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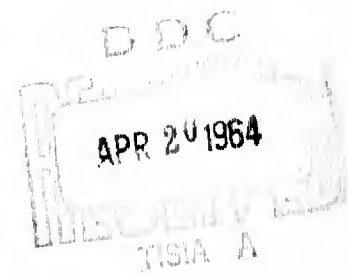
NRL Report 6057

A New Vapor-Securing Agent for Flammable-Liquid Fire Extinguishment

R. L. TUVE, H. B. PETERSON,
E. J. JABLONSKI, AND R. R. NEILL

*Engineering Research Branch
Mechanics Division*

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ABSTRACT

A study and testing program have resulted in the development of new water-soluble surfactants of the perfluorocarbon type capable of forming vapor-securing foams and films on the surface of low-flashpoint flammable fuels of the gasoline type. Equipment has been designed and developed for successful one-man application of these foams immediately following flame extinction with the free-radical quenching agent, potassium bicarbonate dry chemical, on a pound-for-pound basis. Problems of foam collapse, usually encountered where dry chemicals and vapor-securing foam agents are used together, are nonexistent with the new perfluorocarbon foam surfactant. Surface films made up of water solutions of these surfactants continually draining from the foam matrix are capable of regeneration, and the material shows at least a 1200-percent increase in efficiency when compared with protein-type air foams used under identical fire-fighting conditions. Because of its action on low-density hydrocarbon surfaces, the new foam has been named "Light Water."

PROBLEM STATUS

This is a final report on one phase of the problem; work on the problem is continuing.

AUTHORIZATION

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A NEW VAPOR-SECURING AGENT FOR FLAMMABLE-LIQUID FIRE EXTINGUISHMENT

INTRODUCTION

The Combustion Process

In any system involving oxidative combustion, the degree of permanence of extinguishment is in direct relationship to the degree to which efforts are brought to bear on the diminishment of any one (or more) of the four following factors: the heat or temperature of the system, the amounts of combustible fuels or vapors involved and their reactive properties, the amounts of oxygen available to react with the fuel, and the chain reaction of combustion via the mechanism of free-radical quenching using an envelope of ionically active agent.* The student of combustion-inhibition processes will notice that a fourth factor has been added to the familiar "fire triangle" of factors of heat, fuel, and oxygen. This factor has come into existence in an attempt to explain the action of fire-suppression agents such as potassium bicarbonate dry chemical powder and monobromotrifluoromethane gas, which have combustion-extinction properties superior in proportion to the quantities needed. From what very elementary knowledge has been learned about combustion inhibition of such powerful agents, which evidently operate to a great extent through routes involving free-radical quenching or removal, the atomic hydrogen and OH free radicals produced in flames are quickly reacted and removed by ionically active dry chemical powders (and by the halogens) within the combustion zone (1). Their energy absorption and capability toward activation for free-radical removal are high. When active species are removed or neutralized in the combustion zone, the chain reaction of flame propagation is halted, and momentary suppression occurs. It is important to note that continuing flame suppression or fire extinguishment through this mechanism is exceedingly temporary and can operate only as long as a sufficient amount of activated quenching agent is continuously generated to deal with the free radicals produced by the combustion process.

Mechanical Foam - Its Use and Limitations

Of all the common fuels usually involved in accidental fire, gasoline and other flammable liquids are the most demanding in their requirements for special extinguishing methods and materials if complete fire extinguishment is to be obtained. Flammable liquids, in general, are quickly and easily ignited, and flame propagation is relatively rapid as long as fuel remains for continued burning.

The advent of mechanically produced foams was perhaps the most important modern development in giving the fire fighter a satisfactory means for combatting flammable liquid-fuel fires. This material is quickly and easily brought to bear on a fire, and it is a "permanent" extinguishing agent, combining cooling and oxygen-isolation capabilities with functional stability, so that resupply of agent or regeneration of protection on an extinguished fuel is not necessary. In circumstances where progressive extinguishment is required, the advancing front of extinguishment is fully consolidated, and protection against reignition is assured for reasonable lengths of time. Studies at NRL and practical

*A forthcoming NRL report will treat this subject more adequately.

usage over the years have fully justified the superiority of correctly designed foams for flammable-liquid-fuel fire-fighting purposes.

Within the last ten years the progress of development of equipment and methods for generating and applying foams to fires has become increasingly sophisticated; however, some basic limitations of this agent have become evident. These have given rise to the development of newer agents and methods for flammable-liquid fire extinguishment which are more rapid and more efficient in terms of areas of fire extinguished per pound of agent per minute of operation. Unfortunately, each of these has undesirable or restricting properties regarding toxicity, permanence of action, complicated methods of application, or cost, so that the need for foam still exists.

Dry Chemical Powder

The discovery at NRL of the remarkable fire-extinction properties of potassium bicarbonate dry chemical powder and its highly successful use in many types of fire-control problems have pointed up the need for a highly efficient type of flammable-vapor sealing or securing agent containing water, and similar in its action to air foams. Repeated tests and evaluations of potassium bicarbonate powders have substantiated its position as the most powerful flame-quenching agent available within reasonable economic requirements at the present time. It is quickly and easily employed and is non-toxic. However, under some conditions of Class B fire use (gasoline fuels), it may be considered as only a temporary fire-extinguishing agent. These conditions pertain when the entire fire area cannot be completely extinguished with the powder at hand, when hidden fires exist, or when Class A fires persist within a flammable liquid-fuel area. When the dry chemical has become exhausted, the entire Class B fire area will again inflame, negating all progress made toward extinguishment. A byproduct of this action is the disconcerting and sometimes dangerous reflash of flame around and behind the fire fighter as he advances into a fuel-spill area with a dry chemical nozzle.

In the total flooding of enclosed spaces, dry chemical materials, having a density of approximately 2.2 grams/cc, will settle out of air and lose their effectiveness within a short period of time, as opposed to inerting gases. Fuel-blanketing materials are very beneficial in this type of system.

Dry chemicals as a class also suffer from the problem of degree of compatibility with the ordinary protein foams, which are normally used to halt vapor production following extinction of a fire in a liquid fuel. This phenomenon is a reaction of surface forces generated by materials present in all dry chemical powder formulations and which cannot be fully removed at the present state of the art of manufacture of powders. Much progress in the extent of compatibility of powders with foams has been made since the discovery of this mechanism at NRL in 1950, but the problem still exists as a matter of degree.

The present research entails efforts to utilize potassium dry chemical as a prime extinguishing agent for flammable liquid-fuel fires in immediate conjunction with a vapor-securing agent fully compatible with dry chemicals. This agent should demonstrate all the desirable characteristics of air foams for making the temporary action of powder extinction a permanent one, allowing complete consolidation of extinguished fuel areas.

SYNTHETIC-FOAM EXPERIMENTATION

The research described in this report was instituted on the premise that the standard air foams normally used as vapor-securing agents for application immediately

following extinguishment of flammable-liquid fires by means of potassium bicarbonate dry chemical agents are usable but less than satisfactory from points of view of the weight and volume of foam solution required, and from considerations of degree of foam vulnerability to breakdown by dry chemical. The need for research in this area was further heightened by the fact that little, if any, research or development has been devoted to the improvement of the characteristics of protein foam-forming concentrates since their early development in 1938-1940 by Weissenborn, Ratzer (2), and others.

Over this spread of 20 years, the conglomerate "cook-book" mixtures of protein-degradation products in water suspension in conjunction with solutions of chelate-forming iron salts, which constitute our most effective foaming agents, have remained untouched by rapid progress in polymer chemistry and surface-active-agent developments. Accordingly, a clean break with tradition seemed to be in order. Certain selected characteristics of the protein air foams would be used as models, with the addition of highly desirable new requirements.

In order to evaluate and determine fully the effectiveness of new, candidate chemical compounds or mixtures to be used as vapor-securing agents or foaming agents concurrent with dry chemicals for efficient flammable liquid fire extinguishment permanence, certain test criteria had to be established. These criteria were as follows. The securing agent must provide a vapor-sealing thin film or layer of surface-modified water or foam on the fuel surface; it must be fully compatible with dry chemical powders; it should be capable of being applied easily with simple equipment to a fuel surface; on exposure to a heat source in the form of flames it should have an appreciable flame-resistance time; and in order to provide some advance in efficiency, its solution application rate and total application density (gal/ft^2) should be less than the accepted standard minimum rate of $0.10 \text{ gpm}/\text{ft}^2$ required for solutions used in forming air foams when applied to flammable liquid surfaces.

Many of the common commercially obtainable surfactants were tested for their conformity to the above criteria. These were lauryl alcohol sulfate, dioctyl esters of sodium sulfo succinate, alkyl aryl polyether alcohol, condensation products of protein and fatty acid chloride, dicarboxyethyl-N-octadecylsulfo succinate, mixed triethanolamine surfactants, mixed sulfates and polyethoxoxy ethers of branched C_{14} to C_{17} alcohols, and various protein-base foam liquids. These were tested singly and in combination with commercial thickening and film-strengthening agents such as bentonite, especially formulated sodium alginate, polyvinyl alcohols, and carboxyvinyl polymers. Since a vapor-securing agent using water must float on the fuel surface and, therefore, have a specific gravity less than the fuel, water solutions of the above surfactants were necessarily aerated and applied in the form of a foam.

Foams for small-scale tests were made in a laboratory foam generator, where the flow rates of air and solution can be individually controlled to produce foams of widely different physical characteristics. A foam with a high air-to-solution ratio is very stiff and rigid as compared with one with a low ratio, which is fluid and free flowing. The relative abilities of the foams to block fuel vaporization and its subsequent resistance to heat were evaluated by placing them on a $1/8$ -in. layer of gasoline floating on a water base in a $12 \times 12 \times 2$ in. deep metal tray. A torch was periodically passed over the foam surface until combustible vapors penetrated through the foam covering and ignition occurred. The resultant heat and flame after ignition accelerated the rate of breakdown of the remaining foam. The elapsed time until all foam disappeared was termed "burnback resistance time." Foams made with a commercial amine surfactant with expansions from 2 to 40 (one part air plus one part solution, to 39 parts air to one part solution) were applied in depths ranging from $1/4$ to 3 in. The burnback times varied from four to six minutes.

In order to simulate field conditions on a small scale, a standard 2-1/2-gal pressurized portable water extinguisher equipped with an ordinary spray nozzle was used as a foam generator. The unit was loaded with two gallons of a candidate surfactant and pressurized with air to 150 or 200 psi. Various combinations of surfactants and thickening agents were tested in this unit with respect to their foamability, fluidity, and burnback resistance on gasoline fuel contained on a 5-sq-ft concrete surface. Water solutions of surfactants discharged from a spray nozzle normally produced a high-expansion stiff foam that would not flow out in as thin a layer as desired. Despite combination with various commercial thickening agents, the foams produced were found to be very unstable. Different spray nozzles were tried, but very little increase in foam stability was achieved. Since the design of the foam-spray nozzles could not be changed without sacrificing the desirable broad pattern of the foam over the fuel, it was decided to change the pressurization medium from air to carbon dioxide. Foams made with surfactant solutions, modified with synthetic thickening agents and filled with carbon dioxide, appeared to be improved in stability when first produced, but were found to be subsequently less stable than foam made with air due to solubility of the carbon dioxide. Within about one minute after foam production, complete breakdown of the bubble structure had taken place in these foams, even without the destructive influence of heat.

Since both air and carbon dioxide produced unsatisfactory foams, the idea seemed possible that a foam-making unit might be produced using the principles employed in producing "aerosol shaving cream," with a fluorocarbon refrigerant gas as the foam expanding or "blowing" agent. Of these gases Refrigerant-12, dichlorodifluoromethane, appeared to be the best suited for the purpose because of its vapor-pressure-versus-temperature characteristics. At an ambient temperature of 70°F, the vapor pressure of R-12 is 70 psi. The R-12 was added under pressure as a liquid to the surfactant mixture in the extinguisher, and then the system was further pressurized to 150 psi with air. The extra pressure of the air insured that the R-12 would remain in the liquid state until expelled through the nozzle orifice, at which time it would flash into an expanded gas and form a stable foam with the surrounding surfactant solution. The R-12 is insoluble in the solution and of considerably higher density. Thus, it was necessary to shake the container before use in order to disperse the R-12 evenly throughout the solution. By varying the amount of R-12 in the solution the foam expansion could be controlled as desired.

This system proved to be very flexible and permitted variations in the foam output as the progress of the experiments dictated. The foams so produced, using various mixtures of surfactants, were applied by the spray nozzle to gasoline fuel fire areas 7 × 7 ft, enclosed by an earthen dike. To ensure exposure to the foam-destroying effects of dry chemical powder, the fire was first extinguished with potassium bicarbonate type dry chemical in the customary manner, and was followed immediately with application of the candidate foam blanket. Any gasoline-soluble coatings on the dry chemical would dissolve, and if surface active, they would attack the foam from the bottom at the gasoline-foam interface. The foam was immediately tested for flammable vapor diffusion with a lighted torch; then, after a 3-1/2-min period from the time of spreading the foam, a small hole was opened in the blanket and the exposed gasoline surface ignited in order to test the burnback resistance of the foam blanket. The average life of these foams when tested for burnback resistance was one minute.

Using standard protein-type foams in the above test, applied at normal 0.10 gpm/ft² rates (total solution application density, 0.08 gal/ft²), a foam cover had a maximum life of zero to 1.5 min before the entire surface of the gasoline area was alight due to breakdown of the foam. These foams were so subject to destruction by heat when in contact with the potassium bicarbonate powder that the resistance time of 3-1/2 min used with the surfactant foams was never achieved for these protein foams.

A large number of mixtures of the surfactants alone, and in combination with the thickening and film-strengthening agents mentioned earlier, were tested for their characteristics by this fire procedure. It was concluded that R-12 foamed water solution of 1 percent carboxyvinyl polymer and 10 percent alkyl aryl polyether alcohol surfactant solutions showed no advantage when compared to protein-solution foams in their flame-resisting characteristics, when used on hot gasoline surfaces previously extinguished with dry chemicals.

A serious dilemma presented itself concerning the optimization of foams made with these surfactants. Foams produced using relatively large amounts of gas were very stiff but light. Very small amounts of foaming solution were needed to produce a thick blanket over the hot gasoline surface. However, if a fissure developed or an open spot of fuel remained uncovered by the foam, it had no flowability or self-healing ability, and the flames destroyed the high-expansion, low-water-content foam cover very quickly.

Conversely, if a relatively low amount of gas was used to make the foam, a larger amount of solution was needed to blanket the hot fuel fully. The good flowability of this foam assisted in the formation of an integral foam covering with some ability to self-seal after being disturbed.

The best compromise between good coverage and good flowability appeared to be in the form of an expansion 8 foam. In general, an abnormally high application rate of 0.20 gpm/ft² was also found to be necessary to score any advance in resistance to flames over the recognized protection level of 0.10 gpm/ft² for protein foams established for applications when Purple-K-Powder is not present. These results were further confirmed on a 9 × 9 ft fire area using larger scale equipment and an alkyl aryl polyether alcohol foam reinforced with a carboxyvinyl polymer. Obviously, the most favorable of the ordinary surfactant mixtures fell far short of meeting the criterion of economy of application for a vapor-securing agent.

FILM-FORMING-AGENT EXPERIMENTATION

Initial Tests

During the progress of the experimentation described earlier, using ordinary surfactant foams on fires, a series of new synthetic fluorocarbon surfactants containing oriented polar groups became available in very small quantities from a commercial source. Preliminary foaming tests using an ordinary kitchen mixer showed that these materials were extremely efficient foaming agents in water solution, and preparations were made to conduct very-small-scale fire tests of a size commensurate with the amounts of commercial material available.

Air foams were made with a material designated as L-1083 by its manufacturer, using the pressure foam generator described earlier. The foam was applied at a rate of 0.075 gpm/ft² to a one-foot-square pan containing gasoline. The thin layer of foam was impervious to flammable vapor diffusion, and upon opening it in the corner of the pan, the apparently uncovered gasoline surface could not be ignited with a torch. Repeated dusting of the surface of the foam with dry chemical or admixture of dry chemical with the sublayer of gasoline had no breakdown effect on the foam.

Coupled with these desirable characteristics, a new phenomenon was found to exist with this surfactant. Following very slow degradation of the foam with time, new bubbles were formed with what proved to be flammable vapor. When these were ignited they only flashed across the surface, and the gasoline liquid surface did not ignite.

A series of purely qualitative film experiments using water solutions of L-1083 fluorocarbon surfactant were made. By the use of sodium fluorescein dissolved in the solution and an ultraviolet light source, it was possible to observe film generation over fuel surfaces. A very shallow layer of gasoline was used in a small tray 2×8 in. and the dyed solution carefully added drop by drop in sufficient volume to form a round "globule" in the fuel, with its base resting on the bottom of the tray and its top surface protruding slightly above the fuel surface. The exposed surface could be observed as the source of a film which quickly spread over the fuel, and within seconds a vapor-proof film was formed. Mechanical disruption of the fluorescent film only temporarily exposed the fuel. Resealing took place immediately.

Showering fuel surfaces with a very fine spray of the surfactant solution demonstrated no film formation. The use of small amounts of mutual solvents (oleo-hydrophilic compounds) dissolved in the solution was also unsuccessful in promoting film formation.

The transformation of solutions into floating foams prior to application was strikingly beneficial. When air was mixed into the solutions in any proportion sufficient to float the surfactant, the mechanism of foam film drainage at the air-fuel interface invariably yielded a quickly migrating film, protecting and vaporproofing the fuel surface with exceedingly small quantities of solution. This vapor-sealing, flame-impervious film formation from draining foams was demonstrated on JP-4 and JP-5 fuels, on benzene, and on motor gasoline in these tests.

The making of the surfactant solutions into foams as an intermediate step in forming the barrier film is ideal from two points of view. First, the presence of the foam serves as a mechanical barrier in the normal manner of foams on fuels, and second, the slow, gentle drainage of the liquid from the floating foam matrix onto the interface materially assists film formation of the surface-active solution. It has been suggested that the process effects a proper molecular orientation for subsequent efficient film formation. With water sprays the surfactants are in a disoriented state, and the droplets sink before they can contribute to the film formation.

In an attempt to quantify the vaporization-reduction effectiveness of these surface films, some measurements of time-weight loss characteristics of film-protected fuel surfaces were made. A 3-in.-diameter glass crystallizing dish was fitted with an upright barrier which was suspended above the bottom of the dish. With a volume of 20 ml of fuel placed in the dish, the liquid level was just below that of the barrier. Foam placed behind the barrier was restrained from flowing outward; however, the draining liquid from the foam could slide out beneath the barrier and across the remaining 90 percent exposed fuel area of the dish. The exposed fuel area was 10 sq in., and the area covered by foam was 1.4 sq in. The dish was placed on an analytical balance pan within the normal balance enclosure (side windows opened) and weighed at 30-sec intervals. Test runs were made with different surfactants either mixed directly with the fuel or applied as R-12 foams.

The evaporation-rate curves, Fig. 1, illustrate the degree to which gasoline evaporation could be retarded by dissolving the fluorocarbon surfactants directly in the gasoline. The top curve is the rate of loss for gasoline in its natural state at the prevailing temperature of 28°C (82°F). The initial rates were very high as the lower boiling components were lost. The intermediate curve indicates the amount of suppression achieved by adding 15 ppm of L-1086 and 15 ppm of L-1065 to the gasoline. This particular combination and concentration of surfactants was recommended by the manufacturer as being the most effective. The lowest curve indicates the greater retardation accomplished by 15 ppm of L-1083 and 15 ppm of L-1162. The general shape of the two bottom curves did not indicate anything which might be interpreted as a time point when a film had formed completely over the surface, unless this took place before the first 30-sec weighing.

In another series of evaporation-rate tests the surfactants L-1083 and L-1162 were used in a concentration of 1/4 percent each, together with 1/2 percent of an ethylene oxide polymer for a bubble strengthener and foamed to an expansion 8 with R-12 gas. The foam was added to the space behind the barrier in the amount to supply surfactant solution at 0.006 gal/ft² of fuel area within the entire dish. Weighings were started as soon as possible to determine the evaporation rate. Figure 2 shows the evaporation rates of gasoline, JP-4, and JP-5 in their natural state and as covered with the film barrier from this foam. Again the steeply falling curve for pure gasoline indicates the wide range of vapor pressures of its components. As the oriented film-forming solution slid out from under the barrier and moved over the fuel surface, it possessed sufficient strength to trap fuel vapors in bubbles. In this manner a "secondary" foam was built up over the entire dish which helped to retard further evaporation.

As observed in Fig. 2 the suppression of vapors was quite marked with gasoline, but the effect became less with a decrease in fuel volatility. The rate of loss of light ends from gasoline was reduced by 80 percent.

An attempt was made to avoid the rapidly changing evaporation rate of gasoline by using a narrow-range-boiling-point compound, n-heptane. The usual mechanism of film barrier did not take place, and the evaporation rate, although constant with time, was not appreciably lowered through the use of the surfactant foams.

Small-Scale Fire Tests

The extremely favorable results obtained during the experimental testing of the new fluorocarbon type of surfactant focused efforts along lines of determining the extent to which these newer agents as a class met the criteria which had been established for a successful vapor-securing agent. The intriguing characteristic of an invisible water-film formation from foam drainage of the fluorocarbon introduced a heretofore unexpected property requiring new methods of investigation.

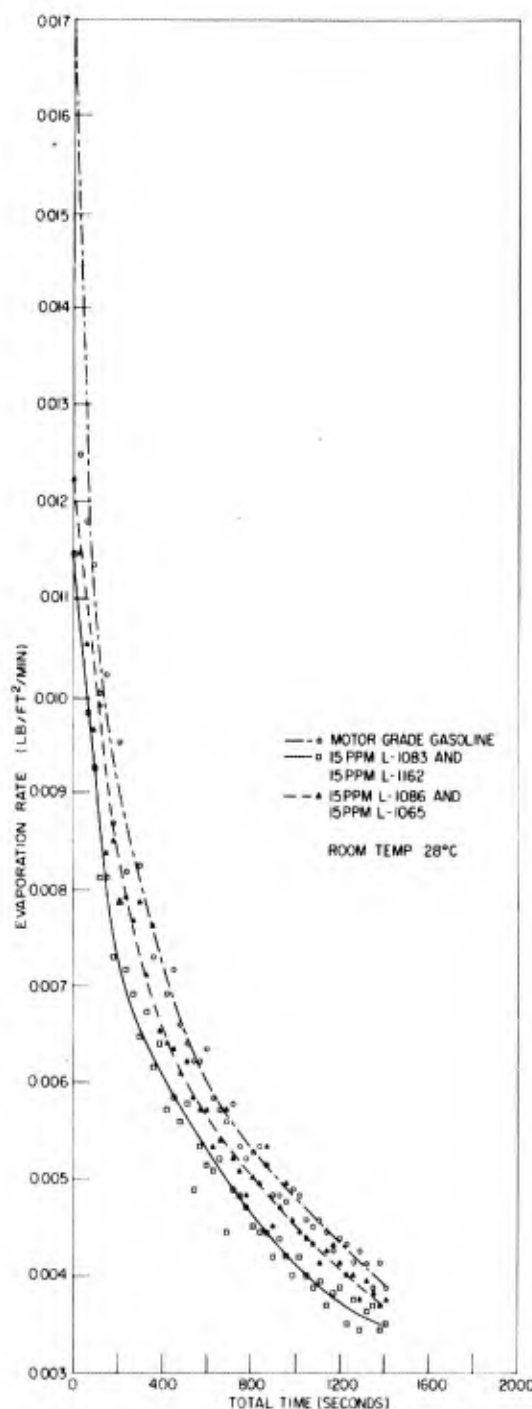


Fig. 1 - Comparison of fuel-evaporation rates from free surfaces, with and without dissolved fluorocarbon surfactants

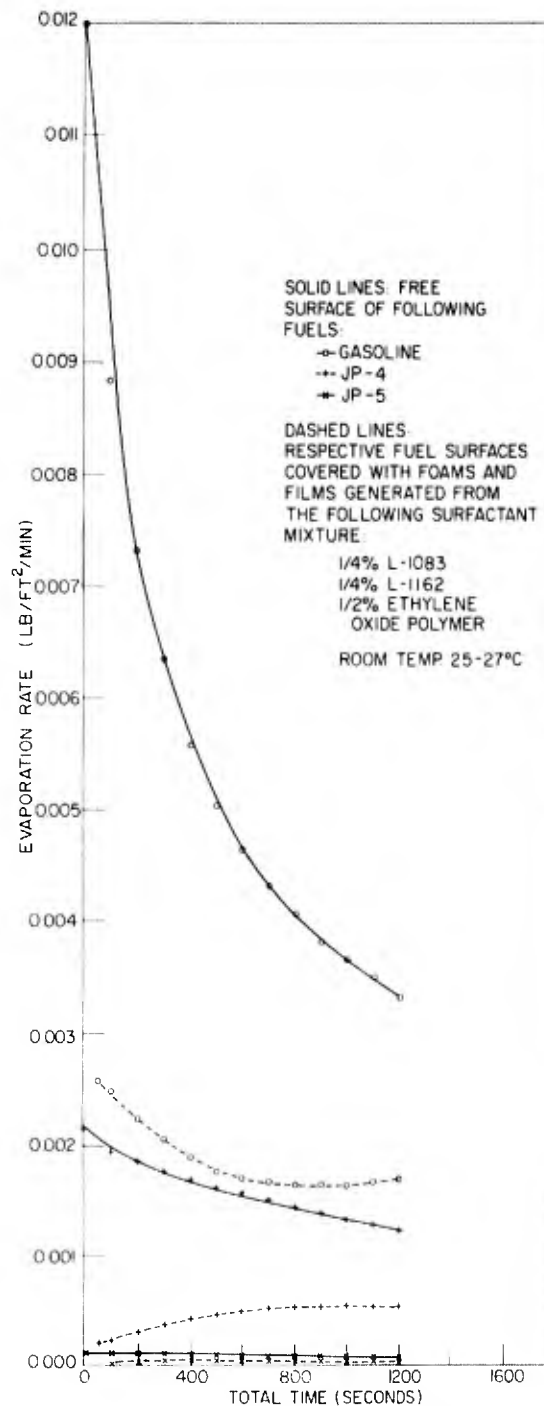


Fig. 2 - Comparison of fuel-evaporation rates from free and foam-film-covered surfaces

A large number of related fluoro-carbon surfactant compounds were received from the manufacturer for test. These were proprietary materials and are known only by the following code numbers: L-1060, L-1074, L-1075, L-1083, L-1155, L-1160, L-1161, L-1162, L-1199, L-1358, and L-1388.

The compounds tested were in the general class of perfluorosulfonic acid derivatives, some being quaternary salts, others alcohols, esters, anionic salts of substituted sulfonamido carboxylic acids, etc. All of these water-soluble, high-molecular-weight fluorocarbons show dramatic surface-tension depression of water to minimums of below 20 dynes/cm. In general, they are insensitive to electrolytes and demonstrate surface activity in organic solutions where they are soluble.

In the small-scale fire-testing work, an attempt was made to screen the candidate perfluoro surfactants available to determine those most suited for additional experimental work. The principal factor thought to be of importance was resistance to flame exposure, hence the term "burn-back time," appears throughout the tests. It is a measure of the resistance of the various foamed materials to successive flame-front attack.

Inasmuch as foam is not a static system, there are two values customarily used to denote physical characteristics of fire-fighting foams. One of these is the expansion of the foam, which relates to its liquid vs gas content at the time it was generated. The second value relates to the rate at which the water is draining out from the bubble walls and bubble interstices of the foam. The "quarter drainage time" or, more simply, "drainage time," is the time in minutes when 25 percent of a foam's original liquid content has collected at the bottom of the mass.

It was desired in the small-scale tests, where conditions and foam characteristics could be readily controlled, to delineate the above values for foams in order to describe fully conditions at optimum performance. The added influence of potassium bicarbonate dry chemical on the foams was also under observation.

For the preliminary heat-resistance tests, an 8-in.-diameter brass pan 2 in. deep was divided into equal segments by placing a vertical barrier across the diameter. Its top edge was flush with the rim, but the bottom edge was terminated 1/8 in. above the pan bottom. Motor grade gasoline, 500 ml, was used for fuel in each test run, leaving a free-board of 1-1/2 in. For each test, one segment was filled evenly with foam (Fig. 3) and the other side ignited. A fixed volume of foam was thus exposed to a constant heat source. The time at which the foam had completely disappeared and the gasoline burned freely in both segments was taken to be the burnback time.



Fig. 3 - Foam addition for small-scale divided-pan fire tests

The candidate surfactant solutions were foamed in an ordinary kitchen mixer with the egg-beater blades. By varying the amounts of solutions in the mixer bowl, mixing speed, and mixing time, foams possessing various characteristics of expansion and drainage time were made. Following the mixing period, the foam was transferred with a spatula into one side of the fire pan. Temperatures of the solution and fuel were 70°F before ignition.

Tests were made both with and without potassium bicarbonate dry chemical (Purple-K-Powder or P-K-P). When P-K-P was used, 30 grams were mixed into the fuel before foam application, and 7 grams were sprinkled over the foam surface before ignition in order to increase the severity of dry chemical exposure.

Figures 4a through 4e illustrate a typical surfactant foam-degradation and burnback sequence during the small-scale divided-pan fire test. Table 1 summarizes the results of the fire tests on the available materials.

Six of the compounds were immediately disqualified because of their lack of foaming ability. Of the remaining five, the L-1083 and L-1162 showed the best burnback resistance. However, the L-1162 was somewhat vulnerable to P-K-P attack, as shown by the reduction in burnback time during its use. The L-1083 foamed easily and appeared to be completely compatible but showed less burnback resistance. A blend of these two picked up the best characteristics of both and showed the most promise for additional testing. The 6-percent protein foam exhibited good flame resistance because of its low expansion and high drainage time, but demonstrated poor compatibility with P-K-P.

In the earlier nonfluorocarbon synthetic surfactant work it was found that certain water-soluble materials imparted some desirable characteristics of greater viscosity to the solution in the bubble wall. One of these, a high-molecular-weight polymer of ethylene oxide, was found to be fully soluble and compatible with L-1083 and L-1162 solutions. Viscosity data are shown in Fig. 5 for the increased polymer concentrations at different temperatures. The increased solution viscosity was expected to decrease the drainage rates of its foam and thereby increase its burnback resistance.

A series of fire tests with the 8-in.-diameter pan was directed toward establishing the relationship of L-1083 concentration with variations in ethylene oxide polymer concentrations. This work was done using an expansion 8 foam (solution application



a. P-K-P addition to the foam surface



b. Beginning of fire exposure of foam



c. Foam breakdown after 1 min fire exposure



d. Foam breakdown after 2 min fire exposure



e. 100% foam breakdown after 6 min fire exposure

Fig. 4 - Results of fire exposure in divided-pan fire test

Table 1
Burnback Resistance of Foamed Surfactants With and Without
Presence of Dry Chemical

Material	Foam Analysis		Burnback Time (Min)	
	Expansion	Drainage Time (Min)	Without P-K-P	With P-K-P
1% L-1060	would not foam	-	-	-
1% L-1074	28	5	1.6	-
1% L-1075	would not foam	-	-	-
1% L-1083	41	10	2.9	3.3
1% L-1155	40	7	1.5	-
1% L-1160	would not foam	-	-	-
1% L-1161	27	9	2.5	-
1% L-1162	24	15	5.0	3.2
1% L-1199	would not foam	-	-	-
1% L-1358	would not foam	-	-	-
1% L-1388	would not foam	-	-	-
0.5% L-1083 plus 0.5% L-1162	40	14	4.4	3.9
6% Protein	11	24	4.8	2.3

Table 2
Burnback Resistance of Foamed L-1083 Surfactant with Ethylene
Oxide Polymer. Foam Expansion 8 with P-K-P Added

Concentration L-1083 (percent)	Polymer (percent)	Foam Drainage Time (Min)	Burnback Time (Min)
1	0	2.3	3.0
1	1	4	5.2
1	2	11	7.2
1	3	18	10.4
1/2	1	5	5.8
1/2	2	12	8.6
1/2	3	20	11.8
1/4	3	20	10.2

density = 0.006 gal/ft²) with P-K-P dry chemical added as previously described. The results are summarized in Table 2.

The increase in the drainage time of the various foams with the increased solution viscosity (due to polymer concentration) was very evident and was taken to be independent of the surfactant concentration. (Figure 5 gives the viscosities of the solutions used.) The burnback time also improved rapidly as the solution viscosity increased, thereby holding more water in the foam mass. Concentration of the surfactant did not appear to be influential, at least down to 1/4 percent. A comparison of these values with the

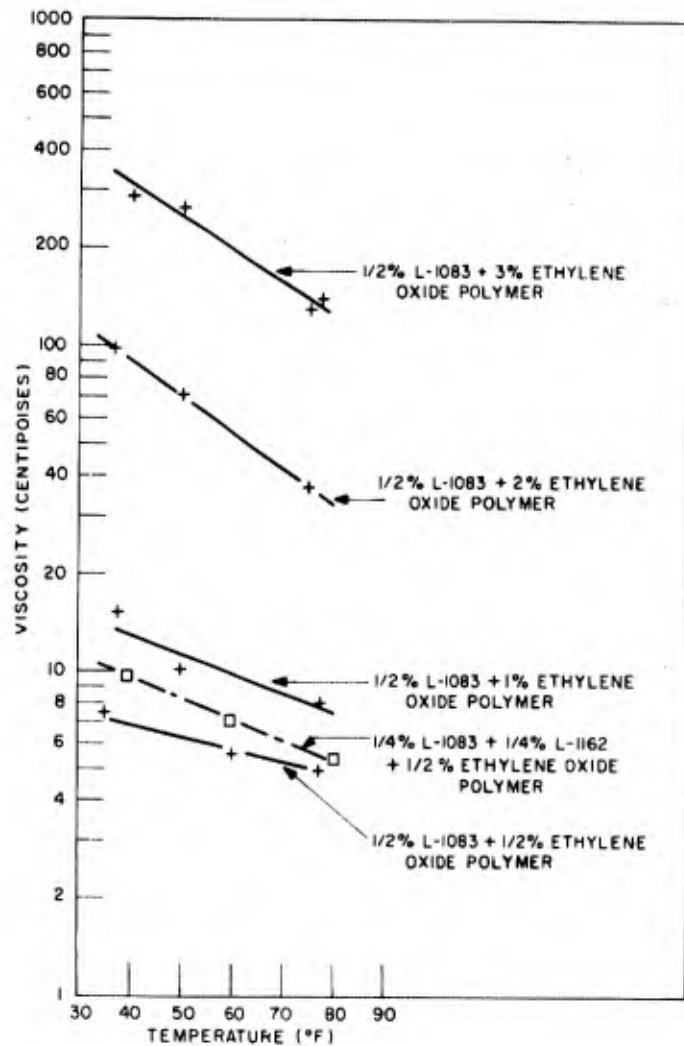


Fig. 5 - Viscosities of various ethylene oxide polymer and surfactant concentrations

protein foam from Table 1 shows considerable improvement in both burnback and P-K-P compatibility.

After establishing the most promising surfactant compound and its working concentration and a suitable bubble stabilizer, it was necessary to determine what expansion should be used for the next scale of testing. A series of tests was then made with the small-scale 8-in. pan fire wherein the volume of solution was kept constant while the expansion was increased. This procedure was used in order to determine the most efficient usage of a fixed amount of solution. To compensate for the differences in foam volume caused by the change in expansion, the gasoline level in the 8-in. pan was adjusted to make the top surface of the foam flush with the pan under each condition of foam volume change due to variation of expansion. The test results are given in Table 3. These values indicated that the foam with the lowest expansion tried was superior in flame resistance for a given amount of solution applied. This occurred in spite of a lower bulk and lower drainage-time value and showed that the available and effective water content was higher.

At this point evidence was at hand to indicate that L-1083 and L-1162 or a combination thereof were important for useful application in solution concentrations of 0.25 to

Table 3
Burnback Resistance of Foamed 1/2% L-1083
and 1% Ethylene Oxide Polymer Solution at
Varied Expansions - Solution Rate 0.025 gal/
ft² with P-K-P Added

Foam Analysis		Burnback Time (Min)
Expansion	Drainage Time (Min)	
27	13	4.1
16	8	4.7
9	5	5.8

1.0 percent. When mixed with low concentrations of a film-strengthening polymer and foamed to an expansion of 8 to 10, they exhibited not only a good flame and P-K-P resistance, but also the ability to form a fuel-vapor-blocking film barrier. The next stage of development would involve problems of foam generation by a continuous process rather than a small foam batch system. Experimentation with dynamic techniques of application to larger fires was also needed.

Intermediate-Scale Fire Testing

The investigator familiar with research problems of the type covered in this report can appreciate the many problems and variables attendant to choosing test conditions for sorting out the critical values in a project of this nature. Small-scale fire tests and equipment design had developed guidelines concerning certain characteristics needing larger-scale testing. Formula development, equipment design, and extinguishment techniques required optimization by the use of a judiciously selected series of model fires and test procedures. Because of a lack of facilities for indoor, weather-protected test fires on the required scale, all testing had to be conducted under outdoor conditions, with variable wind velocity and temperature. Also, the rather high cost of conducting larger-scale test fires restricted the number of tests that could be run.

In the succeeding test series the foam-generating equipment was fabricated on the basis of its final expected design. It utilized the characteristic of self-contained power, using gas pressure as pumping energy. The vapor-securing-agent distribution nozzle used with the equipment was selected from obtainable commercial models after a series of semiquantitative tests.

The choice of fire-model test conditions was patterned after the problems expected in the field. It will be seen that test results caused some modifications in the test conditions as the work proceeded.

Figure 6 depicts the surfactant foam-generating unit developed for the intermediate-scale testing phase. The larger tank, with a capacity of 10 gal, was used for the solutions. The smaller tank, with a capacity of 2-1/2 gal, was for liquid Refrigerant-12 in case it was needed to achieve foaming as employed in the earlier work with the synthetic foams. Both tanks were maintained at 130 psi by means of a regulated nitrogen gas supply from a 220-cu-ft cylinder. The outlet lines from both tanks were piped together near the unit with an orifice plate placed in the R-12 line for control of ratio of R-12 to the surfactant solution under test. Approximately 15 ft of 3/4-in. I.D. hose was coupled to the piping at the system outlet. This carried the mixture of liquid refrigerant and active solution.

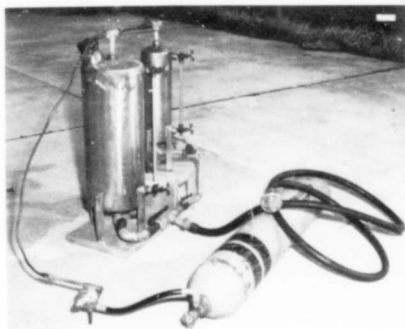


Fig. 6 - Portable surfactant foaming equipment for intermediate-scale fire tests

A commercially available foam-spray nozzle was used as the applicator. This nozzle was constructed in the form of a head with internally impinging liquid jets fronted with a hemispherically shaped screen. The resultant output was a cone-shaped spray discharge pattern of small foamed globules. At a nozzle pressure of 100 psi, the solution flow through this nozzle was 47 gpm. Because of its design this nozzle could serve as a primary foam generator by introducing air through turbulence into the solution. If the candidate solution lacked sufficient ability to form a stable foam through this mechanism, R-12 gas was used as previously described, and the nozzle then served as a distributor tip. Generated foams were analyzed for expansion and drainage-time characteristics by the normal procedures.

A circular fire area 14 ft in diameter (154 ft²) was chosen to permit application densities up to 0.06 gal/ft² with the available 10 gal of solution in the tank. This allowed up to twice the amount of solution used in the small-scale tests. The round area provided better flexibility in fire-fighting attack and wind orientation. The application rate was 0.3 gpm/ft², and the supply of solution permitted a continuous application time of about 13 sec. The area was laid out on a concrete slab with wet clay sloping dikes and was entirely wetted before adding the 35 gal of fresh motor grade gasoline used for each test. Immediately after fueling, a 20-lb P-K-P extinguisher was discharged over the fuel for a period of 5 sec (8 lb). This represented the normal amount of powder which would be applied to extinguish the fire. The fluorocarbon surfactant solution was then applied uniformly in the form of foam over the fuel surface, and then a second 8 lb of P-K-P was discharged over the test foam material. After a one-minute time lapse, a torch was used to detect the occurrence of flammable vapor transmission, and an attempt was made to ignite the fuel. Elapsed time between ignition to full involvement of the fuel area was recorded as burnback time.

The first series of vapor-sealing tests consisted of utilization of a foam formed with air using the distribution nozzle as a foam generator. The solution used consisted of a 0.5-percent solution of L-1083 at 100 psi at the nozzle. The applied foam showed an expansion of 5 with a drainage time of three minutes. Ambient temperatures varied from 40° to 50° F during the tests. Following the application of the foam at area densities of 0.06 gal/ft² to the fuel, combined with Purple-K-Powder discharge as given above, a complete surface coverage was obtained. For a period of ten minutes after application the surface was agitated severely with the torch before ignition could be started. Total involvement of the fuel area occurred only after an additional four minutes flame exposure. At this relatively high density of application, an excellent vapor-proof barrier was formed, and resealing was quickly achieved following any openings made in the protected surface.

A second series of tests utilized a similar testing regime with the same air foam as the vapor sealant on the fuel surface. A 0.5-percent L-1083 solution was used, but the

density of application lowered to 0.03 gal/ft² by halving the application time. A fuel-surface coverage of only 80 to 95 percent was attained at this density, and ignition of the open fuel area took place in five seconds. Total involvement of the fuel area in fire occurred in one minute. It was obvious that with the poor foaming action of the nozzle-solution combination, the application density was below the minimum required, and an incomplete vapor-barrier formation resulted.

A single test using air foam was again made, but with the area density raised to 0.045 gal/ft² in an attempt to achieve better surface coverage. However, again only 90 percent of the fuel was protected, and ignition occurred in five seconds, with 100-percent involvement in one minute. Inadequate foaming action was again observed.

A fourth series of tests was conducted, but an air-foam solution of 0.25 percent L-1083 plus 0.25 percent L-1162 was used. The application density was held at 0.045 gal/ft². The foam from this solution showed an expansion of 5 and drainage time of 1.8 min. The addition of L-1162 decreased the foam quality. About 95-percent coverage of the area was obtained. After a one-minute agitation of the vapor seal, ignition took place, and 100-percent fire involvement of the fuel surface occurred in three minutes after ignition. Thus, the combination of two surfactants exhibited an improved burnback resistance over the L-1083 alone, as was found in the earlier small-scale tests.

In an attempt to increase the overall quality of foam without raising the system operating pressures, the next series of tests incorporated the use of R-12 as an expanding or blowing agent. The ambient air temperature during this period varied from 45° to 55° F. Using a 0.5-percent L-1083 surfactant solution, an expansion 6 foam with a two-minute drainage time was generated. The nozzle pressure was maintained at 100 psi in order to keep the R-12 from vaporizing in the hose line. Tests were run using a low application density of 0.03 gal/ft². The other test conditions were the same as those employed for the air-aspirated foam tests. Total coverage of the 154 ft² area was obtained. It required an average of four minutes of probing with the torch to give sustained fuel ignition. Total fire involvement of the test area occurred in 11 min. The R-12 generated foam was of definite value. No detrimental effect was observed related to the presence of Purple-K-Powder.

A sixth series of tests was made similar to the previous ones, but the solution used to form the securing agent with R-12 as a gaseous blowing agent consisted of a mixture of 0.25-percent L-1083 and 0.25-percent L-1162 to achieve the better film-forming power of the latter. This resulted in a foam of expansion 6.5 with a drainage time of 3.5 min. An increased area density application of 0.045 gal/ft² was used. Because of the better coherency of the foam film on the fuel, an average of 12 min was required before the fired torch was able to ignite the fuel, with considerable probing. Troubles were experienced in obtaining a good 100-percent involvement figure for these fires after initial ignition because of the wind velocity at the time. In general, the entire fuel contents of the test area burned away, leaving about 20 percent of the surfactant foam untouched. Good burnback resistance of the foam was shown.

Wind orientation and velocity were very influential factors in the burnback process. The heat and flame blowing over the foam greatly increased the severity of exposure. The original point of burnback ignition, being variable, sometimes took place on the leeward edge of the area and other times on the windward edge. Burnback results on this basis were impossible to correlate properly. Because of this wind-condition variable, it was decided that the next series of tests should be run with a temporary cover over the center of the fuel pool; this cover would be removed after coating the fuel with foam film, and thus a reproducible ignition point would be achieved regardless of wind direction. Laboratory viscosity determinations of limits of usefulness of the soluble ethylene oxide polymer film-strengthening agent (Fig. 5) in the solution formula had also been completed at this time, so the solution for the next series of tests incorporated 0.5-percent

soluble polymer with 0.25-percent L-1083 and 0.25-percent L-1162. Solution viscosity was limited by friction losses in the hose lines to about 10 centipoises. At minimum temperatures this value was reached at about a 0.5-percent solution of polymer. The resulting R-12 gas-filled foam showed an increased expansion of 8.6, with a drainage time of 5.5 min.

Using an area density application of 0.03 gal/ft² at an ambient temperature of 60° F in the doughnut-shaped foamed area created by the 15-in.-diameter center shield, it was found that upon removal of the shield the open center was quickly coated with the vapor-securing film from the foam, and an average of some four minutes of agitation was required to obtain sustained ignition of the fuel in the center spot. Excellent flame resistance was demonstrated in these tests, and after ten minutes of center burning the flames spread to involve only 50 percent of the area, and only 80 to 90 percent of the foam film was destroyed after 15 to 17 min of burning, by which time the complete volume of fuel had burned away.

Ignition was not always of the sustained type when the test area was probed after the agent application. In some instances after disruption of the covering, ignition occurred, but would be self extinguished as the foam and film barrier flowed in to close the opening within a few seconds. With a fresh application, holes up to one square foot could readily be sealed by this mechanism. As indicated in previous intermediate-scale test results, this effect was noticeable for periods up to ten minutes before the film barrier could be broken down sufficiently to allow a continuous supply of fuel vapor for combustion. In other instances the presence of the secondary foam was observed, as characterized by flammable vapor-filled bubbles, which would burn off as a traveling flame front but leaving no continuing burning behind it. After a sustained burning occurred, its spread was retarded in varying degrees by the combination of foam and surface film barrier.

The favorable results of the previous testing period led to efforts to design equipment utilizing dual-agent application to the same fire. A bracket was developed that held the discharge nozzles of the two agents, dry chemical and vapor-securing agent, side by side at a suitable angle of divergence to prevent interference between them or intermixing of agent discharge patterns. In addition, a hood was attached to the securing-agent nozzle, cutting off the portion of the securing-agent cone-shaped discharge pattern on the side of the Purple-K-Powder discharge pattern.

Two fire tests were run using the dry chemical discharge alone on the 154 ft² round fire-test area. The fire was readily extinguished with a 20-lb P-K-P extinguisher in four seconds, with a favorable wind velocity of 3 to 8 mph behind the operator helping to propel the agent across the area, and at the same time holding back the fire from reflash over the extinguished portion until final extinguishment was obtained. Two more fire tests were run with an obstacle in the form of a 55-gal drum lying on its side in the center of the fuel area. These fires were impossible to extinguish with the 20-lb Purple-K-Powder extinguisher discharge. The fire was chased around the drum but never completely extinguished, and after the powder supply was finally exhausted the entire surface was again aflame. This drum was used as an obstacle in the fire area for the testing of the dual-agent application technique, in order to determine the advantage gained by following the dry chemical application with a securing agent.

The surfactant formulation used in this test series was chosen to be 1/4-percent L-1083, 1/4-percent L-1162, and 1/2-percent soluble polymer. Two tests were run with a solution application density of 0.06 gal/ft². The test technique employed was to attack the fire with the dry chemical first, then, after allowing a couple of seconds lead time, to start the securing-agent application (as the dry chemical discharge continued), applying it where the fire had been knocked out. This "follow-up" action proceeded in the direction of the remaining fire until it was completely extinguished, at which time the dry chemical was shut off and all remaining fuel surface secured with application of the

securing agent. An average of ten minutes of probing the foam and fuel surface with a torch was required in order to obtain sustained ignition of the fuel. After eleven minutes more, only 80 percent burnback of the area was recorded.

Further testing was conducted to determine the lowest application density feasible under these test conditions. One test was run at 0.03 gal/ft^2 , and similar reignition and burnback resistance were found as for the 0.06 gal/ft^2 density runs. Another test was run in which the solution application density was lowered to 0.02 gal/ft^2 . However, this density was judged to be below the acceptable minimum, because only 90-percent foam coverage of the area was achieved. The expansion 8, drainage time 6 min, securing-agent foam employed was fluid enough to flow around the obstacle, but the amount of foam available was not enough to cover the area completely. Because of this condition, the integrity of the foam blanket was considered marginal and was found to be subject to wind disruption. The 10-percent exposed area was readily ignited in 0.5 min. After a 2-min burnback time, the size of the area aflame had only increased to 15 percent, but the 10 to 13 mph wind, often blowing from the ignited side, broke the blanket open on both sides, allowing the fire to advance rapidly across the area. The minimum application density, therefore, appeared to be between the values of 0.02 and 0.03 gal/ft^2 for this test-fire configuration.

On three occasions during this testing period, the 14-ft-diameter fire had been only partially extinguished by the application of Purple-K-Powder when used in conjunction with fluorocarbon surfactant securing agent. These fires were then completely extinguished with the continuing application of securing agent to obtain application densities of 0.03 , 0.04 , and 0.06 gal/ft^2 . No detrimental effect on the final burnback resistance of the foam blanket was observed because of the more severe heat exposure.

For comparative purposes, three runs were made using a 6-percent regular protein foam solution in lieu of the fluorocarbon surfactant solution formula. The same foam-spray nozzle was used, with the commonly employed air aspiration instead of R-12 gas as the blowing agent for foam generation. An expansion 5 foam with a drainage time of 1.3 min was characteristic of this nozzle using protein foam solutions. For the first fire test, protein foam alone (no P-K-P) was applied for 43 sec, achieving only 95-percent extinguishment. The solution application density reached was 0.21 gal/ft^2 . Within a time period of 4 min, 50 percent of the area was burned back. The dual application of dry chemical and protein foam applied at a density of 0.21 gal/ft^2 was employed for the second fire test. In this test only 70-percent fire extinguishment of the area was achieved, and within 0.5 min, 50-percent fire involvement occurred. For the third test, the foam-solution application density was increased to 0.36 gal/ft^2 , requiring 72 sec foam application. Almost total (95 percent) extinguishment of the area was obtained, and it required a two-minute time period for 50-percent fire involvement of the area. The extinguishing ability and burnback resistance of the protein foam used in this test series was seriously hampered because of the factor of degree of incompatibility between the Purple-K-Powder and protein foam. Comparing these results with fluorocarbon surfactant foam, it was observed that even twelve times as much protein foam did not achieve extinguishment nor approach the degree of burnback protection obtained with the fluorocarbon surfactant.

From the intermediate-scale testing program, the following general conclusions were reached:

1. The superiority of fluorocarbon surfactant mixtures when suitably transformed into foams and used as vapor-securing agents on flammable fuel surfaces was adequately established.

2. Within the limits of self-powered equipment which were established, the use of the vaporizing refrigerant gas, dichlorodifluoromethane (R-12), enabled a superior quantity (and quality) of foam to be generated.

3. A mixture of 0.25-percent L-1083 surfactant with 0.25-percent L-1162 was needed to obtain satisfactory foam. Admixture of 0.5-percent ethylene oxide soluble polymer with these surfactants aided the flame-resisting properties of the foam to some extent.

4. Minimum area density requirements of this solution in the form of foam were about 0.03 gal/ft² for a fire of 154 ft².

5. Interference with the superlative extinguishing ability of potassium bicarbonate, when used simultaneously with a spray of fluorocarbon surfactant foam as a "following-up" securing agent, was avoided by discharge separation of the two agents. Complete compatibility of the two agents was found during fire tests where maximum admixture and exposure was experienced.

6. Preliminary experimental combined-agent tests show that techniques of combined operation of the two agents require that a type of dual equipment be designed to give maximum operator control of each agent, with flexibility of agent application.

Surface-Film-Forming Studies

The ability of the mixture of perfluorocarbon surfactants to form surface films on gasoline substrates is intriguingly novel and deserved additional study on a quantitative basis. A test regime was needed to accumulate data concerning the characteristics of this water film on an oil substrate system similar to that appearing in the literature for oil films on water substrates.

The foam-solution drainage mechanism removed the problem of reversed densities of the liquids concerned, but it also required a new approach to film studies rather than the traditional Langmuir film-balance technique or some adaptation of it. The factor of rate of film formation from this system was also important.

To cope with these characteristics, a procedure was devised to permit the evaluation of the film-spreading characteristics of the fluorocarbon surfactant films on a quantitative basis using a metal tray 23.5 in. in diameter (443 in.² area) and 1 in. deep to hold one quart of a gasoline-type hydrocarbon fuel with an appreciable vapor pressure, used as the substrate liquid. The tray was water jacketed in order to permit holding the system at other than ambient temperatures. This test arrangement is shown in Fig. 7. Solutions for film-formation measurement were placed in a Waring blender and beaten with air to give the desired foam characteristics. After foaming, a measured quantity was poured out into the center of the tray area and allowed to spread freely over the fuel surface as its flowability and volume permitted (Fig. 8).

The initial spread of foam usually took place within a few seconds, and then it appeared as in Fig. 9. In the case of the synthetic surfactants and protein foam materials, this pattern represented the maximum extent of their fire-extinguishing and vapor-securing capability. However, with the perfluorocarbons, the foam continued to progress outward in an irregular pattern. Radiating out in front of the foam, although they were almost invisible, were streamers of the surface-barrier film. Within the film-covered area, the "secondary" foam began to form, consisting of fuel-vapor-filled bubbles. This foam could be distinguished from the original or "primary" foam by the larger size of its bubbles. The spreading action continued until the film was observed to seal to the outer rim of the container. At this point the integrity of the barrier-film covering was tested by exploring the surface with a small torch (Fig. 10). Although the presence of the bubbles indicated that the surface-active material was present and had been elevated to form the bubble walls, an additional vapor-proof barrier film still remained beneath the bubbles on the fuel surface. This was demonstrated when the flaming torch was



Fig. 7 - Water-jacketed fuel tray for film-forming tests

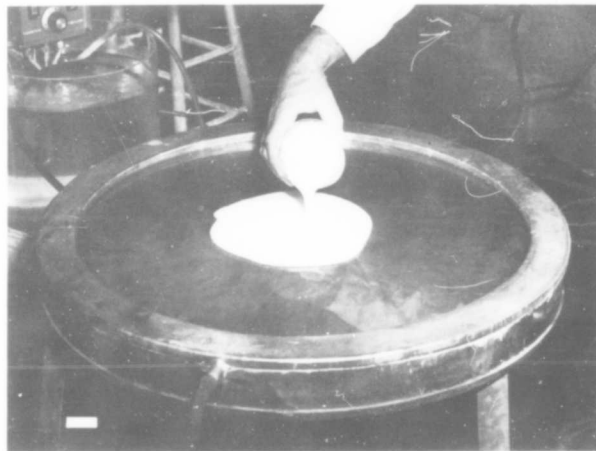


Fig. 8 - Application of surfactant foam to fuel surface

touched to the bubbles; a flame front could be seen to travel across the surface of the container, being fed by the vapors from the bubbles as they collapsed from the approaching heat. Once the bubbles had burned off there was no continued burning, even though the gasoline surface appeared to be completely exposed. Furthermore, it could not be ignited by passing the torch over the fuel surface. On further standing a new secondary vapor-sealing foam covering would form, which could again be flashed off without igniting the gasoline beneath (Fig. 11). This process could be repeated for many cycles before film effectiveness was finally destroyed. The film was very vulnerable to

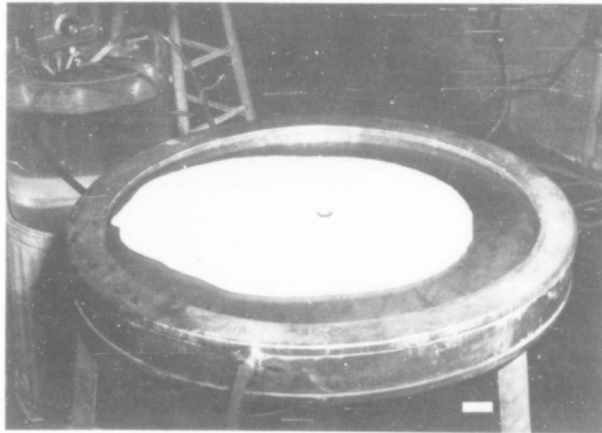


Fig. 9 - Typical initial spread and "level-off" of foam on fuel surface

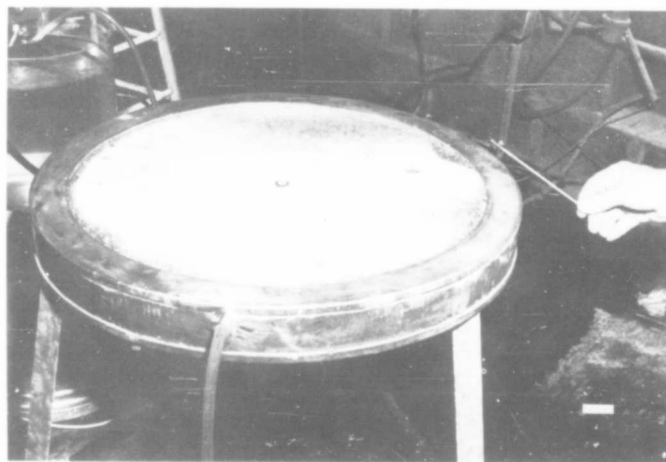


Fig. 10 - Flame test of surfactant foam, film, and vapor-filled foam-covered fuel surface

mechanical disruption when foam in depth was not present surrounding the break to afford some hydraulic head to supply the necessary force toward closing.

Figure 12 compares the spreading rate and ability to secure gasoline vapors for three materials when applied as surface foams to gasoline fuel substrates at identical solution application densities, 0.0040 gal/ft². The protein foam spread to a circular



Fig. 11 - Flame-resistance test of aged "second-generation" foam-covered fuel surface

pattern approximately 7 in. in diameter (40 in.^2) and stopped with no further activity observed. Fuel beneath the pattern was well secured from ignition, but the fuel area outside was completely unprotected. The synthetic surfactant foam, being more fluid, flowed out to a larger circle, 11 in. in diameter (95 in.^2), in less time but then stopped. Two characteristic types of foams were used with the fluorocarbon composition, one an expansion 4 to compare with the ordinary foaming materials, and the other an expansion 8 foam to illustrate the retarded spreading resulting from a more stable foam. Both of these latter foams demonstrated their ability to generate a film of great surface activity by creating a surfactant area four times their original area within a few minutes time.

The data shown in Fig. 12, and data from a number of semiquantitative tests performed, showed that the measurement of the limiting area of fuel secured with a vapor-proof film of perfluorocarbon surfactant solution involved also a function of time. The spreading velocity of the film varied with its application density. From an academic viewpoint, the application of very small quantities of solution per square foot merely meant that longer periods of time were required to seal completely the open-tray fuel surface used in the tests. For instance, a quantity of foam containing a solution which would yield an application density of only 0.00009 gal/ft^2 completely vapor-secured the 23-in.-diameter tray, but it required the excessively long time of 960 min.

Since the spreading rate (or the spreading velocity) of vapor-securing agents on a fuel is important from a fire-fighting standpoint, this factor was studied as a function of application density of foamed surfactant solutions, and the curve of Fig. 13 was obtained. The minimum elapsed time after foam application at which no point within the limiting area of the tray (443 in.^2) could be ignited by an open flame was taken as the observed endpoint. The curve is drawn through these minimum values, representing a "go" or "no go" ignition situation.

At the highest application density shown, 0.0214 gal/ft^2 at a fuel temperature of 70°F , the applied foam volume was sufficiently high to cover the entire pan surface within ten seconds, and no additional film spreading was necessary. All the region above the curve and to the right represents the "secured-vapor" condition; i.e., the surface

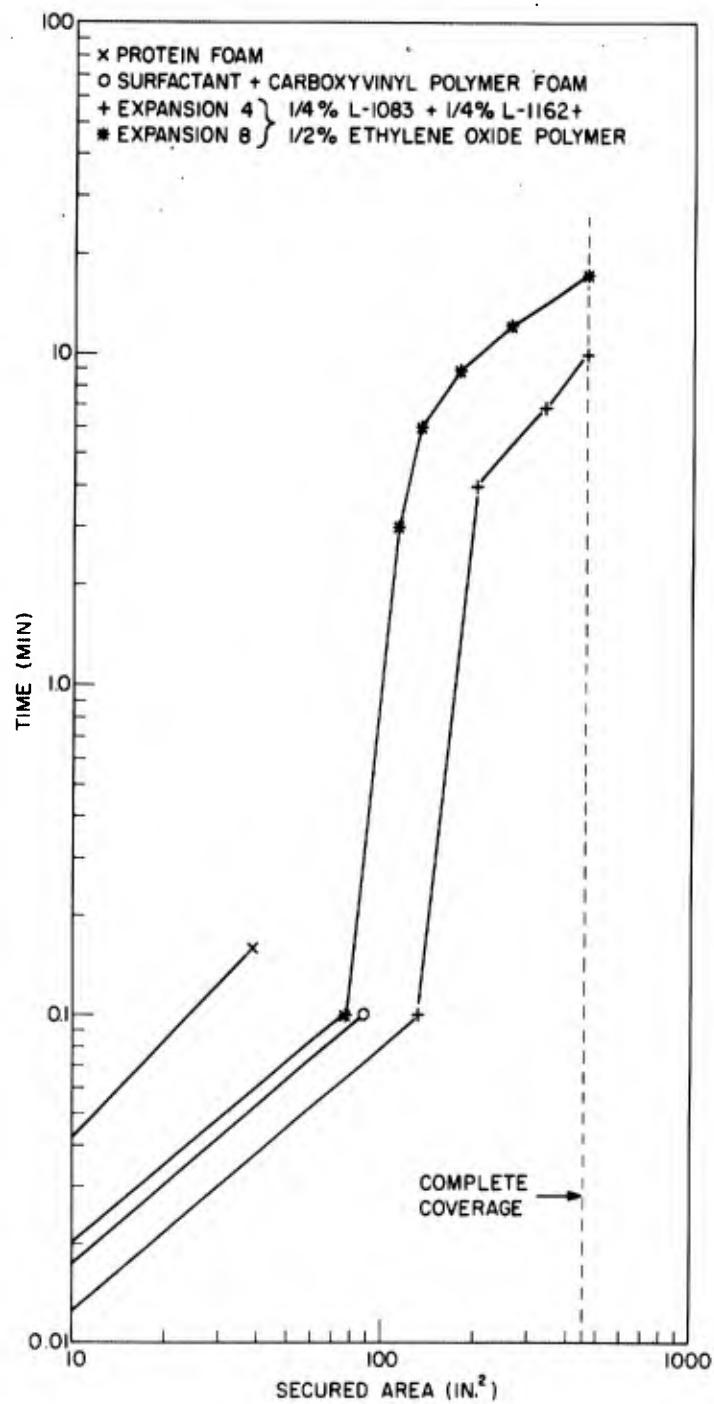


Fig. 12 - Comparative spreading rates and vapor-sealing capabilities of three agents at a fixed application density of 0.0040 gal/ft²

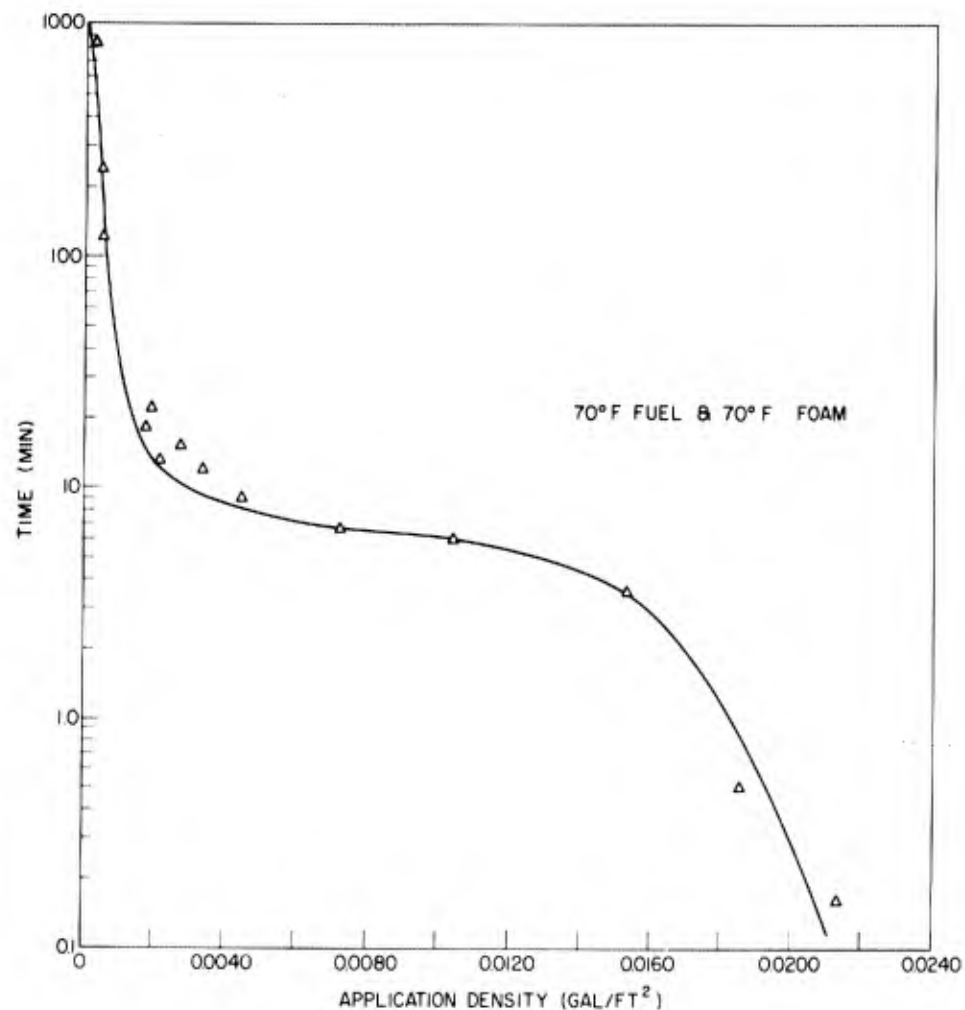


Fig. 13 - Time required at 70°F for complete pan-area vapor sealing as a function of application density (1/4% L-1083 + 1/4% L-1162 + 1/2% ethylene oxide, expansion 4)

could not be ignited. With applications from 0.0160 down to 0.0020 gal/ft², the time for securing the area did not change very rapidly; however, below 0.0020 gal/ft² it began to increase sharply. It can be seen that if permitted 960 min spreading time, one gallon of perfluorocarbon surfactant solution applied as a foam could restrain vapor efflux from a gasoline fuel surface of over 11,000 ft². Maximum life of the barrier film, once it is formed, is not known, but applications of 0.0040 gal/ft² have prevented sustained ignition for periods up to 48 hr.

The role of temperature in film formation was also investigated with the same apparatus. By circulating thermostatically controlled water through the jacket of the tray, the fuel temperature was maintained at 40°, 70°, and 100°F during the respective runs. Surfactant foam solutions were pretempered, permitting application of foams with temperatures comparable to that of the fuel substrate. The minimum securing times for halting vapor production are again plotted as a function of application density in Fig. 14 for the three temperatures. The 70°F curve is identical to that of Fig. 13 and serves as a basis for comparing the higher and lower temperatures. The minima through which the curves are drawn provide "go" or "no go" ignition conditions.

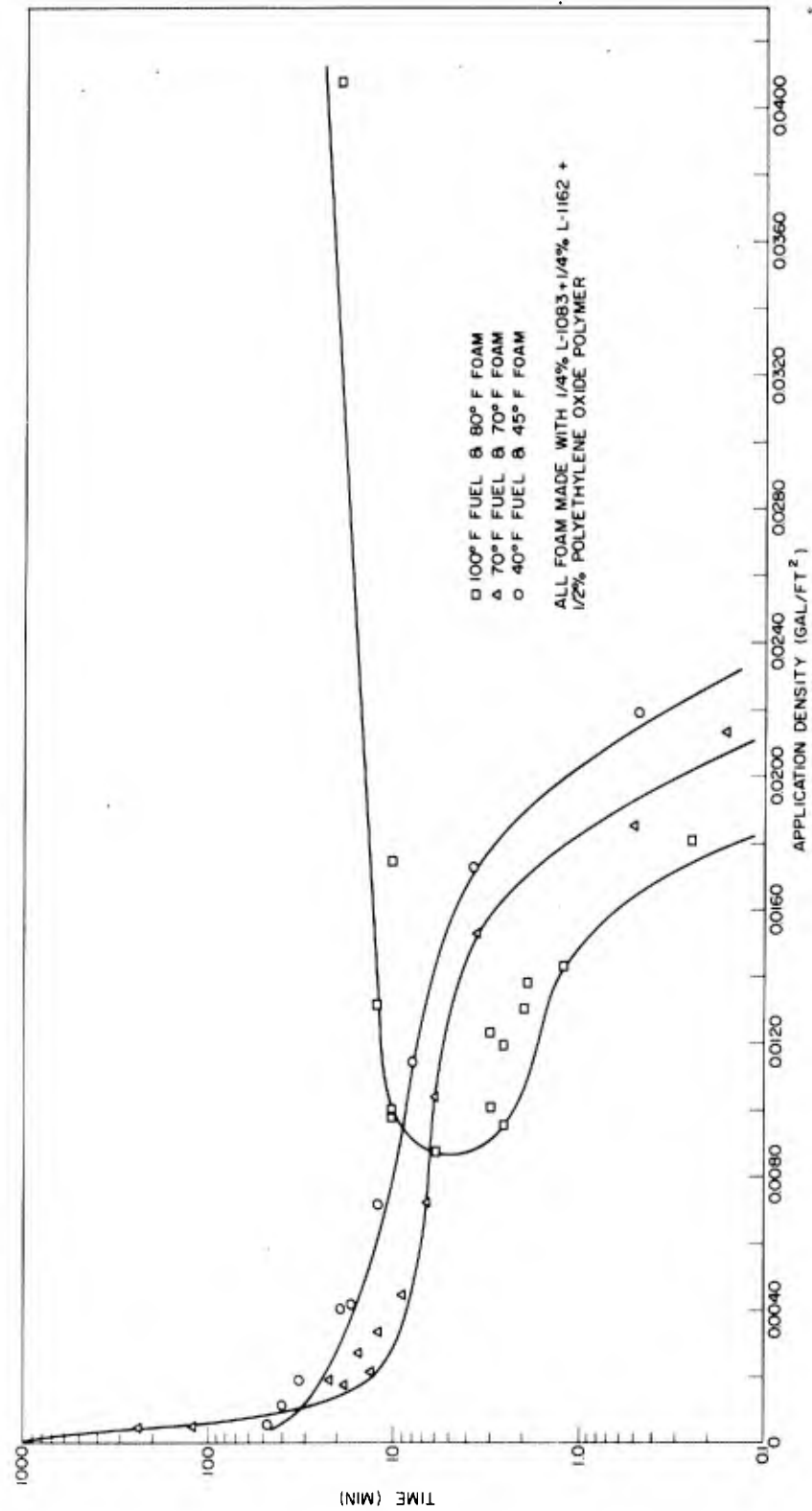


Fig. 14 - Influence of temperature on time required for complete vapor sealing at varied application densities

With the lower temperature, the speed of film spreading was somewhat diminished, but the same application densities would cover the same fuel areas, if given a longer time. At the very low density of 0.00066 gal/ft² the performance exceeded that at 70°F. At the high temperature of 100°F, the securing process seemed to run a different course, and a distinctly different curve was obtained. The lower viscosity of the foam permitted a faster foam spread (and also a faster film spread) at higher application densities (0.018 to 0.009 gal/ft²). Time to effect a vapor seal at the lower density was six minutes, the same as at 70°F. At this point, a new phenomenon became manifest. Application densities less than 0.009 gal/ft² never did effect a complete seal. Further, the vapor seal formed in six minutes or less was found to have a relatively short life at 100°F, and this life was obtained only by increases in application density. The portion of the 100°F curve rising slightly to the right as application densities increase from 0.009 toward 0.04 gal/ft² shows essentially the time at which the vapor seal broke down, instead of the time at which it was formed. For example, the lower limb of the 100°F curve indicates that a vapor seal is effected in a little over one minute by application of 0.014 gal/ft², and the upper limb indicates that the seal fails a trifle after ten minutes. To prolong the seal to 20 min, an application density of 0.032 gal/ft² would be required.

It is probable that the curves at 40°F and 70°F could be extended into the region of seal breakdown if the time of observation were greatly increased; durations of two or three days have been observed. There has not yet been time for adequate investigation of the nature and cause of the decrease in seal life with increase of temperature. Initial speculation is that the major cause may be either the greater vapor pressure of the fuel or change in surfactant film properties. Vapor pressure of the fuel used in these tests increased from approximately 2.5 psi at 40°F to 10 psi at 100°F.

By substituting JP-5 for gasoline as the substrate, it was possible to divorce the temperature and vapor-pressure relationship. The JP-5 when heated to 170°F was above its flash point and could be ignited by the small torch; however, its vapor pressure was only 0.3 psi. Perfluorocarbon surfactant foams applied on this hot fuel did demonstrate some vapor-suppressing ability, but they could not preclude ignition when used at a density of 0.0088 gal/ft². This led to the belief that the decreased effectiveness was more a direct result of high temperature rather than high vapor pressure.

The use of refrigerant gas to blow foams for the above test procedure showed such foams to be much more fluid and capable of faster film formation than their air-bubble counterpart. Their stability, however, was reduced, and the film protection did not persist for equivalent time periods.

As shown in Fig. 12, the difference between barrier-film-generating materials and non-film-forming materials was readily detectable by the testing technique employed. This difference could be used as a screening test for determining the film-forming ability of other candidate compounds. Also (Fig. 13), the results at any fixed application density in the 0.0020 to 0.0140 gal/ft² range could be duplicated within close limits when working in the 70°F or below temperature range. The method was judged to be a suitable basis for future specification performance requirements. For instance, employing a modification of the equipment and agent application procedure described earlier, and using the solution application density of 0.0080 gal/ft² with the gasoline and solution maintained at a constant 70°F, a film barrier must generate, move across the pan surface, "lock in" to the pan wall, and prevent sustained ignition of the gasoline surface when proofed by a live flame within five minutes elapsed time in order to demonstrate a satisfactorily performing material.

Large-Scale Combined-Agent Fire Testing

The problem of selecting a suitable large-scale test-fire size and equipment adequate for dealing with it is subject to many solutions. In the case of this research it was decided that for dual-agent experimentation the nominal 150-lb-capacity dry chemical unit (normally charged with 125 lb P-K-P) would be of the correct capacity for the maximum size fire which could be handled in a test program within the scope of test facilities available at NRL. Approval laboratories' test evaluations of the capacity of this size unit have shown that it can successfully cope with a 400 ft² gasoline pool fire of a square configuration, without obstacles in the fire area.

A dual-agent unit was constructed around the 150-lb wheeled unit, so that it was completely self-contained. Figure 15 illustrates the finished equipment.

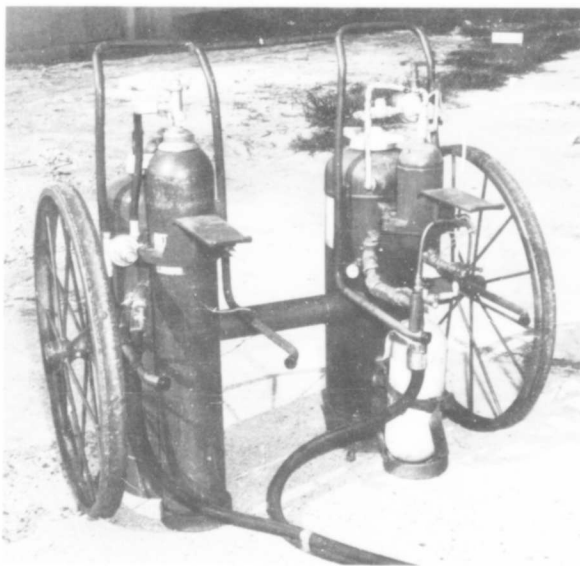


Fig. 15 - Experimental dual-agent extinguishing unit with dual hose.

One wheel from the 150-lb dry chemical extinguisher and one wheel from an identical second 150-lb dry chemical extinguisher were removed to allow a side-by-side axle mounting of the two cylindrical containers. The only changes made in the shell to accommodate the vapor-securing-agent surfactant solution were the removal of the gas pressurization tube, addition of a bottom drain, and addition of a 1/2-in. top pressurization tap. Exterior mounting brackets were installed to hold the refrigerant type R-12 liquified gas and the compressed air for pressurizing the vapor-securing-agent portion of the system. The dry chemical container retained its own pressurization system, using the original 110-cu-ft nitrogen cylinder and was operated in the normal manner.

Liquid capacity of the active surfactant solution container was 16.5 gal, weighing 150 lb. In order to expand this volume of solution into a securing-agent foam of desirable test characteristics, 130 gal of vaporized R-12 refrigerant gas were required. When stored in a liquid state, a container of one gallon capacity is adequate for this volume of refrigerant gas.

It was calculated that 40 cu ft of compressed gas at STP was needed to expel properly the contents of the solution of vapor-securing agent and the refrigerant gas tanks. The air tank used normally for emergency breathing apparatus provided this capacity when under its rated pressure, and was conveniently available for quickly recharging the unit. Its gas-pressure regulator was set for 150 psi and supplied both the active solution and the refrigerant-gas storage containers. This common pressure source served to proportion properly the flow rates of both materials into the hose line and to the nozzle. For proper flow characteristics, it was desired to keep the refrigerant under sufficient pressure to keep it liquified up to the discharge nozzle. In order to do this, the nozzle pressure had to be maintained at a minimum of 80 psi under the prevailing testing temperatures, even after undergoing the friction losses in the hose line.

Figure 16 is a sheet illustrating the flow of materials and the essential components of the surfactant foaming unit of the system. A valve on the inlet and outlet of the refrigerant-gas container isolates it so it can easily be recharged, and unions outside the valves provide for ease of removal. This material must be kept sealed at all times to prevent its boiling off. A check valve in the outlet line prevents any backflow into the tank. A 1/8-in.-diameter orifice plate was mounted in the outlet union. This orifice meters the flow of gas into the surfactant solution line to achieve the correct proportion in the final mix. The solution tank has an outlet line with a check valve, a shut-off valve, and a drain line.

At the time of desired operation, the system is pressurized by opening the air-cylinder valve and the refrigerant-tank inlet valve. The quarter-turn outlet valves on the refrigerant tank and solution tank are opened, thereby allowing material to flow to the nozzles, where it is then under the finger-tip control of the fire fighter.

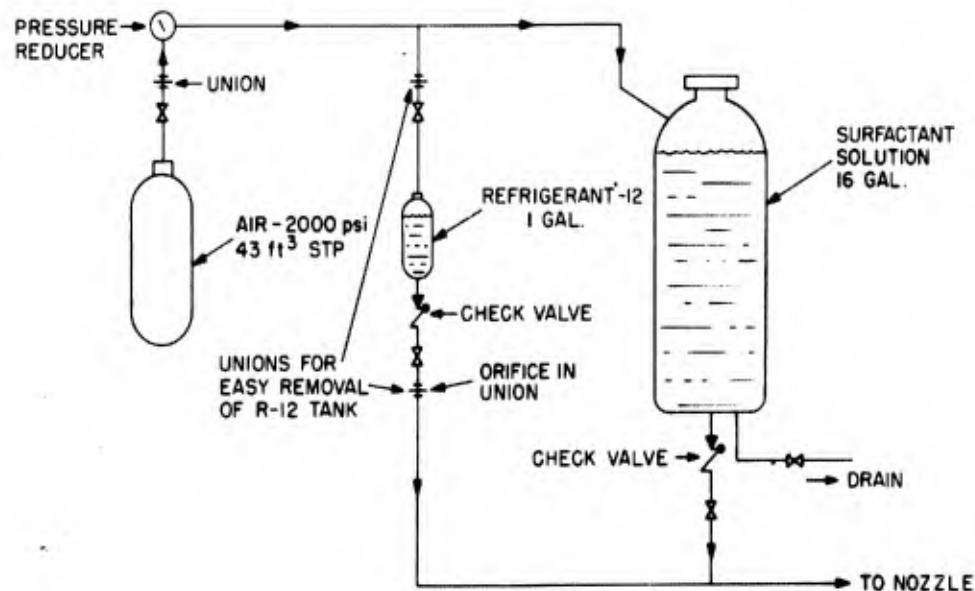


Fig. 16 - Flow sheet of surfactant unit for "twinning" with dry chemical unit

The nozzle chosen to form and distribute the foamed securing agent was a commercially available device used on an aspirating "fog-foam" producer. Its liquid-flow capacity was rated at 47 gpm at 100 psi. Thus, the discharge rates of agents were 6.5 lb/sec of securing-agent solution and about 3 lb/sec of dry chemical, or a ratio of 2.2 to 1.0 on a weight basis.

A double rubber hose, known as "Twin LP Gas" hose, was found to be available commercially in a 3/4-1 in. combination with a 400-psi working pressure rating. The 3/4-in.-diameter section was used for dry chemical and the 1-in. section for securing-agent solution. Friction losses of 50-ft-long discharge hose were well within the available pressure heads. At the outer end, the hoses were separated for a short distance to permit separation of the discharge for ease of control and to allow the operator to stand in the center of the nozzle holder. Figure 17 shows the mounting and method of nozzle

operation. The use of two nozzles for agent application, each of which must be capable of independent and intermittent operation, required adapting of various available pistol-grip controls with trigger valves, since nothing fully meeting requirements was commercially available.

Duration of discharge of the dry chemical with this unit is approximately 40 sec, and the surfactant foaming solution 20 sec, with continuous flow. The trigger controls make it possible to use the agents intermittently as required, thus prolonging the time of operation. Maximum effective range of the dry chemical nozzle is 25 ft and that of the securing agent is 20 ft. The respective discharge patterns of the twin-nozzle holder are shown in Fig. 18a and 18b.

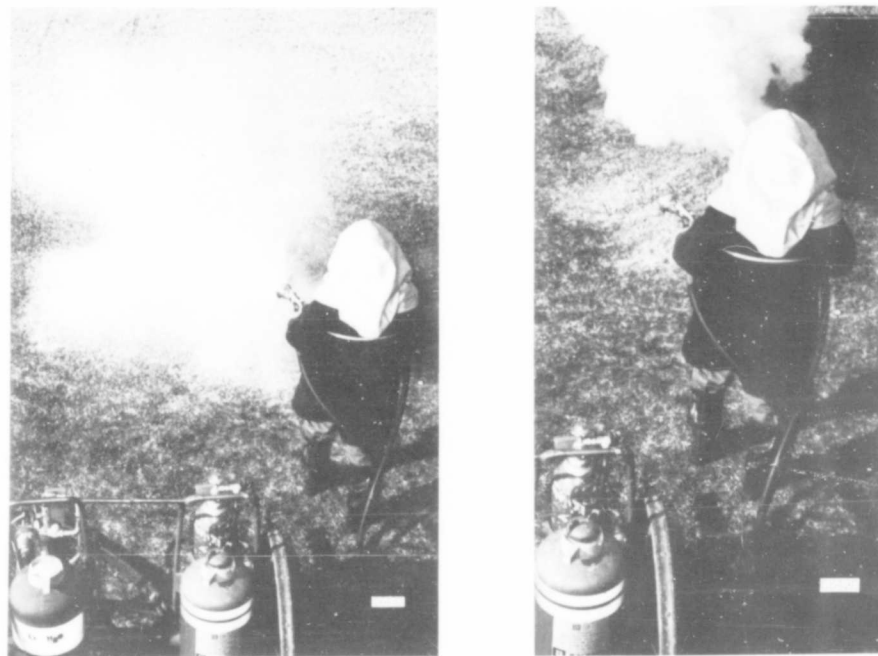
The fire-test area was 20×20 ft (400 ft^2) and consisted of a wetted concrete surface with the fuel restrained by a mud dike approximately two inches in height. Fresh motor gasoline fuel in the amount of 90 gal used in each fire formed a layer 0.36 in. deep. An open top, steel 55-gal drum was placed on its side in the center of the fuel area to introduce the added impediment of an obstacle. Figure 19 shows the area layout.

The selection of the dimensions of the fire area determined that the total amount of dry chemical available from the dual-agent unit was 0.31 lb/ft^2 . With the existing nozzle-flow rate of approximately 3.0 lb/sec, the application rate was $0.0075 \text{ lb/sec/ft}^2$. Application of the entire 16.5 gal surfactant foam-forming solution would provide 0.04 gal/ft^2 on the fuel surface.



Fig. 17 - Twin-nozzle mount, showing trigger valves and breast bar

The standard test procedure decided upon was to dump the 90 gallons of fuel quickly, ignite, allow a 15-sec preburn period, and then attack the fire with the dual-nozzle-equipped handline. Dry chemical alone was applied to initiate a knockdown from the left side. Within a few seconds, and after fire knockdown had started, the surfactant solution



a. Vapor-securing surfactant discharge
from left-side trigger-valved nozzle

b. Dry chemical discharge
from right-side trigger-
valved nozzle

Fig. 18 - Discharge patterns from the twin-nozzle mount

nozzle was opened, and this material was applied to the already extinguished fuel surface. During the next phase the operator worked with both agents flowing, attempting to extinguish the fire areas with the dry chemical and then to secure the extinguished areas with foamed surfactant. The finger-tip nozzle controls allowed some choice of agent to the fire fighter, subject to his degree of coordination. Presence of the securing-agent vapor-proof blanket permitted the fire fighter to move around the barrel obstacle with ease and without the problem of the fire reflashing around behind him. This enabled him to extinguish the fire readily, progressively, and consistently.

Dry chemical was normally applied until the flames were completely or almost completely extinguished. Securing-agent foam was continued after this point, extinguishing any remaining flames, until the operator judged that a sufficient covering had formed to preclude reignition. At this time the fuel surface area was probed over its entire surface with a lighted torch to determine the presence of any flammable vapors. The lighted torch was then used to agitate the fuel in an effort to effect an ignition. This was continued until ignition took place, and served to evaluate the effectiveness of the securing-agent film. Ten such tests were conducted with winter and summer grade motor gasoline and one each with JP-4 and JP-5 aircraft turbine fuels. The series of photographs in Fig. 20a through 20i illustrates the steps in a typical fire test.



Fig. 19 - Large-scale (400 ft²) fire-test area with obstacle in center

Attempts to extinguish this fire with the 125 lb of P-K-P alone were not successful. The steel drum effectively shielded the dry chemical from cleanly sweeping the fuel surface. When the operator moved his discharge in an attempt to reach this fire, the flames continued to move around behind him. This "chase" continued until the dry chemical agent supply was exhausted, at which time the entire area again became involved in flames (rate applied: 0.0075 lb/ft²/sec, amount applied: 0.31 lb/ft²). The failure of this relatively dense application was attributed to the presence of the obstacle.

Where the surfactant foam was used on fires with simultaneous application of potassium bicarbonate, the dry chemical application times were from 20 to 28 sec, requiring about 60 to 85 lb of Purple-K-Powder. The powder application rate was 0.0075 lb/ft²/sec, and the amount needed was 0.18 lb/ft². This gives a guide to the effectiveness of the perfluorocarbon surfactant securing agent as a back-up aid to dry chemical; a fire not extinguishable with 0.31 lb/ft² of P-K-P could be easily extinguished with slightly more than half that amount when using securing agent in conjunction with the dry chemical.

In all instances, the total amount of 16.5 gal of surfactant solution was used in building an adequate cover in the estimation of the operator. Thus, the amount applied was 0.04 gal/ft². At the end of the application time there normally existed some open fuel surfaces, where the force of the stream held the back area of the square fuel pool from sealing. The fluid securing-agent foam immediately flowed in after shutting off its application, and all fuel was visibly covered with a substantial blanket of foamed agent (Fig. 20e). The surface-tension forces, being very low, permitted the foam film to form an effective seal around the edges and up to the obstacle.

It was not possible to detect with a lighted torch any spots or sources of flammable vapor above the fuel area. This technique was not continued for an extended time period, because it did not seem to be a severe enough type of test. Under undisturbed conditions it was estimated that the fuel-vapor suppression would remain effective for several hours. In order to observe the characteristics of the film, the torch was used to sweep it open. This permitted subdued burning in the bared area, but the film rapidly reformed and the flames were self-extinguished within a few seconds. The length of time this process could be successfully repeated was noted. Resistance to sustained burning, which could be maintained for ten minutes of agitation, was considered excellent.



a. Ignition stage of 400 ft² large-scale test fire using gasoline fuel



b. Start of attack, using combined-agent unit (initial dry chemical discharge)



c. Combined-agent discharge on test fire; operator proceeds to right

Fig. 20 - Results of combined-agent test in large-scale fire area



d. Last stages of fire extinguishment
(note white vapor-securing cover on fuel)

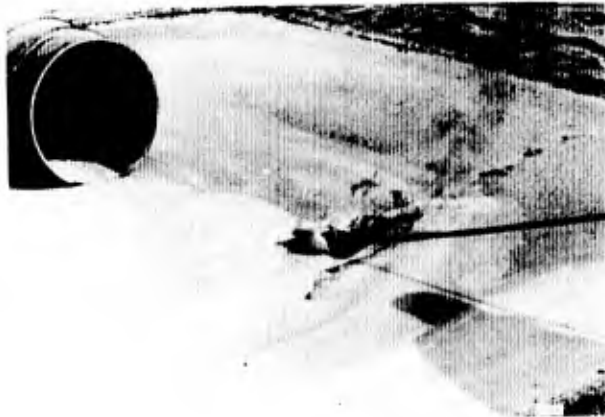


e. Fire extinguished, fuel
vapors secured

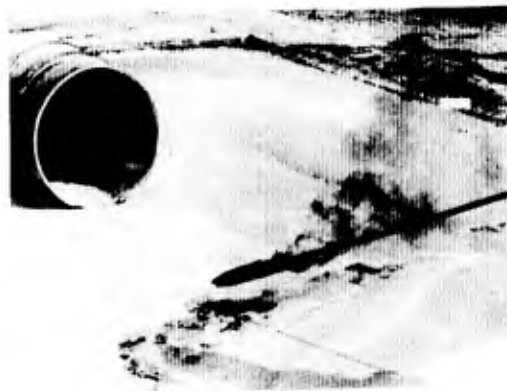


f. Lighted-torch proofing of vapor blanket

Fig. 20 - Results of combined-agent test
in large-scale fire area (continued)



g. Disturbance of fuel blanket with lighted torch
(dark streaks are P-K-P powder)



h. Failure of fuel to sustain ignition
from action in Fig. 20g because of
surfactant film closure



i. Open-area ignition made possible after
repeated torch agitation of vapor-securing
agent. This area will self-extinguish after
removal of the torch

Fig. 20 - Results of combined-agent test
in large-scale fire area (continued)

A difference was noted in the reignition resistance between the three runs made in the spring and the seven runs made early in the summer. After checking back into possible variations in the preparation and handling of the surfactant solution and making the laboratory investigations cited earlier, it was concluded that the higher ambient and gasoline temperatures caused the lower resistance to reignition. The early runs were made with temperatures in the 40° to 50°F range, while the later runs were made with temperatures in the 80° to 90°F range. The corresponding decrease in reignition time was from ten minutes down to two to three minutes.

One run was made using 100 gal of JP-4 as the fuel in place of the gasoline. The ambient temperature was in the 85° to 90°F range. The knockdown of fire by the P-K-P was slightly faster than with gasoline, but the amount of securing-agent solution applied was the same, 0.04 gal/ft². The resistance-to-ignition period was between two and three minutes. Thus, the JP-4 fuel as used in this test gave results essentially equivalent to gasoline.

One run was also made using 100 gal of JP-5 as the fuel. Ambient temperature was 90°F. Because of the low rate of flame spread across the fuel, it was necessary to extend the preburn time to one minute to reach an equilibrium burning state. The dry chemical knockdown was slightly faster than with the JP-4, but again the same amount of solution was applied. The resistance to reignition was rated excellent, being on the order of ten minutes. As expected, this fuel was much more difficult to reignite than either the JP-4 or gasoline.

There was no evidence of breakdown of the fluorocarbon surfactant foam in the presence of the MIL specification P-K-P. In this type of usage, wherein both agents are applied from the twin nozzles, a high degree of intermixing is unavoidable. The large-scale test results indicated complete compatibility.

The program of large-scale testing confirmed the concept previously demonstrated in the laboratory, and in small-scale tests, that a film barrier could be formed on a liquid-fuel surface in a manner to reduce appreciably its normal flammability characteristics. This film could be generated and formed from a surfactant foam with sufficient rapidity to be of material assistance in preventing reflashes when extinguishing a fire on volatile hydrocarbon fuels with dry chemical. The film is free flowing, which enables it to be self-sealing after being disturbed by agitation, by walking through it, or by other actions. The duration of ignition protection of the film is variable with ambient or fuel temperature and drops from about ten minutes at 50°F to three minutes at 90°F.

The proportion between the amounts of dry chemical and securing agents used was 80 lb of P-K-P to 16 gal (135 lb) of securing-agent solution, or 1:1.7 by weight. This ratio was higher than was indicated by the preliminary work leading up to this scale of operation. No attempt was made in the large-scale tests to determine the effect of using a lower application density than the 0.04 gal/ft². With the resistance to ignition down to three minutes in the high-ambient-temperature range, it was not deemed advisable to use a lower application density on fires of this size or larger.

DISCUSSION

Existing Fire-Fighting Foams and Their Comparison with Fluorocarbon Surfactant Foams and Films

The present fire-fighting procedures of using protein types of air foam as vapor-securing agents on Class B fuel fires constitute a valid yardstick for determining the comparative usefulness of the fluorocarbon surfactant foams and their films as agents for accomplishing the same purpose. In the experimental program reported here, efforts

have been constantly directed toward parallel testing procedures employing standard protein foam under conditions identical to those to which the fluorocarbon surfactant foams were exposed. These test conditions almost always included the factor of potassium bicarbonate dry chemical admixture in the combustion area, since one of the principal objectives of this work was the enhancement of the fuel-fire extinguishing characteristics of the latter superior, nontoxic, and useful extinguishant.

The intermediate-scale fire-test results, using a 14-ft.-diameter circular gasoline-fueled area with an obstacle in its center, are useful in comparing these very dissimilar foams. A basic level of protection for the test area was established by applying 0.03 gal/ft² of fluorocarbon surfactant mixture solution in the form of a gas-blown foam (expansion 8, 6 min drainage time) while simultaneously extinguishing the 14-ft-diameter, 154-ft² fire with dry chemical from a 20-lb P-K-P extinguisher. The solution application rate was 47 gpm (0.3 gal/ft²/min) and of 6-sec duration to give an application density of 0.03 gal/ft². This effected a 100-percent extinguishment, required 3 min agitation to relight, and allowed a burnback of only 50 percent of the total area ten minutes after reignition started.

Protein-type foam from an aspirating nozzle of standard design, yielding a foam of expansion 5, 1.3 min drainage time, did not make rapid progress against the fire, and application was continued for 43 sec. Thus, the application density rose to 0.20 gal/ft², or seven times that used with the surfactant foam. Even at this point the fire was only 70 percent extinguished. The 50-percent burnback time was only 30 sec. By increasing the foam application time to 72 sec and the application density to 0.36 gal/ft², the fire was 95-percent extinguished, but the 50-percent burnback time was still only 2 min. In the latter application the amount of foam solution used was twelve times that of the surfactant mixture water solution.

To be fully candid, it should be brought out that the relatively high degree of incompatibility of protein foams intimately mixed with dry chemical when they are used together on a fire is the principal factor responsible for large quantities of protein-type foam being necessary to achieve a suitable level of fuel-fire protection. This is caused by several controlling conditions. The present status of protein-type foam-concentrate specification requirements does not impose a need that foam-forming solutions demonstrate a compatibility with existing dry chemical materials. As a result no effort has been made by foam-concentrate manufacturers to improve their materials so as to allow simultaneous use of foams with dry chemicals. The quality of foam generated by the device in use also governs the degree of compatibility of foams. In the NRL tests, the aspirated type of foam nozzle which was used results in an air foam of increased vulnerability to dry chemical attack. Foam generators of the vane-pump type obviate this latter problem.

Under fire-test conditions similar to those of the 14-ft-diameter test, except not using P-K-P, protein foam applied for 43 sec (0.20 gal/ft²) resulted in a 95-percent extinguishment. The 50-percent burnback level was reached within four minutes and 100-percent burnback in seven minutes.

In the light of the fire-test data, it is also of interest to compare the economics of the two materials. A concentrated form of the mixture of surfactants found most effective in our tests, showing no gelling tendencies at ordinary temperatures, is supplied by the manufacturer according to NRL recommendations. It is denoted as product No. FX-183 and can be obtained from the Minnesota Mining and Mfg. Co. at a current cost of approximately \$8.00 per gallon. The concentrate is diluted with three parts tap water, thus resulting in a finished cost of \$2.00 per gallon, which, when applied at 0.03 gal/ft², would represent a cost of \$0.06/ft² of fuel area protected to the basic protection level cited previously. On the other hand, protein-foam concentrate, at \$1.50/gal, is used in a 6-percent solution to give a cost of \$0.09/gal of finished foam solution. If the protein

foam is applied as a securing agent with P-K-P, at least 0.36 gal/ft² of foam solution, at a cost of \$0.03/ft², would be required, and even then the degree of protection would be below that of the basic protection level needed. It is believed that the new surfactant formula agent is clearly competitive costwise with protein foam when used to secure fuel areas after extinguishment with "P-K-P" dry chemical.

Although work in the area of fluorocarbon surfactant foams as a primary extinguishing agent has not been extensive, it is believed that this type of material may be developed to a point where it will be considered competitive with protein foam per se for equal degrees of effectiveness.

In the category of weight and volume comparisons of the amounts of material required, the fluorocarbon surfactant agent showed a saving of 90 percent over protein foam agent when employed as a securing material. These favorable savings make fluorocarbon surfactant mixtures very attractive, even regardless of cost factors, for applications where weight and volume of agent are extremely critical, such as extinguishing units to be airlifted by helicopters or transported by truck. Aircraft firefighting and rescue equipment falls in this category, and as experience is gained in the use of surfactants and improvements in the formulation and equipment requirements permit foaming in simpler ways, fluorocarbon surfactants should find a wide application.

The new material offers the first possible firm lead toward a completely synthetic foaming agent which is chemically identifiable and capable of being produced to definite chemical and physical standards. The diluted solution can be premixed and stored indefinitely without problems of bacteriological attack or deterioration. Protein foam concentrates have always been a difficult material to manufacture and store. Their exceedingly complex chemical nature has made it almost impossible to control the manufacturing process or to identify the final product. Fairly large-scale fire performance tests have been the only method of quality control available to the purchaser. During storage, proteinaceous concentrates have always been susceptible to the formation of sludges and precipitates, which indicate deterioration and interfere with proper utilization.

Some Surface-Activity Considerations of These Surfactant Systems

The various surface-active properties exhibited by the foams and solutions of the perfluorocarbon surfactants are exceedingly alluring to the physical chemist interested in studying the various mechanisms occurring at the interface of immiscible liquids and air. These compounds confer properties to water so that the latter can make use of the surface "skin" of hydrophobic liquids, such as gasoline, as a platform on which the solution may spread in very thin but completely coherent films; this ability is not obtainable with ordinary surfactant solutions. Considering the low density of hydrocarbon fuel, the surface forces acting at its interface are evidently capable of equilibrating the gravitational forces of a liquid of some 20-percent greater density than the substrate fuel. Much remains to be learned concerning this mechanism. This report contains the engineering applications of the phenomenon.

The formation and subsequent surface application of gas (or air) foams of lesser density than the substrate fuel happily accomplishes several actions simultaneously; it establishes a floating, vaporproof, coherent seal over the fuel of very low interfacial tension with the solid walls of the fuel container, and at the same time it provides the mechanism for spreading an interfacial film, also coherent and vaporproof, over the surface of the fuel not already coated with foam or opened by mechanical disruption. The latter mechanism eventuates from the process of drainage of the very surface-active water solution from the foam mass, a necessary consequence of the aging process of a foam bubble. Thus, as the foam breaks down—a sequence which has been studiously

avoided heretofore in fire fighting using other foams—more and better surface vapor efflux protection is obtained by the use of the fluorocarbon surfactant solutions.

Because of the novel mechanisms involved in accomplishing a heavier-than-substrate liquid film on gasoline fuel, the measurements ordinarily performed on surface spreading agents on aqueous substrates are of little significance. One such property would be the spreading velocity of the liquid draining from the foam.

The curved portions of the time-vs-area relationships shown in Fig. 12 indicate that a liquid-film transport over the fuel takes place, following the formation of a foam area which seems to halt abruptly after about 0.1 min from the time the foam is applied to the fuel surface. The spreading velocity of this film is about 1.5 cm/min. The velocity of an oleic acid film on pure water was found by Cary and Rideal (3) to be 20 cm/sec.

The curves of Fig. 14 indicate the proportionality of spreading velocities of these surfactant films to the sizes of the initial foam areas on the fuel substrate (given as application density in gal/ft²). The function of temperature also operates to change film-spreading velocity, and at high temperatures (100°F) a limiting surface area capable of being formed at these temperatures is demonstrated.

Information available concerning the purity of the perfluorocarbon surfactants L-1083 and L-1162 used in this work indicates that they consist of mixtures of several possible compounds. In general, these are quaternary nitrogen compounds derived from perfluorocarboxylic and perfluorosulfonic acids. For the present, their ability to form monomolecular films on hydrophobic substrates has not been determined because of their lack of complete characterization as individual compounds. However, the figure of film-area coverage of 11,000 ft²/gal, which was derived from the film-forming tests described earlier, indicates an approach to a film of monomolecular thickness on gasoline fuel.

It is of considerable interest that these properties of synthetic perfluorocarbon chemical materials were known to some extent several years ago to the authors. In 1956 or thereabout, other workers at NRL, working with a modified Langmuir film balance, demonstrated surface activities of compounds similar to those described in this report (4). At that time attempts were made to reduce the evaporation rate of gasoline by very small amounts of these perfluorocarbons dissolved in the fuel and adsorbed at the interface as a film, thereby reducing the fire hazard. Only very meager success could be demonstrated, and the mechanism was all but forgotten.

A similar barrier-layer mechanism using these surfactants had been reported in 1962 (5). It was formed by dissolving 0.003 percent of a fluorochemical in the hydrocarbon fuel. The resulting migration and cohesion of surfactant provided an adsorbed barrier film at the surface to halt escape of fuel vapor from the fuel bulk. These films apparently consisted of a solid form of the surfactant and required an appreciable time to form effectively. Similarly, if disrupted by mechanical force, film reformation would take several minutes.

A Proposed Nomenclature

Quite early in this research it became apparent that a considerable amount of difficulty ensued in correctly describing the goal of this work. Early objectives were laid down concerning the type of material which might be used to form a vaporproof coating on flammable fuels immediately following flame extinguishment by dry chemical powders or other temporary agents. Obviously, ordinary fire-fighting foams could not be employed because of their relatively high ratios of weight and volume per square foot of exposed fuel surface necessary to provide vapor protection. From economic viewpoints,

water was the most desirable nonflammable liquid with which a coherent film could be formed, but the problem of floating water on fuels of densities less than 1.0 was insurmountable until the surface-active characteristics of the soluble perfluorocarbon surfactants was discovered.

The film-forming mechanisms obtained from the solutions draining from foams produced with the perfluorocarbon mixtures became a means of making water "light" in weight. Since it was also a practical necessity that these foams and their films be easily differentiated from the existing protein types of fire fighting foams, it became expedient in the laboratory to refer to the new material as "Light Water," which it indeed was. The newly coined name became easy to use, and after a number of years of reference to this new agent as Light Water and its recording in patent application form (6) and in certain military specifications (7), the name promises quick and accurate reference without confusion.

The liquid mixture of L-1083 and L-1162, containing suitable amounts of ethylene-oxide-soluble polymer, is named Light Water Concentrate and is available from the manufacturer, Minnesota Mining and Manufacturing Co., as FX-183. This concentrate is diluted on a basis of one part concentrate to three parts fresh, potable water to give a solution containing 0.25-percent L-1083, 0.25-percent L-1162, and 0.5-percent ethylene oxide soluble polymer. This is called "active solution."

The Dilemma of Flame Vulnerability of Light Water Foam Formulations

In the formulation of Light-Water foams with a high resistance to heat, which characteristic is normally desired in fire-fighting operations, we are confronted with problems identical to those governing the usefulness of ordinary protein foams, with one exception. This exception is concerned with the fact that the surfactant solution draining from a degraded foam on the surface of the fuel exhibits properties of vapor retention similar to those of the foam from which it came.

The ability of fire-fighting foam to resist flame is dependent on its water-solution content. Foams with high water content (low expansion) are highly resistant to flame, but they are unstable "emulsions" of air and liquid and lose water rapidly by drainage to the interface of fuel and foam. Large quantities of water are needed per unit area with this type of foam.

Foams with low water content (high expansion) are increasingly vulnerable to flame attack but are highly stable and hold their water in the foam matrix for long periods of time. Small quantities of water per unit surface area of fuel yield equivalent vapor control using the high-expansion foams.

In the small-scale work described earlier in this report, an effort was devoted to find how to utilize best a fixed amount of water to delay ignition of fuel beneath. It was determined that fluorocarbon surfactant solutions expanded into a high expansion or volume of foam would best serve the intended purpose, and the next larger scale of testing was initiated following this plan.

The intermediate-scale tests required that the Light Water be applied from a nozzle instead of being spread evenly by means of a spatula in a fixed container. The new manner of application raised new problems not indicated by the previous tests. Flame burn-back rate over a surface was exponential in character; i.e., the rate of disappearance of securing agent becomes faster as the resultant exposed fuel area and fire grows larger. Thus, the amount of fuel originally covered by the Light Water application became the most important factor in evaluating performance.

A good application of Light Water, which effectively sealed off 95 percent of the fuel area when reignition was effected by a torch, might show a time to complete burnoff of agent of ten minutes. The same amount of identical material, but poorly distributed, so that only 75 percent of the fuel area was effectively sealed, might show a complete agent burnoff time of only two minutes. Location of the on-fire area to the secured area in relation to the wind also was a factor of considerable importance. When the fire was on the leeward side, the wind carried the heat away from the secured area; when the fire was on the windward side, the heat and flame were swept over the secured area, accelerating the rate of burnback. In order to achieve maximum effectiveness of the agent it was imperative that the fire fighter strive for as complete a coverage as possible and that he take special pains not to leave any voids on the windward or his normal approach side.

On further testing, it was found difficult to obtain good vapor sealing of Light Water securing agent of the high-expansion type because of its stiff, resistant-to-flow nature. Often wide fissures occurred during application, and also the wind sometimes moved the Light Water around as islands on the fuel. Any disruption of the covering, such as footprints, also left exposed fuel which added to the fire area and thus promoted rapid burnback. The stiffer, higher-expansion foams, being more stable, were slower to drain liquid, which beneficial action formed the barrier film on the fuel and which was an essential part of the securing mechanism. These undesirable characteristics were ameliorated by using a lesser amount of air or "blowing" gas in the foam-generating system, so that a more fluid foam was formed.

Through the use of a low-expansion "Light Water" foam, a net gain in effectiveness was established. The same amount of applied "active solution" formed a 100-percent or near 100-percent foam cover and left little or no foothold for reignition to start. Burnback resistance per se, as measured by the small-scale static test, did not adequately reflect the dynamic conditions of actual use and therefore was an inadequate test. Light Water foam of expansion 8 and six minutes drainage time appeared to offer the best compromise in characteristics. It provided a readily flowable foam which would seal up against obstructions, promoted the rapid formation of a surface-active film barrier on the fuel, and provided a sufficiently stable foam to resist burnback, if ignition did occur. The presence of the continuously forming film barrier governs the prevention of ignition. Its aggressive spreading tendency on fuels permits it to move ahead of the "mother" foam matrix, and this also gives it a self-healing ability to cover over mechanical disturbances, such as a man's footprints. Further, the stability of the film is so great that it can re-form even under the flames of a burning fuel area, presenting the appearance of a self-extinguishing fire. Once a sustained point of burning was present, either from a hole or beyond the edge of the securing-agent blanket, the physical presence of a foam containing water governs the rate of burnback across the fuel. Thus, Light Water involves both the presence of a film surface barrier and a foam. Both work hand in hand, with each performing a vital role.

Application Engineering of "Twinned-Agent" Systems

The commonly accepted and most useful criterion for comparing and evaluating dry chemical extinguishers and dry chemicals is the maximum area of burning fuel surface which can be extinguished per quantity of powder. The Underwriters' Laboratories have established a certain procedure designed to be replicatable for this purpose. It requires a relatively low-flash fuel to incorporate the reflash problem. The test-fire fuel surface is clear and unobstructed, except for the confining tank walls.

When fire-test data are compared on such a basis, it is observed that the weight of dry chemical required to extinguish one square foot of fuel surface varies somewhat, depending on the size of the fire area. In Fig. 21, Underwriters' Laboratories values

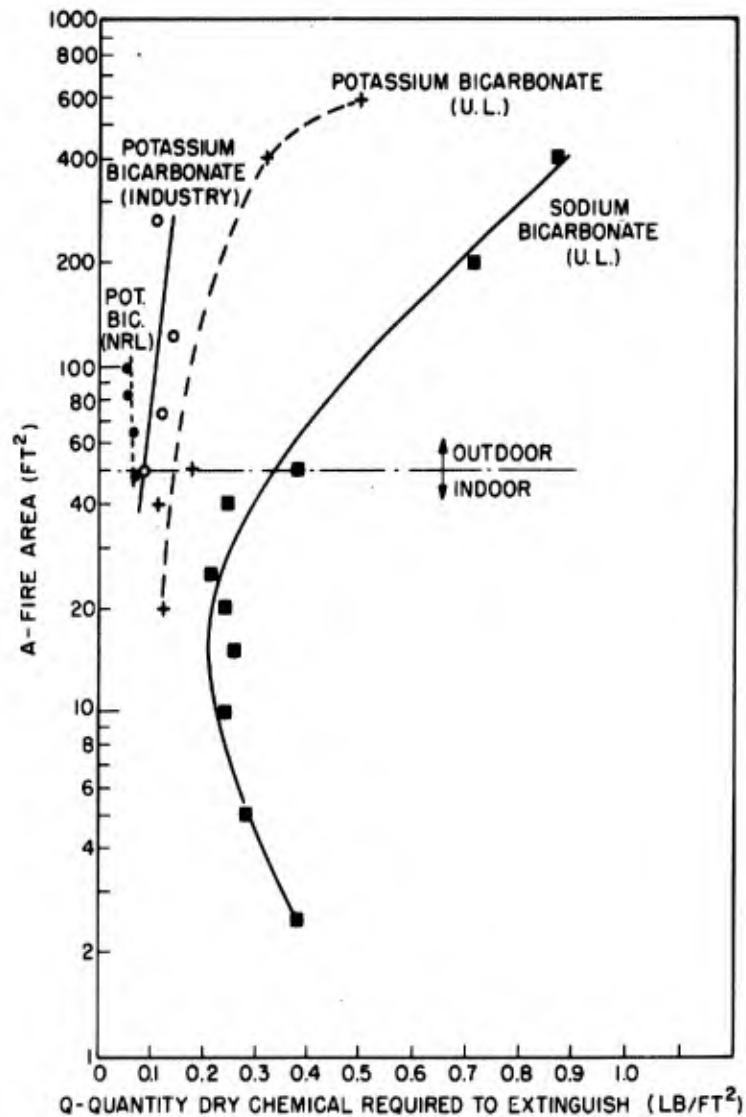


Fig. 21 - Dry chemical extinguishment--comparison of area-quantity relationships from several sources

for square feet of fire extinguished per pound are shown for sodium bicarbonate type dry chemical from a 2-1/2-ft² fire to a 400-ft² fire. (Fires below 50 ft² in area are conducted inside, with larger sizes being done outdoors.) A minimum quantity per square foot is indicated with a fire of about 20 ft²; however, this may not be significant, because of the fact that the fire-test pans and extinguishers used come in fixed size increments, which will result in some irregularities. The available comparable UL data for potassium bicarbonate dry chemical are also shown in Fig. 21. At the far left are plotted quantity potassium bicarbonate ratios from two other testing sources, using outdoor fires only.

The Underwriters' values naturally run higher than the others because of their conservative ratings, intended to allow for unskilled operators. Their values also show a minimum of a 2 to 1 advantage of potassium bicarbonate over sodium bicarbonate with the small-size fires. The superiority of potassium bicarbonate in their tests increases with increasing size of fire area.

The quantities of potassium bicarbonate required per square foot by the other sources, in addition to being lower than Underwriters', also differ in the relative change of quantities as the fire size increases. NRL results showed no higher ratios in going from a fire 40 ft² in area to one 100 ft². The industrial data indicates only a slight increase in powder requirements per square foot between 50 ft² and 275 ft² fires. In contrast, the Underwriters' shows an increase from about 0.35 lb KHCO₃ per square foot with a 50 ft² fire to 0.7 lb with a 700 ft² fire. Thus, the quantity per square foot doubled. This increase is not believed to be an inherent property of the fire on the chemical, but rather a problem of distributing chemical over the burning surface.

Dry chemical effectiveness is quite severely limited by the presence of objects or "clutter" within a burning fuel area. The powder does not readily diffuse into blind or "shadowed" spaces, and the particles are also slowed in velocity. These hidden flames are a chief source of reflash ignition. Because of the infinite sizes and configurations of possible obstacles, it would be impossible to foretell their effect on decreasing the effectiveness of powder per square foot of fire extinguished.

A designer faced with the task of developing a combination unit of equipment affording immediately successive application of dry chemical and vapor-securing agent is immediately aware that he cannot accurately predict how much fire a fixed amount of dry chemical can extinguish. It will depend on the magnitude of fire area plus the degree of "clutter" present within the fire area. Curves such as those in Fig. 21 can be of assistance in considering fire size alone, but the effect of "clutter" remains pure conjecture. On the other hand, the amount of vapor-securing agent required per square foot of exposed fuel surface has been well defined by the test program described previously. It does not vary with the size of the fire area. All of the above factors enter into making the decision on the ratio of securing agent to dry chemical for a finished piece of large equipment.

Relatively small sizes of hand portable dry chemical extinguishers are presently carried aboard foam fire-fighting vehicles, and foam is thus available in large quantities as a back-up or primary agent, and the degree of foam-vs-powder compatibility factor becomes of lesser concern. The recently developed spherical container, dry chemical air-lift unit, with its 400 lb of Purple-K-Powder, is the first piece of dry chemical equipment made available which is capable of serving as a primary fire-fighting and rescue device on a fire of any size. Knockdown and/or extinguishment of fires normally associated with the small training type aircraft should be within its ability. If a vapor-securing agent were used in combination with it, it could be relied upon to be a much more capable device, obviating possibility of flashback of incompletely extinguished fires, and it could even supplant the need for ordinary foam in connection with its use. This design area is one of the immediate objectives of this research.

The full extinguishing capability of the air-lift unit has not been determined by large-scale field test. However, by extrapolation of the curves of Fig. 21, an approximation can be reached concerning the maximum fire extinguishable with the 400-lb unit. Extrapolation is difficult in these cases because of the shapes of the curves. Using the UL potassium bicarbonate extinguishment-area curve, it is estimated that fires of the magnitude challenged by this size extinguisher would require 0.5 to 0.6 lb/ft² for extinguishment. The 400 lb would thus extinguish a maximum of 670 to 800 ft² of unobstructed fuel surface. This would assume dissemination of the powder at a fully efficient discharge rate. (A similar extrapolation of the other potassium bicarbonate curves gives values in the 2000 to 6700 ft² range (0.2 to 0.06 lb/ft²). The known practical difficulties in efficiently distributing chemical over fire areas of this size would rule out any possibility of such an achievement.

In the combined-agent usage, which is contemplated for this new material, the fire-extinguishing action would be an incremental one; each successive small area would be

quickly extinguished by powder and then covered by vapor-securing agent before proceeding to the next area. For this reason it seems justifiable to use a nearly equivalent application density ratio for the two agents. If such was done, a ratio of about 0.25 lb/ft² dry chemical would be used with the 0.03 gal/ft² (which is 0.25 lb solution per ft²) of the vapor-securing agent. The densities of both dry chemical and vapor-securing-agent solutions are very close to being equal, so that equal sizes of containers for the two agents can be used.

As a result of the foregoing considerations, it follows that the companion unit to the 400-lb air-lift extinguisher should be designed to contain approximately 45 gal (377 lb) of active solution. This balance should provide sufficient vapor-securing-agent solution to match the capability of 400 lb of potassium bicarbonate dry chemical with an adequate safety factor, particularly in the dry chemical amount.

For this size unit the design ratio conveniently works out to one pound of vapor-securing-agent active solution to about each pound of potassium bicarbonate dry chemical. It should be pointed out that capacities of other dry chemical extinguishing agents may require different ratios. Additionally, it was considered that from a practical design viewpoint, a tremendous advantage would be attained by using the same basic containers for each unit and coupling them together for fire-fighting use. This led to the terminology of a "twinned" unit.

The Application of "Twinned-Agent" Systems

Considerations of efficiency of application of dry chemical should be remembered in the application of "twinned" systems. In the case of small fires needing small extinguishers, where the operator can deliver dry chemical to its best advantage, there probably exists little or no need for a vapor-securing agent such as Light Water. However, as the size of hazard increases, and as the size of dry chemical extinguisher needed also increases, the need for a securing agent becomes more evident. With its aid, an operator achieves freedom of movement due to incremental consolidation of fire extinguishment gains. Since the basic water constituent of the Light Water securing agent possesses the cooling ability of water, coupled with the penetration power of surface-active solutions ("wet water"), it becomes an unequaled extinguishing agent for "mixed class" fire hazards when twinned with dry chemical. Class B flammable liquid fires which contain Class A combustibles of the difficultly penetrated type (rags, upholstery, etc.) cannot be extinguished solely with dry chemical agents of any type. Such fires are not easily evaluated, but this may need to be done in future experiments with the twinned system.

Although experimentation at NRL has not been conducted using the Light Water agent in combination with other gaseous or vaporizing liquid fire-extinguishing agents, there appears to be no reason that the attractive characteristics of these latter agents would not be enhanced by twinning them with Light Water. Carbon dioxide, for instance, even though it is a less effective extinguishing agent for Class B fires than is dry chemical, has the superior ability to "flood" an area on fire, flowing completely around obstacles. This action would be fully safeguarded by the addition of a securing agent with film-forming properties, and the tendency of the combustion-retarding envelope of gaseous CO₂ to be swept away from the area by wind currents would be rendered unimportant. The same general properties of certain of the vaporizing liquids would be aided by concomitant application of an effective twinned, Light Water unit.

In summation, it is worth noting that the twinned, Light Water concept provides an efficient solution to the problem of separation of fuel, oxygen, or heat, from a fire system utilizing temporary but highly efficient free radical mechanisms or gaseous inerting atmospheres as primary extinguishants and highly surface-active cooling and vapor sealing foams, films, and solutions as permanentizing agents.

Light-Water System Operation at Temperatures Below Freezing

In any fire-fighting equipment of this nature, protection against below-freezing temperatures is an important consideration. The use of auxiliary heaters introduces a serious maintenance problem which should be avoided if possible. The addition of freezing-point depressants to the active solution was investigated and found to be feasible down to low temperatures of the level which might be expected in usual naval applications. A solution of Light Water concentrate in a 30-percent ethylene glycol, 69-percent water mixture was usable at temperatures of +8°F. No trouble was experienced with the foaming ability or the fire performance of this material.

CONCLUSIONS

An involved study and testing program has resulted in the discovery and development of a new water-soluble surface-active material capable of forming vapor-securing foams and films on low-flashpoint flammable fuels. Consisting of proprietary perfluorocarbon compounds mixed with a proprietary water-soluble thickener of the ethylene oxide polymer type, the material has been developed with a view toward combining it with concomitant discharge of potassium bicarbonate dry chemical devices in the larger sizes. Tests indicate that the new material (called Light Water) can be economically employed in a pound-for-pound ratio with dry chemical devices to result in a permanent flame extinguishment of low-flashpoint flammable liquids of the gasoline type, with no sacrifice in efficiency of the present superior dry chemicals.

When the new Light Water agent is properly employed in correctly designed dual-discharge twinned one-man equipment, a completely vaporproof covering is attained on the fuel similar to the action of the present protein type air foam, but very superior to this agent because of its complete compatibility with dry chemical material and its approximately 1200-percent relative superiority on a weight basis.

Degradation of Light Water due to aging effects results in a vapor-securing water film which retains its properties for long periods of time on the fuel. Heat exposure or flame attack results in reformation of the film.

Fully satisfactory twinned equipment has been developed for use of the new Light Water agent (7), and specifications have been prepared for procurement of the concentrated agent mixture (8) to be employed in the equipment by suitable dilution of the commercially obtained liquid.

RECOMMENDATIONS

Field Applications of Light Water Systems

A sufficiently large amount of evidence has been gathered in the research program described here to indicate that these perfluorocarbon surfactants possess characteristics not obtainable with other materials for use in fire-fighting operations where flammable-vapor efflux must be prevented or where obstacles prevent the fire fighter from fully extinguishing a fuel surface practically simultaneously. These functions are very often encountered in aircraft-crash fire-fighting situations, where foam is considered to be the primary extinguishant principally because of its permanency of fuel-vapor control.

The system advanced by this report, i.e., where fast flame extinction is achieved through the use of potassium bicarbonate followed immediately with Light Water foam discharge on the surface, promises a capability of excellent and efficient performance in aircraft-crash fire-fighting operations.

The employment of existing 400-lb and 150-lb dry chemical units with twinned Light Water units needs immediate field evaluation. Fire-fighting situations containing "mixed-class" hazards of the A and B type should be readily controllable with the twinned-agent system, and using agencies should also explore these possibilities.

Future Research in Synthetic Film-Forming Surfactants for Fire-Fighting Purposes

The employment of fluorocarbon surfactants as fire-fighting foams reported here constitutes an important development from the point of view of improvement of our presently available foam-forming materials. Sufficient evidence has been accumulated to show that these new materials may be used with various synthetic bubble-strengthening agents to develop fully practical and efficient air foams for Class B fire-fighting purposes. The employment of synthetic, specific compounds of predictable properties for foam-forming solutions and concentrates would considerably ameliorate the present problem of stability of such concentrates, where hydrolyzed protein mixtures of uncertain nature and composition defy accurate specification or control.

The film-forming characteristic of the fluorocarbon surfactants, when employed for fighting fires in hydrocarbon fuels, is an important and valuable co-property of these foams. The film pressure, or spreading power, of these agents needs further study and definition, as does the composition and character of the film. It is highly probable that since this is a surface-force mechanism, the properties of this surface film will vary widely with chemical and physical characteristics of the substrate liquid and the "condition" of the interface. Temperature effects on the film are also important and need further study.

Research and experimentation will be devoted in the near future to the above phases of this new departure in fire-extinguishment systems by the fire research staff at NRL, within existing limitations of time, finances, and capability.

ACKNOWLEDGMENTS

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