuel composed of a mixture of low to high volatility hydrocarbons. The evaporometer and the surfactant solutions were the same as used in the previous tests with cyclohexane. One-tenth ml ($100 \mu\text{l}$) of surfactant solution was applied to JP-4 fuel, since this quantity of surfactant was found to produce ample vapor suppression with cyclohexane (Fig. 4). As in previous tests, the surfactant solution both spread and formed a drop, or lens, hanging down into the fuel layer so, presumably, the film thickness exceeded the critical value. Vapor concentrations over the fuel were measured before addition of the surfactant solution, 2 minutes after applying the surfactant, and at 5 or more minute intervals thereafter. One test was carried out with the 0.2% FS-2 solution for a period of 69 minutes. This test was repeated twice for a long enough time to establish the maximum vapor suppression. The data obtained are presented in Fig. 7. Similar tests were conducted with FC-195 solutions on a surface of JP-4 fuel. The data from the FC-195 tests are presented in Fig. 8. The results show that the fluorochemical solutions reduce the rate of evaporation from the JP-4 fuel surface by about 90% and maintain it at this low level for longer than 60 minutes. The FS-2 solution and the FC-195 appeared to be equivalent in this regard.

Flammability Tests

Surfactant solutions (either commercial concentrate or fluorochemical alone in water) applied to the surface of cyclohexane reduced the vapor concentration from 2 to 5% of that for the untreated cyclohexane. These values correspond to 0.2 to 0.5 of the lower flammability limit for cyclohexane-air mixtures; hence, the fuel vapor-air mixture in the vapor space should not be in the flammable range. To confirm this point, a pilot flame (Meeker burner flame) was impinged on the surface of the filmed cyclohexane.

Fig. 8 - Change in hydrocarbon vapor concentration over jet fuel JP-4 with 0.1 ml of FC-195 film-forming solution on the surface. (Unfilmed JP-4 = 100%)



No ignition was obtained until after the pilot flame had been applied long enough to destroy the aqueous film. Similar results were obtained with filmed JP-4 fuel. Thus, by suppressing evaporation of the fuel, aqueous fluorochemical-derived films can prevent the accumulation of flammable fuel-air mixtures in the vapor space above volatile hydrocarbon liquids.

Fire Fighting Applications

The critical film thickness required to suppress evaporation of a hydrocarbon liquid, as determined in this study, is about 10μ . This corresponds to about 0.00025 gallons of surfactant solution per square foot. By contrast, the amount of water which must be applied as a foam to extinguish a burning hydrocarbon liquid is 0.03 to 0.10 gallons per square foot. Thus, it appears that in fire fighting applications, the aqueous film serves mainly as a vapor barrier, capable of preventing ignition of fuel or of preventing reignition of the fuel after the original fire has been extinguished by the cooling and blanketing action of the AFFF.

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