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SUPPRESSION OF EVAPORATION OF HYDROCARBON LIQUIDS AND FUELS BY FILMS CONTAINING AQUEOUS FILM FORMING FOAM (AFFF) CONCENTRATE FC-196

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Washington, D. C.

31 December 1974

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Report 7842	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD/A-006650
4. TITLE (and Subtitle) SUPPRESSION OF EVAPORATION OF HYDROCARBON LIQUIDS AND FUELS BY FILMS CONTAINING AQUEOUS FILM FORMING FOAM (AFFF) CONCENTRATE FC-196		5. TYPE OF REPORT & PERIOD COVERED An interim report on the NRL problem. 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J. T. Leonard and J.C. Burnett		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, D.C. 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project SF 38-451-001-03350 NRL Problem C05-19.201
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Naval Sea Systems Command Washington, D.C. 20360		12. REPORT DATE December 31, 1974 13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Evaporation
Evaporation suppression
Aqueous fire-fighting Foams
Hydrocarbon liquids
Hydrocarbon fuels

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Suppression of evaporation of hydrocarbon liquids and fuels by aqueous films containing a fluorocarbon surfactant has been examined as a function of film thickness, time, and hydrocarbon type. The hydrocarbon liquids included the homologous series of n-alkanes from pentane to dodecane, aromatic compounds, motor and aviation gasolines and jet fuels JP-4 and JP-5, and Navy distillate fuel. The surfactant solution used to form the films was a 6% solution of Aqueous Film Forming Foam (AFFF) concentrate FC-196. Films of the surfactant

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solution, ranging in thickness from 5 to 100 μm, were placed on the surface of the hydrocarbon liquid to test the ability of the film to suppress evaporation over a 1-hr period. Results indicated that for the n-alkanes and the hydrocarbon fuels a certain critical thickness of surfactant solution was required for optimum vapor suppression. Increasing the film thickness beyond this point did not lead to a significant increase in evaporation suppression but rather to eventual failure of the film. The critical film thickness for the n-alkanes was found to increase with increasing volatility of the hydrocarbon.

In comparison with the n-alkanes, it was considerably more difficult to suppress evaporation of the aromatic compounds. For example, the maximum vapor suppression obtained with benzene was less than 40% as compared with over 90% for the n-alkanes. The difference was attributed to the greater solubility of the aromatics in the aqueous film.

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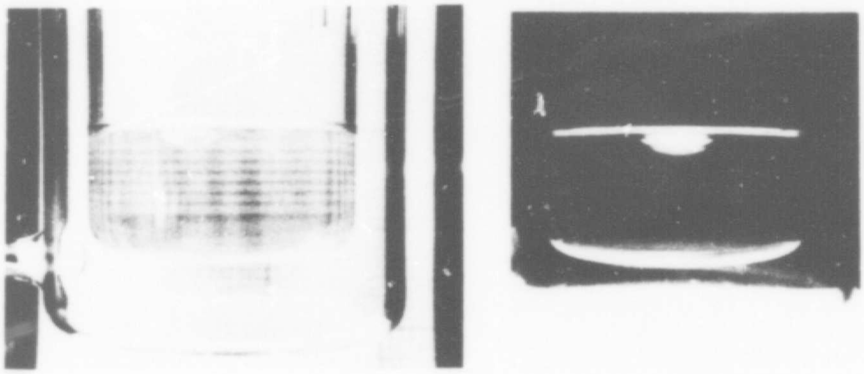
"Suppression of Evaporation of Hydrocarbon Liquids and Fuels by Films Containing Aqueous Film Forming Foam (AFFF) Concentrate FC-196," by J. T. Leonard and J. C. Burnett, December 31, 1975.

Page 10, Figure 7a and b, should be as shown below:



(a) (b)

Fig. 7 — Formation of a pendant drop of the surfactant solution on toluene prior to breakthrough (a) Showing the evaporometer and (b) Highlighting the pendant drop

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INTRODUCTION

Films based on insoluble surface-active compounds can be used to suppress evaporation of water even in large reservoirs [1]. The requirements for such compounds are that they contain at least 16 carbon atoms and have the ability to orient themselves perpendicularly to the surface in a closely packed array. Bernett et al. [2] attempted to apply this concept to the suppression of evaporation of hydrocarbon liquids. They examined a series of partially fluorinated surface-active compounds which were spread at a hydrocarbon liquid/vapor interface. The hydrocarbon liquids tested were toluene, 2, 2, 3-trimethylpentane, and nitromethane. None of the surfactants were successful in suppressing evaporation of the hydrocarbon liquids despite the fact that in several instances they formed essentially continuous films on the surface. Failure to achieve evaporation suppression was attributed to the fact that the fluorinated surfactants employed contained at the most eight carbon atoms per molecule, as compared with 16 which were found necessary to suppress evaporation of water, and to the inability of the fluorine-containing molecules to form a sufficiently-close-packed monolayer. However, these workers did establish that thin films (5 μm thick) based on an aqueous solution of a fluorocarbon surfactant would retard the rate of evaporation of toluene and n-octane by 40 to 50%. Evaporation suppression was attributed to the ability of the film to reduce the rate of transport of the hydrocarbon molecules across the interface to a value substantially less than the rate of diffusion through the saturated nonturbulent layer above the liquid.

Suppression of evaporation of hydrocarbon liquids and fuels by aqueous films is of practical importance in fire fighting and may even be of potential value in preventing air pollution in the event of large-scale spills involving these liquids. In the area of fire fighting, Tuve et al. [3, 4] have described the use of aqueous solutions containing fluorochemical surfactants for combatting hydrocarbon fuel fires. In this application the surfactant solution is applied as a foam which extinguishes the fire by virtue of its cooling and blanketing effect on the burning liquid. As the foam breaks down, it leaves an aqueous film on the fuel surface which tends to suppress evaporation and thereby prevent reignition of the hydrocarbon liquid.

In an earlier work [5] the present authors demonstrated the use of aqueous films based on solutions of fluorocarbon surfactants to control evaporation of certain hydrocarbon liquids and fuels. In the present study the list of hydrocarbon liquids is extended to include the homologous series of n-alkanes from pentane to dodecane (C_5 to C_{12}) plus selected aromatic compounds and hydrocarbon fuels.

Note: Manuscript submitted October 31, 1974.

EXPERIMENTAL PROCEDURE

Materials and Methods

The hydrocarbon liquids and fuels used in this study are listed in Table 1 together with an indication of their purity. As a further step in purification, the hydrocarbons were percolated through alumina and silica gel to remove polar impurities. Since the fuels contain additives which might be removed by percolation through silica gel, this treatment was not applied to them.

The surfactant solution used to form the aqueous films was a 6% solution of Aqueous Film Forming Foam (AFFF) Concentrate FC-196, which is manufactured by the 3M Company, St. Paul, Minn. The structure of the surfactant has been described by 3M as a long-chain perfluoroaliphatic radical combined with a water-solubilizing group*. Fluorocarbons of this general type, which are capable of producing fire-fighting foams, have been described by Tuve [4].

Prior to the measurement of evaporation rates, the entire list of hydrocarbon liquids and fuels was screened to determine on which hydrocarbon the surfactant solution could be expected to spread and form a vapor-suppressant film. For this purpose, surface and interfacial tensions were measured by the ring method using a Cenco du Nouy Tensiometer following the procedure described in ASTM Standard D-1331 [10], and spreading coefficients were calculated from the formula [11]

$$S_{b/a} = \gamma_a - \gamma_b - \gamma_{ab}$$

where

$S_{b/a}$ = initial spreading coefficient;

γ_a = surface tension of the lower liquid phase;

γ_b = surface tension of the upper liquid phase;

γ_{ab} = initial value of the interfacial tension between the surfactant solution and the hydrocarbon liquid.

If $S_{b/a}$ is positive, the surfactant solution should spread on the hydrocarbon liquid; if not, film formation will not occur. It should be pointed out that on contact either liquid may dissolve in the other sufficiently to cause a change in either γ_a or γ_b or both, with a resulting change taking place in the value of the spreading coefficient. Thus the final value of the spreading coefficient $S_{b'/a'}$ may differ in both magnitude and sign from the initial spreading coefficient. In the case of benzene on water, for example, the spreading coefficient changes from an initial value of $S_{b/a}$ = 8.9 dyne cm^{-1} to a final value of $S_{b'/a'}$ = −1.6 dyne cm^{-1}, due primarily to the lowering of the surface tension of water by dissolution of benzene [11]. In view of this limitation, spreading coefficients

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*J.D. LaZerte, personal communication, 1972.

Table 1
Surface and Interfacial Tensions, Spreading Coefficients, and Evaporation-Suppression Behavior for Hydrocarbon Liquids and Fuels

Hydrocarbon Liquid or Fuel	Source and Grade*	γ_b (25° C) (dyne cm^{-1}) Literature †	γ_b (25° C) (dyne cm^{-1}) Experiment	γ_{ab}(25° C) (dyne cm^{-1})	$S_{b/a}$ (25° C) (dyne cm^{-1})	Evaporation Suppression
n-Pentane	a	15.46	15.42	2.46	2.46	no
n-Hexane	b	17.90	17.94	3.06	-0.54	no
n-Heptane	b	18.80 19.80‡	19.58	3.40	0.76	yes
n-Octane	a	21.25	20.95	4.09	1.44	yes
n-Nonane	a	22.40	22.04	4.35	2.27	yes
n-Decane	a	23.42	23.10	5.03	2.65	yes
n-Undecane	a	24.27	23.78	5.21	3.15	yes
n-Dodecane	a	24.96	24.50	5.64	3.44	yes
Cyclohexane	c	24.34	24.11	3.48	5.21	yes
Isooctane	a	18.33	18.26	2.06	-0.22	no
Benzene	d	28.20	27.82	1.27	11.13	yes
Toluene	d	27.92	27.62	1.10	11.10	yes
Xylene	d	27.76**	27.98	1.69	10.87	yes
Aviation gasoline	e	n.a.¶	19.27	2.72	1.13	yes
Motor gasoline	e	n.a.	19.70	1.86	2.42	yes
JP-4	e	n.a.	22.36	3.75	3.19	yes
JP-5	e	n.a.	26.05	4.43	5.20	yes
Navy distillate	e	n.a.	28.59	4.87	8.30	yes

*a Phillips, Pure Grade, 99 mol % minimum
b Fisher, Certified Spectranalyzed
c Fisher, Certified
d Allied Chemical, Reagent ACS
e Military or federal specification [6]
† Graphical interpolation of literature data [7, 8]
‡ Based on data from Ref. 8. There is good agreement between Refs. 7 and 8 on all compounds except n-heptane
** Data for p-xylene
¶ n.a. = not available

are used in this study mainly as a guide in predicting initial spreading behavior of the surfactant solution on the hydrocarbon liquids and fuels.

Apparatus for Studying Evaporation Rates

To study the effectiveness of surfactant solutions in suppressing evaporation of hydrocarbon liquids and fuels, a specially designed evaporometer was employed. Details on the construction of this apparatus are given in an earlier report [5]. Basically the apparatus consists of an evaporometer (Fig. 1) and a Beckman GC-5 chromatograph. A Hewlett-Packard electronic integrator has been added to the system to facilitate handling of the chromatographic data.

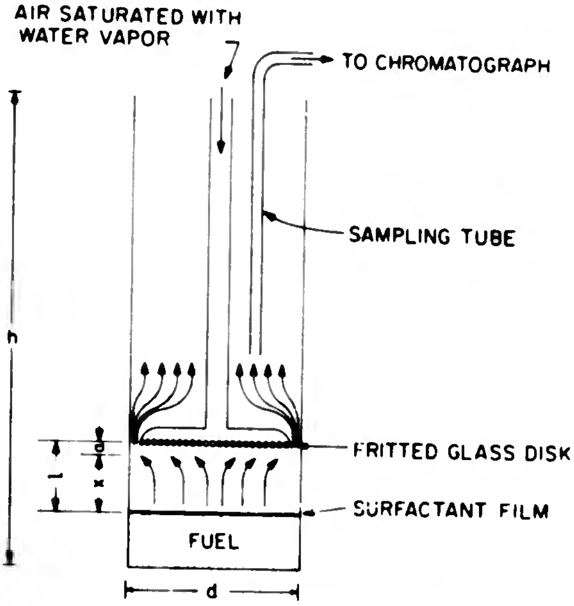


Fig. 1 — Apparatus for measuring evaporation rates. The dimensions are $h = 25$ cm, $d = 5.1$ cm, $1 = 2.8$ cm. The sample size is 50 ml.

Measurement of Evaporation Rates

To measure evaporation rates, the evaporometer was charged with hydrocarbon liquid and allowed to equilibrate at 25° C. The composition of the gas in the vapor space above the sample was measured at 2-min intervals until the evaporation rate was constant, i.e., until the area under the curves for three successive runs were reporducible to within 1%. The average of the three areas was taken as the reference concentration for the unfilmed hydrocarbon. Then the surfactant solution was placed on the fuel surface by means of a syringe with a long (31-cm), fine-bore, Teflon tube. For small volumes, a 50-μl syringe with 0.001-μl graduations was used; for larger quantities of surfactant, a

100-μl syringe was employed. The surfactant was injected at the wall of the evaporometer about 5 mm above the sample in the form of a slow ($\approx$ 1 μl/s), steady stream.

A waiting period of 2 min 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 valve on the chromatograph was actuated and the vapor concentration determined. The analysis was repeated at 2-to-5-min (minimum) intervals for single hydrocarbons and at 5-min intervals for mixed hydrocarbons. The area under the peak for each sample analyzed after applying the film-forming solution was divided by the corresponding value for the unfilmed 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.

Flammability Tests

Flammability tests were conducted on all of the fuel samples and on those hydrocarbon liquids that had flash points below 25° C and on which film formation occurred. Both the Fisher/Tag Cleveland Open Cup Flash Tester and the Fisher/Tag Closed Cup Tester were used. The open-cup method was chosen because the nonequilibrium conditions inherent in this procedure simulate the conditions existing in the evaporometer or in an open pool where the vapors cannot accumulate. The closed-cup apparatus was used to determine if in a closed environment sufficient vapors could collect in the vapor space above a filmed hydrocarbon liquid or fuel to cause ignition. These results are particularly important in assessing the behavior of the more volatile liquids which, although they may be covered by a film, may still release sufficient vapors to constitute a flammable mixture if allowed to accumulate.

In using the open-cup method, the sample was placed in the cup at 25° C, and a flame was passed over the sample to determine if the vapors could be ignited. If so, a fresh sample was placed in the cup, and a film of surfactant solution 23 μm thick was spread over the surface. After a 2-min wait the flame was passed over the cup. If no ignition occurred, the flame was passed over after 5 min and again at 10 min. If the hydrocarbon vapors could not be ignited in the absence of the surfactant film, no further tests were carried out.

The procedure for testing with the closed cup was essentially the same except that instead of passing the flame over the sample, the flame was introduced through an opening in the lid of the sample holder. At all other times, the opening was closed. Also, after applying the surfactant film, a stream of air was blown over the sample cup for 1 min to remove residual hydrocarbon vapors. The cup was then closed for another minute before testing with the flame.

RESULTS AND DISCUSSION

Spreading Coefficients and Evaporometer Studies

Table 1 lists the measured surface- and interfacial-tension data and the calculated initial spreading coefficients for the various surfactant solution/hydrocarbon liquid pairs. Negative initial spreading coefficients were obtained for the following liquids: n-pentane, n-hexane, and isooctane. When these same liquids were tested in the evaporometer, no indication of evaporation suppression was found. Instead, when the surfactant solution was placed on the surface of these liquids, a droplet formed which almost immediately broke through the hydrocarbon surface and fell to the bottom of the container. The remaining 15 hydrocarbon liquids and fuels in Table 1 gave positive spreading coefficients and positive indications of evaporation suppression when examined in the evaporometer. Thus spreading coefficients provided a reliable qualitative prediction of evaporometer performance in this work.

A plot of the initial spreading coefficients for the surfactant solution on the n-alkanes (C_5 through C_{12}) as a function of hydrocarbon surface tension is given in Fig. 2. The resulting straight line intercepts the axis at $S_{b/a} = 0$ when the surface tension of the hydrocarbon is 18.5 dyne cm^{-1}. Thus the critical surface tension for the n-alkanes with this surfactant solution is 18.5 dyne cm^{-1} at 25° C; if the surface tension of the hydrocarbon is below this value, the surfactant solution will not spread and form a film on the hydrocarbon surface.

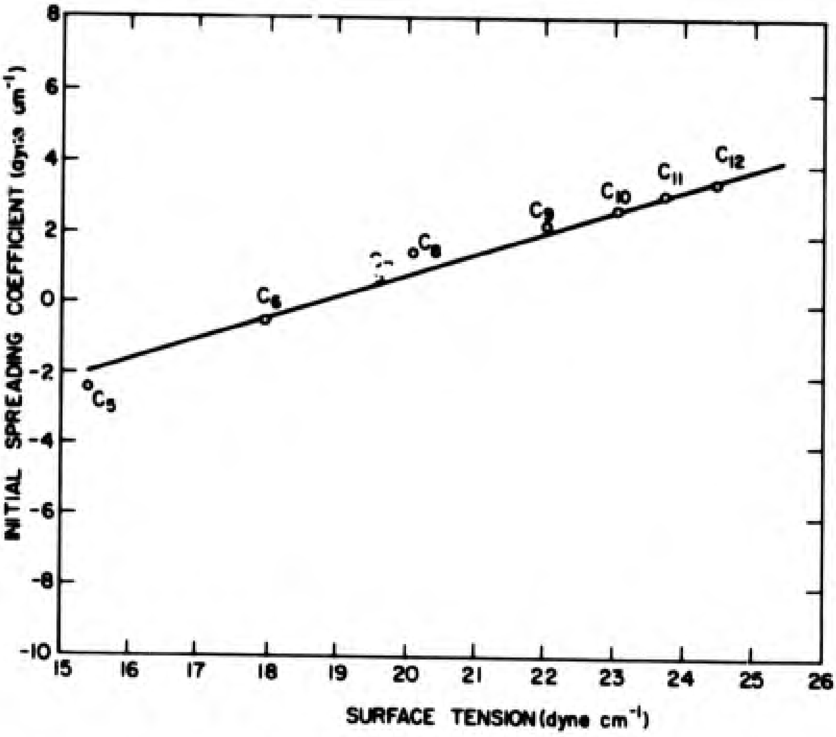


Fig. 2 — Spreading coefficient as a function of surface tension for the n-alkanes at 25°C

The results of a typical evaporometer study showing the effect of film thickness on suppression of evaporation of n-octane are given in Fig. 3. The data show that as the thickness of the surfactant film is increased, the rate of evaporation of the hydrocarbon is suppressed. Also, the time at which maximum vapor suppression occurs shifts from 20 to 2 min as the film thickness is increased. With optimum film coverage, the concentration of the hydrocarbon vapor is reduced to less than 5% of its original value. If the minimum values from Fig. 3 are replotted as in Fig. 4, it can be seen that once the thickness of the film reaches a certain critical value, called the critical film thickness in this work, additional amounts of surfactant solution do not lower the evaporation rate. Instead, as the film thickness is increased beyond the critical point, evaporation is suppressed for longer periods of time (up to 30 to 40 min). Ultimately gravitational effects take over, and the surfactant solution begins to collect in the form of a pendant drop. If more surfactant solution is added, the pendant drop will break through the hydrocarbon surface, and evaporation suppression will cease.

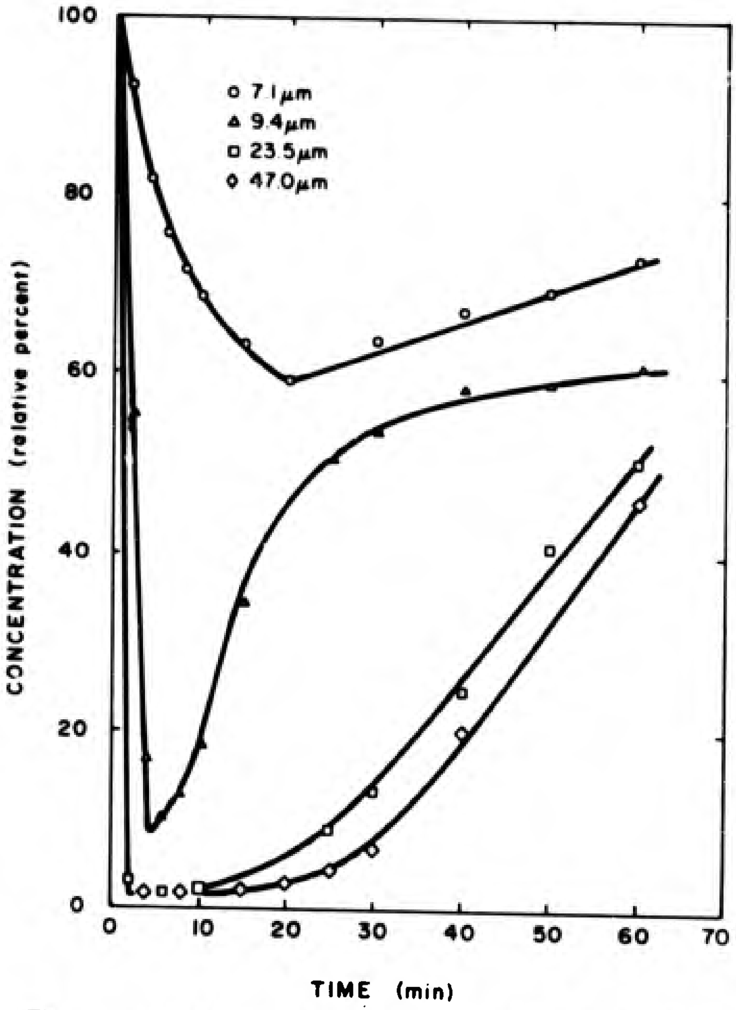


Fig. 3 — Change with time of hydrocarbon vapor concentration over n-octane at various film thicknesses. (Unfilmed n-octane = 100%).

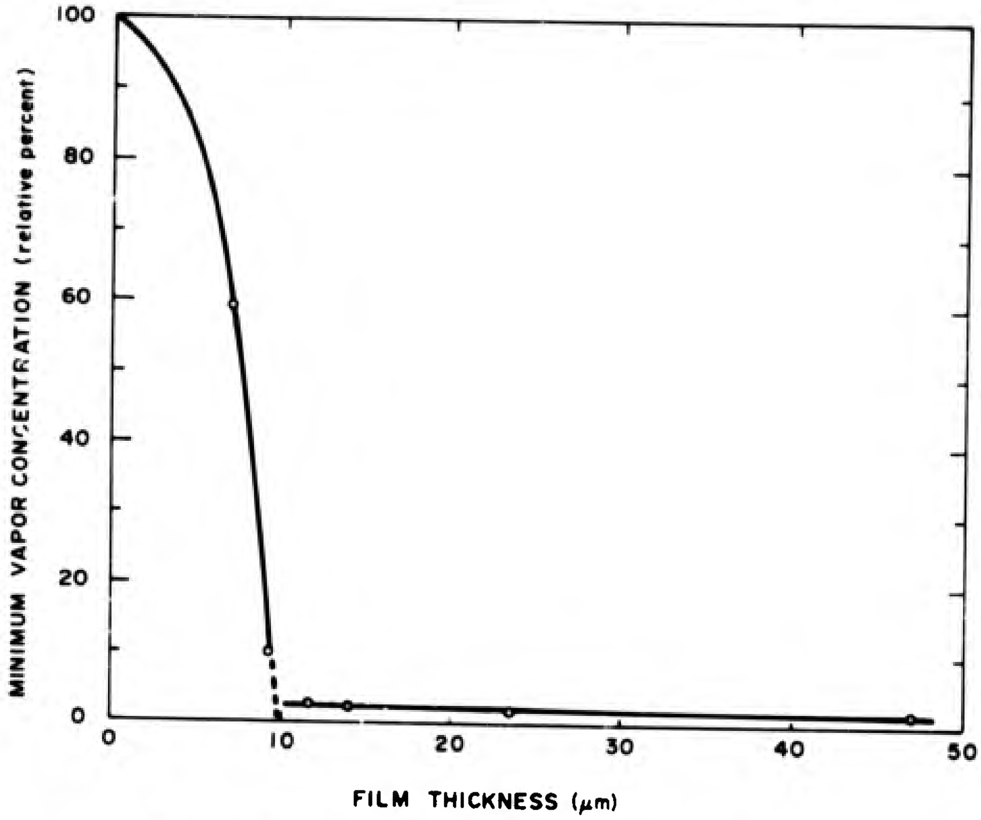


Fig. 4 — Effect of film thickness on the minimum concentration of n-octane in vapor space. Extrapolation of the vertical curve to the abscissa gives the critical film thickness.

A series of plots similar to Figs. 3 and 4 were made for n-alkanes containing from 7 to 12 carbon atoms to determine the critical film thickness for each of these liquids. When these data are plotted as a function of the vapor pressure of the hydrocarbon liquid (Fig. 5), it can be seen that the more volatile hydrocarbons require a thicker film of surfactant solution for evaporation suppression. Although cyclohexane is not a member of the same homologous series, the datum point for this compound also falls on the curve, indicating a critical film thickness of 14.1 μm. This value is in fair agreement with the critical film thickness of 10 μm reported earlier for cyclohexane [5] using another fluorocarbon surfactant, namely Dupont FS-2.

Suppression of evaporation of aromatic compounds by the surfactant films is considerably more difficult than with the n-alkanes, as can be seen by a comparison of Figs. 4 and 6. (The curve for toluene falls between the curves for benzene and xylene but is not shown to eliminate crowding). At a film thickness of 23.5 μm, the rate of evaporation of benzene was suppressed less than 40%, as compared to over 90% for the n-alkanes. Plots of the evaporometer data for the aromatic compounds (Fig. 6) reveal another difference when compared with the n-alkanes, i.e., the aromatic hydrocarbons did not exhibit a critical film thickness. As the thickness of the film on the aromatic hydrocarbons was increased, evaporation suppression increased until a pendant drop formed which eventually broke through the interface. The last datum point for each compound in Fig. 6 corresponds to the maximum film thickness achieved without breakthrough. The formation of a pendant drop on toluene is shown in Fig. 7.

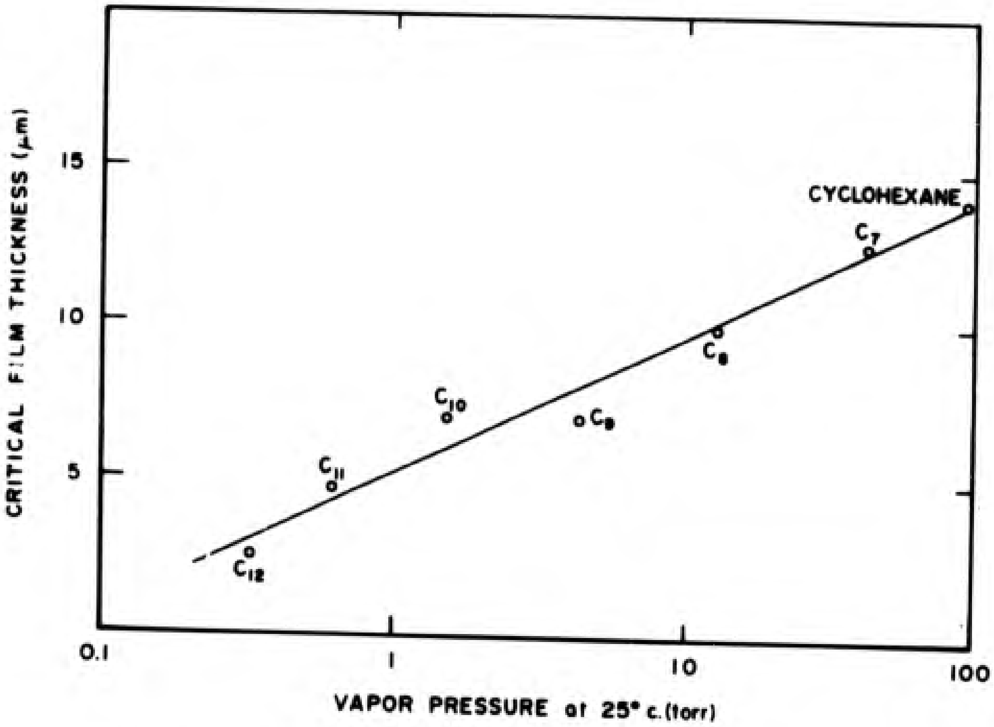


Fig. 5 — Effect of vapor pressure on the critical film thickness for the n-alkanes and cyclohexane

The inability to obtain better evaporation suppression with the surfactant films on the aromatic compounds relative to the n-alkanes is attributed to the greater solubility of the aromatic compounds in the aqueous film [11]. On a mole-fraction basis (Table 2), benzene is 140 times more soluble in water than n-octane. Presumably a similar relationship would apply to the relative solubilities of aromatic and aliphatic hydrocarbons in the surfactant solution which constitutes the vapor-suppressant film. It is noteworthy that the ability of the surfactant film to suppress evaporation of the hydrocarbon liquids in this study was found to decrease as the solubility of the hydrocarbon in water increases (Table 2).

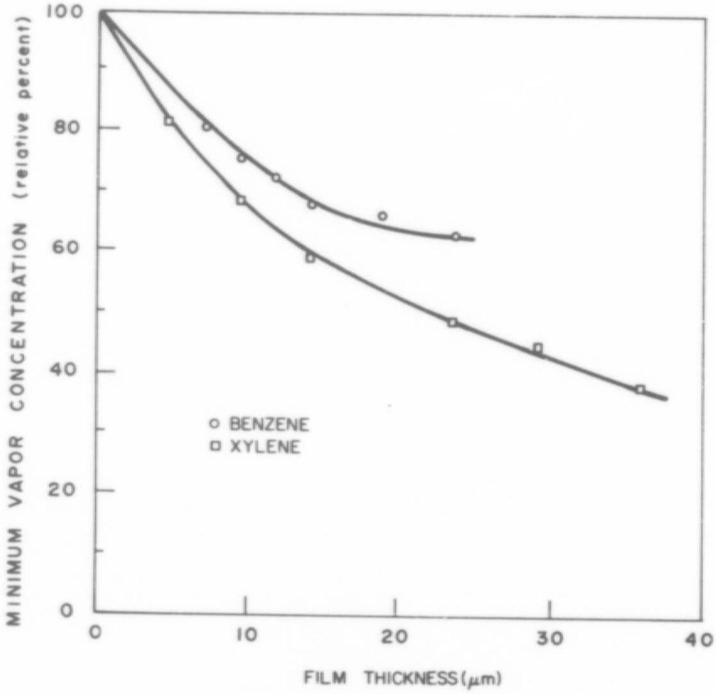
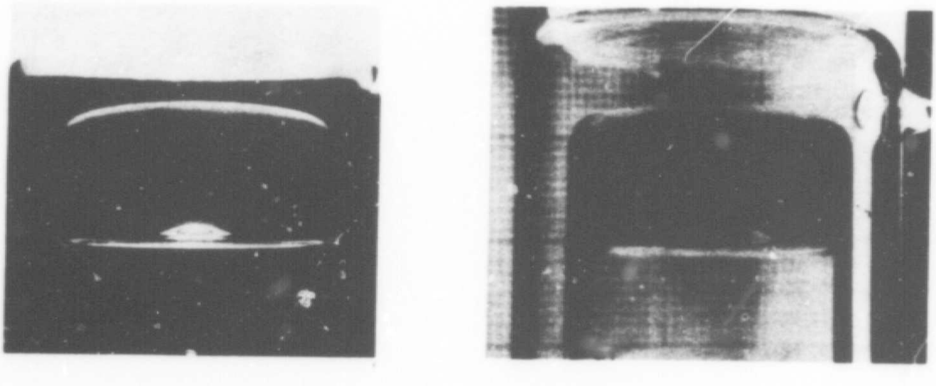


Fig. 6 — Effect of film thickness on the minimum concentration of aromatic hydrocarbons in vapor space.



(a) (b)

Fig. 7 — Formation of a pendant drop of the surfactant solution on toluene prior to breakthrough (a) Showing the evaporometer (b) Highlighting the pendant drop

Table 2
Solubility of Water in Organic Liquids and of Organic Liquids in Water at 25°C [11] and Evaporometer Data for Aliphatic and Aromatic Compounds

Hydrocarbon Liquid	Mole Fraction of Water in Organic Liquid	Mole Fraction of Organic Liquid in Water	Evaporometer Data — Minimum Vapor Concentration (rel. %)
n-Pentane	0.00048	0.00015	n.a.*
n-Hexane	0.00060	0.000029	n.a.
n-Heptane	0.00084	0.000009	0.8
n-Octane	0.00090	0.000003	1.5
Benzene	0.0031	0.00042	62.4
Toluene	0.0025	0.00010	47.9
Xylene	0.0023	0.000024	35.4

* n.a. = not available since film did not form.

Since the hydrocarbon fuels JP-4 and JP-5 may contain as much as 25% aromatic hydrocarbons [6], a simulated jet fuel was prepared to determine the effectiveness of the surfactant solution in suppressing evaporation of mixed hydrocarbons. The simulated jet fuel consisted of 25% benzene and 75% n-octane. The thickness of the surfactant film was 14.1 μm. The results of these tests are presented in Fig. 8 together with data obtained when the individual liquids were covered with a surfactant film of the same thickness. The data show that in the simulated fuel, the evaporation of the aromatic portion was only slightly affected by the presence of the aliphatic constituent, whereas the evaporation of the aliphatic compound was almost completely suppressed. Although this represents an extreme case (jet fuels seldom contain more than 17% aromatics [12]), it does indicate that the evaporation of the aromatic portion of jet fuel would be only partially retarded by the film.

The evaporation-suppression data for the hydrocarbon fuels are summarized in Figs. 9 and 10. As with the n-alkanes, the fuels exhibited a critical film thickness beyond which the rate of evaporation was suppressed in excess of 90%. However, for JP-4, JP-5, and Navy distillate fuels, the critical film thickness was not too well defined. Rather, the curves for these fuels (Figs. 9 and 10) indicated a more gradual change, as opposed to the fairly sharp transitions found for aviation and motor gasolines as well as for the n-alkanes (Fig. 4). This behavior is not too suprising, considering the wide variety of hydrocarbon types, including aromatic compounds, which can be found in these fuels. However, it is evident that the hydrocarbon fuels resembled the aliphatic compounds in evaporation-suppression behavior in that the more volatile fuels (aviation and motor gasolines) required a greater film thickness for evaporation control than the low-vapor-pressure product

(Navy distillate fuel). Extrapolation of the vertical portion of the curves in Fig. 9 yields a critical film thickness of 16.4 μm for aviation gasoline and 11.4 μm for motor gasoline. By application of the data in Fig. 5, it would appear that aviation gasoline resembles an n-alkane in the range of C_5 to C_6 in evaporation-suppression behavior, whereas motor gasoline resembles between an n-alkane C_7 and C_8. The critical film thickness for Navy distillate fuels is 2.2 μm (Fig. 8), which places this fuel fairly close to C_{12} in evaporation-suppression behavior. These results are consistent with the volatility characteristics of these fuels.

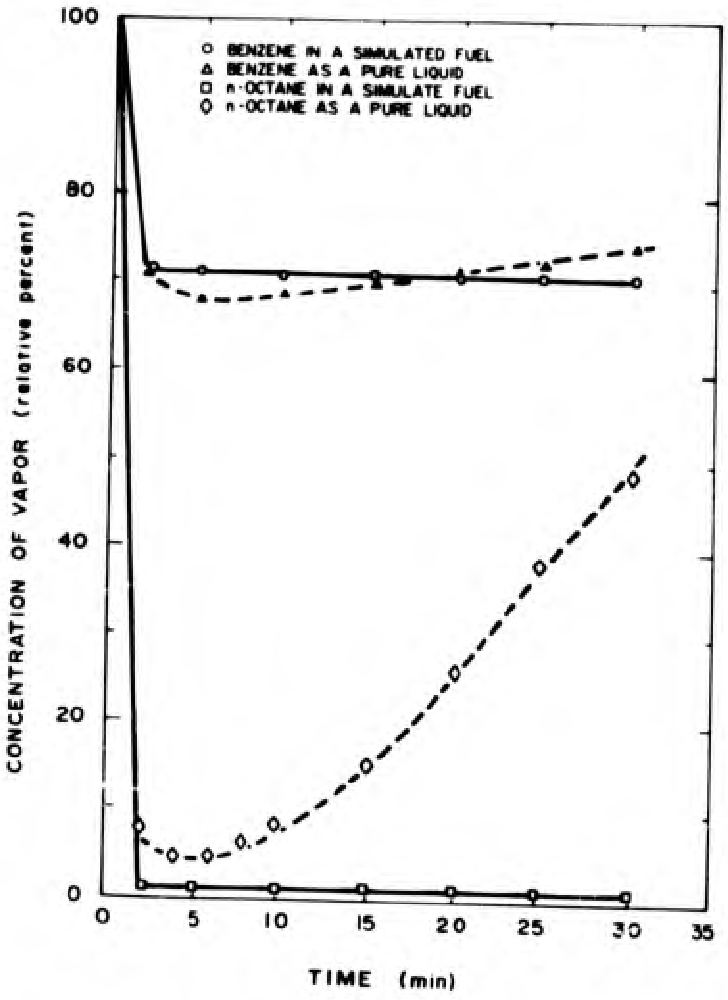


Fig. 8 Concentration of hydrocarbon vapors over the simulated fuel as compared with pure liquids, at a film thickness of 14.1 μm

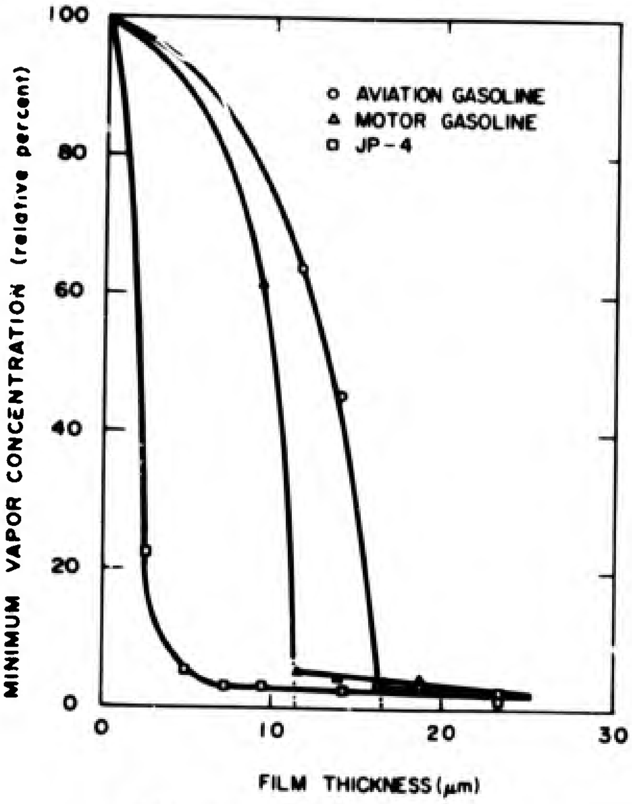


Fig. 9 — Effect of film thickness on the minimum hydrocarbon vapor concentration for volatile fuels

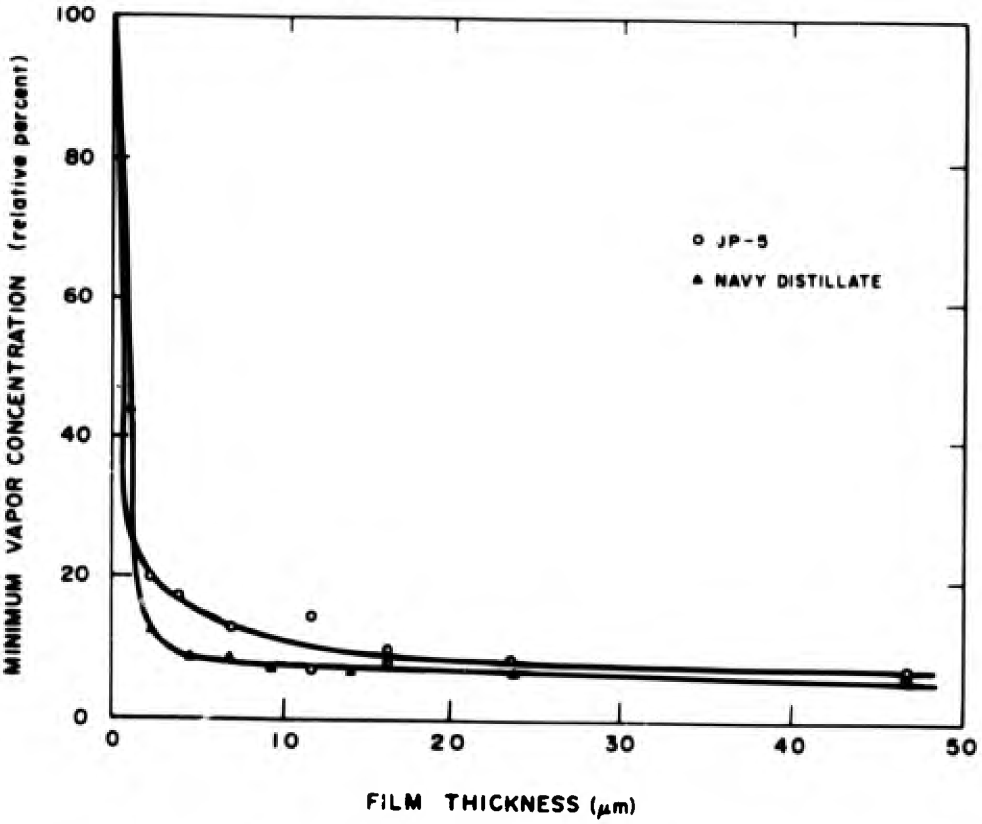


Fig. 10 — Effect of film thickness on the minimum hydrocarbon vapor concentration for low-vapor-pressure fuels

The remaining fuels, JP-4 and JP-5, do not fall in line. If the critical film thickness is obtained by extrapolation of the vertical portions of the curves in Figs. 9 and 10, then the critical film thickness becomes 2.6 μm for JP-4 fuel and 1.0 μm for JP-5. Although this value for JP-5 is in accord with the volatility characteristics of that fuel, a critical film thickness of 2.6 μm for JP-4 is entirely too low. Alternatively, if the critical film thickness is taken as that point beyond which evaporation suppression is not improved by increasing the film thickness (as determined by the horizontal portion of the curves in Figs. 8 and 9), then the critical film thickness becomes 7.0 μm for JP-4 and 16.6 μm for JP-5. Neither of these values is consistent with the volatility characteristics of these fuels. Thus it appears that the correlation between critical film thickness and volatility which was derived for the n-alkanes is of limited value in describing the behavior of complex mixtures such as jet fuels.

Application to Fire Research

From the standpoint of fire research, reducing the concentration of hydrocarbon vapor by 90% or more is of considerable importance, especially if in the process the hydrocarbon is taken below its lower flammability limit and hence cannot be ignited. The effectiveness of the surfactant film in reducing the concentration of hydrocarbon vapors in the evaporometer is summarized in Fig. 11. Vapor concentrations corresponding to the lower flammability limits for the hydrocarbon liquids were calculated from the literature values for the lower flammability limits [13] and from vapor-pressure data [14] at 25° C. For three compounds (n-heptane, n-octane, and cyclohexane), it can be seen that the surfactant film reduced the concentration of vapors below their respective lower flammability limits. The concentrations of five hydrocarbon liquids (n-nonane, n-decane, n-undecane, n-dodecane, and xylene) were already below their lower flammability limits before the surfactant solution was applied. In these cases application of the surfactant film further reduced the possibility of ignition. For the remaining compounds (benzene and toluene), the surfactant film appears to offer no protection from ignition since the vapor concentrations of these compounds were still above their lower flammability limits after the film was applied.

To further demonstrate the effectiveness of the surfactant film in preventing ignition of hydrocarbon vapors, flammability tests were also carried out. The results of these tests using an open-cup flash point tester are summarized in Table 3. Closed-cup flash point data are also included in this table for reference since open-cup data are not available for all of the liquids. As predicted from the evaporometer data in Fig. 11 both n-heptane and cyclohexane were protected from ignition by the surfactant film. However, n-octane did not ignite in the absence of the film since the flash point of this compound in this apparatus is three degrees above the test temperature. Burgoyne et al. [15] have shown that flash points obtained by the open-cup method are often considerably higher than the values obtained in a closed cup. Thus n-octane, which has a closed-cup flash point of 13° C, gave positive ignition in the closed-cup tests (Table 4) but not in the open cup.

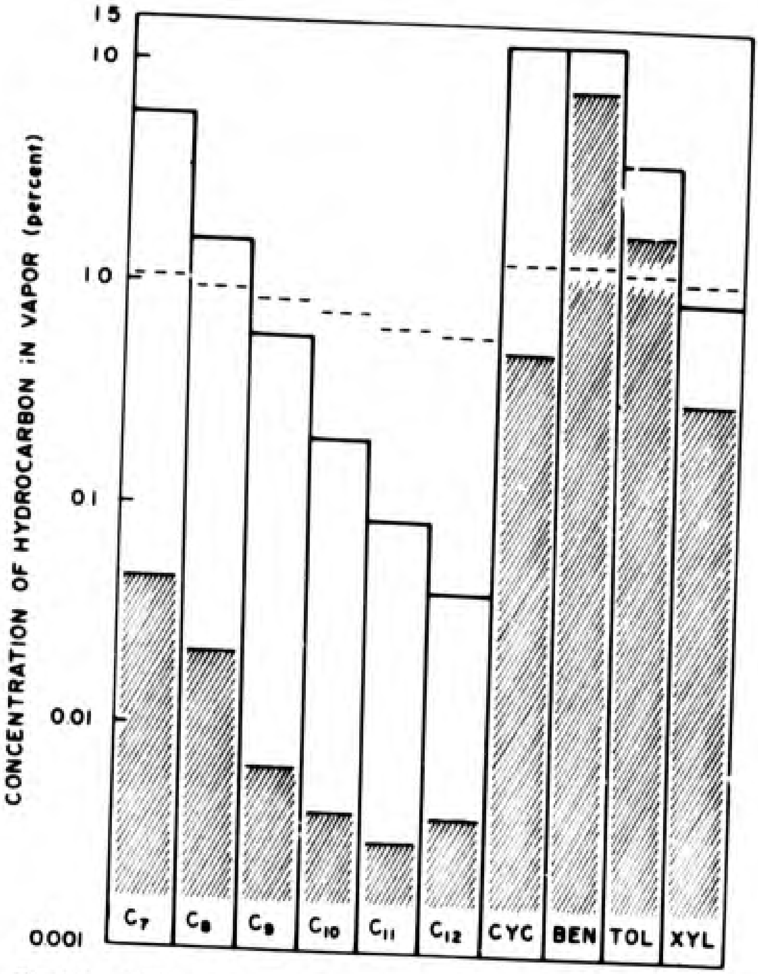


Fig. 11 – Effectiveness of the surfactant film in reducing the concentration of hydrocarbon vapor below the lower flammability limits (dashed horizontal lines). C_7 through C_{12} = n-heptane through n-dodecane; CYC = cyclohexane; BEN = benzene; and XYL = xylene. The unshaded area represents the concentration of hydrocarbon vapor before applying the film; the shaded area represents the minimum hydrocarbon concentration with the film.

Table 3
Observations on the Flammability of Hydrocarbon Liquids and Fuels Before and After the Application of the Surfactant Film in an Open-Cup Apparatus

Hydrocarbon Liquid or Fuel	Flash Point - Closed Cup [13] (°C)	Film Thickness (μm)	Observation on Flammability*(25° C) - Time Since Surfactant Applied		
			2 min	5 min	10 min
n-Heptane	−4	none	+		
		23.5	—	—	—
n-Octane	13	none	—		
Cyclohexane	−20	none	+		
		23.5	—	—	—
Benzene	−11	none	+		
		23.5	+		
Toluene	5	none	+		
		23.5	—	—	+
75% n-Octane, 25% Benzene		none	+		
Aviation gasoline	−46	none	+		
		23.5	—	—	+
Motor gasoline	−38	none	+		
		23.5	—	—	+
JP-4	−23 to	none	+		
	−1	23.5	—	—	—
JP-5	60	none	—		
Navy distillate	66	none	—		

* + = ignition
— = no ignition

Table 4
Observations on the Flammability of Hydrocarbon Liquids and Fuels Before and After the Application of the Surfactant Film in a Closed-Cup Apparatus

Hydrocarbon Liquid or Fuel	Film Thickness (μm)	Observations of Flammability*(25° C) - Time Since Surfactant Applied		
		2 min	5 min	10 min
n-Heptane	none	+		
	23.5	–	+	+
n-Octane	none	+		
	23.5	–	–	–
Cyclohexane	none	+		
	23.5	+	+	+
Benzene	none	+		
	23.5	+		
Toluene	none	+		
	23.5	+		
75% n-Octane, 25% Benzene	none	+		
	23.5	+		
Aviation gasoline	none	+		
	23.5	+		
Motor gasoline	none	+		
	23.5	+		
JP-4	none	+		
	23.5	–	–	+
JP-5	none	–		
Navy distillate	none	–		

* + = ignition
– = no ignition

Also, as predicted from the data in Fig. 11, benzene was not protected from ignition by the surfactant film. Toluene did not produce ignition in the open cup during the first 5 min but gave a positive test at 10 min. In a separate experiment the flame was positioned above the toluene sample after the surfactant film was applied and allowed to remain there throughout the test. After a 5-min wait the sample flashed several times but the flame went out. A minute later a stable flame was obtained. Thus toluene appears to be more of a borderline compound than would appear from the data in Fig. 11. From the evaporometer data for toluene, which are presented in Fig. 12, it can be seen that the concentration of toluene increased steadily with time after the minimum value was reached. Thus it is not surprising that toluene eventually produced a flammable concentration in the open cup. Similarly, the simulated fuel, which contained 75% n-octane and 25% benzene, passed from a no-flame to a flammable concentration between 2 and 5 min.

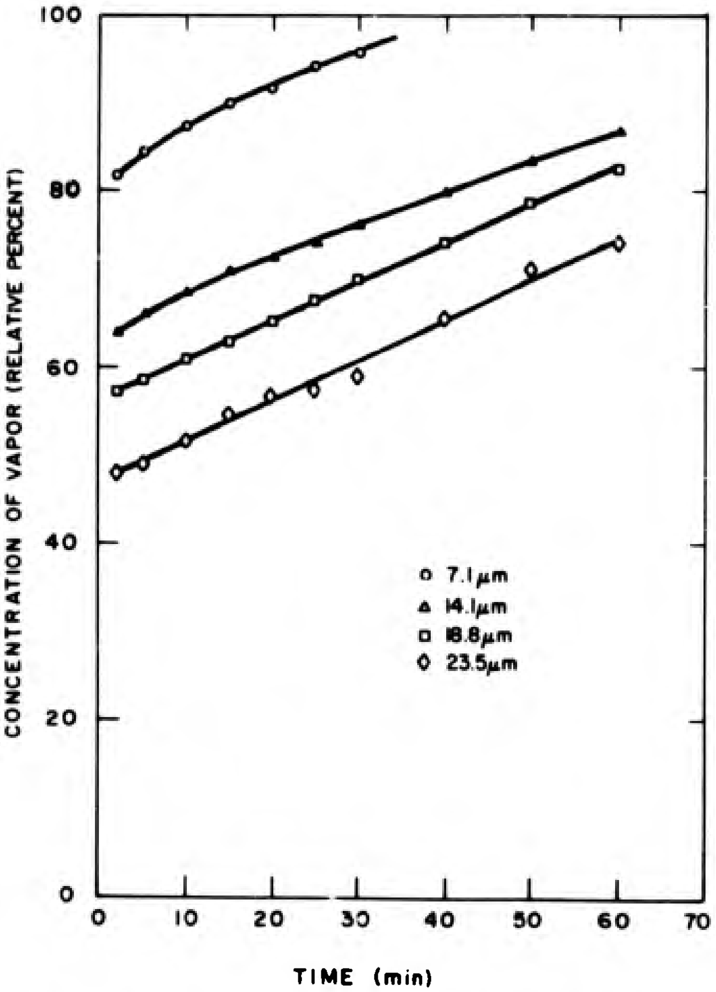


Fig. 12 — Change of hydrocarbon vapor concentration over toluene with time at various film thicknesses. (Unfilmed toluene = 100%).

Of the three fuels which ignited in the unfilmed condition, only JP-4 was maintained below its lower flammability limit for the entire 10-min test period. The other fuels, aviation and motor gasolines, both began to produce vapors in the flammable range between 5 and 10 min. Thus the degree of protection afforded by the surfactant film is limited in the case of these fuels.

The flash points of the remaining fuels are so high (JP-5, 60°C minimum; Navy distillate, 66°C minimum) that they pose no flash-ignition hazard at room temperature.

The results obtained using the closed-cup apparatus are given in Table 4. It is obvious that the surfactant film offers little or no protection in a closed tank for the more volatile hydrocarbons (n-heptane and cyclohexane) and the high-vapor-pressure fuels (aviation and motor gasolines). Although the evaporometer studies indicated that rate of evaporation of these liquids had been suppressed in excess of 90%, it is apparent that sufficient vapors can escape through the film which, if allowed to accumulate in a closed tank, will eventually reach a flammable concentration. By contrast, when these same liquids were tested in an open cup, n-heptane and cyclohexane were protected for the entire 10-min period, and aviation and motor gasolines failed to ignite for at least 5 min. As predicted, n-octane gave a positive ignition in the closed cup in the unfilmed condition and no ignition after the film was applied. Also, in accordance with the predictions based on Fig. 11, the rate of evaporation of benzene and toluene was not suppressed sufficiently by the film to prevent ignition in a closed cup. Limited protection was afforded to JP-4 in that ignition did not occur during the first 5 min after the film was applied. Due to their high flash points, ignitions were not obtained with JP-5 and Navy distillate fuels in the closed cup.

SUMMARY

Aqueous films based on solutions of fluorochemical surfactants can be used to suppress evaporation of hydrocarbon liquids and fuels provided that the initial spreading coefficient for the surfactant solution/hydrocarbon liquid pair is positive. For the homologous series of n-alkanes, the critical surface tension for evaporation suppression with the surfactant solution employed in this study is 18.5 dyne cm^{-1} at 25° C. Spreading did not occur on the n-alkanes which had surface tensions less than the critical value, namely n-pentane and n-hexane, nor on isooctane. Films did form on the remaining n-alkanes (n-heptane to n-dodecane), and the evaporation rates of these compounds were suppressed in excess of 90%. It was also found that for the n-alkanes there exists a critical film thickness for evaporation suppression. Increasing the film thickness beyond this value does not lead to improved vapor suppression but rather to eventual failure of the film.

In comparison with the n-alkanes, it is more difficult to suppress evaporation of aromatic compounds. The maximum vapor suppression obtained with benzene was less than 40%, as compared to over 90% for the n-alkanes. The difference appears to be related to the greater solubility of benzene in the aqueous film, which facilitates the transport of benzene molecules through the surfactant film. Toluene and xylene are less soluble in water than benzene, and hence the evaporation of these compounds was suppressed to a greater extent than was that of benzene.

Hydrocarbon fuels responded to the surfactant solution in the same manner as the n-alkanes in that their rates of evaporation were suppressed in excess of 90%. Also, with the exception of JP-4 and JP-5, the fuels exhibited a critical film thickness which increased with the volatility of the fuel.

Flammability studies showed that although the surfactant film was able to suppress evaporation and thereby prevent ignition of the n-alkanes and the hydrocarbon fuels in an open cup, sufficient vapors could escape from the more volatile hydrocarbon liquids and fuels (n-heptane, cyclohexane, and aviation and motor gasolines) to permit ignition in a closed-cup apparatus. Of the aromatic compounds tested, benzene was not protected from ignition in either the open or the closed cup, whereas toluene was suppressed sufficiently to prevent ignition from 5 min in the open cup but not in the closed cup. Jet fuel JP-4 was completely protected from ignition in the open cup for the entire 10-min test period and for at least 5 min in the closed cup. Due to their high flash points, ignitions were not obtained with JP-5 and Navy distillate fuels in either apparatus.

From the standpoint of fire suppression, it appears that a surfactant film may be an effective means of retarding evaporation and thereby preventing ignition of the n-alkanes and hydrocarbon fuels in an open environment but not in a closed tank.

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Specification Title	Number
Gasoline, Aviation, Grades 80/87. 100/130, 115/145	MIL-G-5572E
Gasoline, Automotive	VV-G-72b
Turbine Fuels; Aviation Grades JP-4 and JP-5	MIL-T-5624H
Fuel, Navy Distillate	MIL-F-24397 (SHIPS)

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