

Fuel Neutralization to Prevent Flashback on Aircraft Fires

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burning JP-4 fuel spilled from an aircraft. Present methods of extinguishing aircraft fuel fires use Aqueous Film-Forming Foam (AFFF). The AFFF is primarily a two-dimensional agent, because it forms a water film on the surface of the JP-4. When the fuel's surface is not flat, such as when the fuel is spilling or running on the terrain, the protective water film/foam blanket is not formed or is broken. Further, when the fuel pours from under the edges of the AFFF blanket or splits the AFFF film/foam blanket, reignition can occur. The objective of the Fuel Neutralization Program is to find a method or additive which will neutralize the fuel and prevent it from igniting. Since AFFF is widely used by the Air Force, the most desirable method would be used in conjunction with the AFFF. The objective of this Phase I study is to						
determine the most feasible co	determine the most feasible concepts for fuel neutralization. The most promising concepts					
include fuel thickening and neutralization by: emulsification with water and/or HALON;						
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use of chemical kinetic modifying additives. During the Phase II Program, these concepts will be experimentally developed, with the most promising concept tested in a full-scale aircraft fire.

PREFACE

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This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this effort was to study concepts which are the most feasible for fuel neutralization to prevent flashback on aircraft fires. This report discusses methods which will neutralize burning JP-4 fuel spilled from an aircraft.

B. BACKGROUND

Present methods of extinguishing aircraft fuel fires use Aqueous Film-Forming Foam (AFFF). This compound belongs to a class known as perfluorocarbon surfactants, with substituted polar radical end structures to render them partially soluble in both hydrocarbons and water, and capable of the Langmuir orientation at the interface. These compounds are highly surface-active in both water and organic liquids, lowering the surface tension of water about 80 percent and JP-4 36 percent.

By using these AFFF compounds, it is possible to form a foam having two desirable properties. First, the foam can be designed with respect to its ability to spread rapidly over a JP-4 surface, protecting the surface from heat and enabling resealing of breaks; second, with the foam floating on the surface of the JP-4, the water film drains from the bubble, orienting the surfactant solution to yield a film of water floating on the JP-4. The water film floats on the top surface of the JP-4 due to the surface forces of the oriented surfactant on the "skin" of JP-4.

The floating film of surfactant solution vapor proofs a JP-4 surface, even after the foam is gone. Figure 1 shows the suppression of fuel vaporization with AFFF ("Light Water") for JP-4 and gasoline. For a liquid fuel to burn, vaporization is necessary, since combustion only occurs in the vapor phase. Further, it is necessary that the fuel/air ratio be above the "lower explosive limit." If the vaporization rate can be reduced, the time required to reach the combustion limit will be extended, giving the firefighters valuable seconds to extinguish the fire and/or blanket the fuel pool surface. Once combustion occurs, the slower the fuel vaporizes, the easier it is to extinguish the fire.

While AFFF is extremely efficient in extinguishing an aircraft fuel fire, the foam is primarily two-dimensional because it forms a water film on the surface of the JP-4.

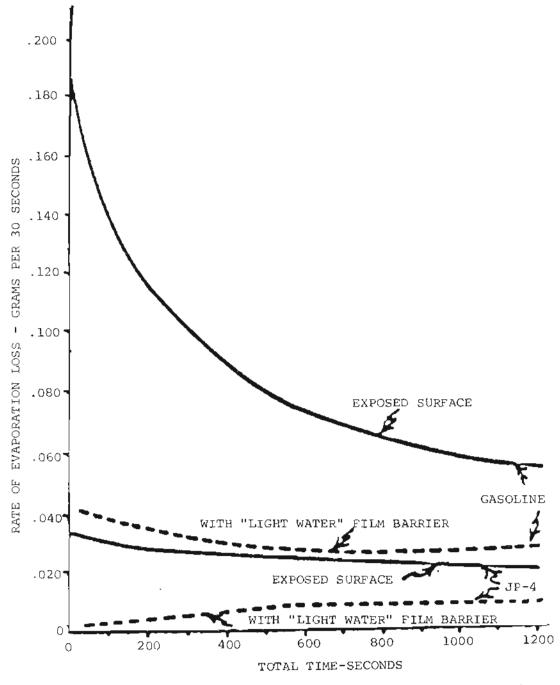


FIGURE 1. Suppression of Fuel Vaporization with AFFF Foam (Light Water).

When the fuel surface is not flat, such as, when the fuel is spilling or running on the terrain, the protective water film/ foam blanket is not formed or is broken. Further, when the fuel pours from under the edges of the AFFF blanket or splits the AFFF film/foam blanket, reignition can occur.

C. SCOPE

The objective of the Fuel Neutralization Program is to find a method or additive which will neutralize the unburned JP-4 fuel, during a fire, to prevent it from reigniting. Since AFFF is widely used by the Air Force, the most desirable method would be used in conjunction with the AFFF. The problem with extinguishing aircraft fires is primarily that of getting a limited quantity of extinguishant to the fire site in the minimum time. Since the amount of extinguishant that can be transported to the fire site is fixed by the number and capacity of the fire vehicles, any additive or method must be more efficient, on a weight basis than AFFF.

Water would be one of the most efficient materials for extinguishing fires in flammable fuels, except for its disparity in density which causes it to sink below the burning surface of JP-4. From Figure 1, it can be seen how the water film formed by AFFF can reduce the vaporization of JP-4 from If JP-4 could be emulsified with water, the fuel surface. several useful conditions could occur: 1) If a JP-4 inwater emulsion is formed, vaporization of the JP-4 fuel droplets would be reduced by the water film around the droplet; 2) The emulsion would result in the reduction of vaporization from the fuel pool and also stabilize the fuel spill so it could be covered with the AFFF; and 3) The formation of fine droplets causes the JP-4-in-water emulsion to float in the JP-4 fuel for longer periods of time before settling. emulsions would be stable and JP-4-in-water droplets could float at the JP-4 surface, forming a fuel-neutralizing barrier.

The JP-4-in-water emulsifier can be added to the water either by premixing or on-line adding to the AFFF. The emulsifier will drain with the water from the foam, forming an emulsion on/in the JP-4 fuel surface. The advantage of such a system would be the small amount, perhaps a few percent by volume, of emulsifier required with the water. Emulsion formation usually requires mixing energy; however, using technology developed to disperse oil spills at sea, it was found that emulsifiers can be self-mixing (Section IV). Finding a suitable self-mixing emulsifier to form a JP-4-in-water emulsion is an experimental process which will be conducted in a Phase II Program.

Halon materials are extremely efficient at extinguishing fires and flame inhibition. Fiala (Reference 6) showed results

that halon added to AFFF enhances the foam efficiency. It is also possible to form halon/water emulsions which can be dispersed with the AFFF. The halon/water emulsion will drain from the foam bubbles and form a halon/water emulsion with the JP-4 fuel surface. The halon/water/JP-4 emulsion will inert the fuel surface and form an inert thickened layer in the fuel. Other chemical kinetic modifiers are more than an order of magnitude more effective at flame inhibition than the halons. These modifiers are discussed in Sections VI and VII. Most of these modifiers have not been used as practical fire extinguishants, but their outstanding performance merits further evaluation.

As discussed in Section III, evaporation rate is considerably reduced and flame spread rates are 60 to 150 times lower for thickened JP-4 compared to liquid JP-4. Thickening the JP-4 fuel would increase the time before the vapors would reach their lower explosive limit. thickening the fuel would stabilize the spill and make it easier to cover with an AFFF blanket. Considerable work conducted on fuel thickening, using gelling agents and emulsifiers, is reviewed in Section III. Most of the work was related to the FAA and Army programs for safety fuel. The Army concluded that fuel gelling was not compatible with aircraft fuel systems, because extremely high mixing energy was required to form the gel. Since it would not be possible to vigorously mix the gelling agent into an open JP-4 fuel pool, it was felt that self-mixing emulsifiers would be more applicable for fuel neutralization.

Another method of thickening JP-4 fuel would utilize solid absorbents and solid inorganic materials as discussed in Section V. Materials, such as silica, clays, or vermiculite can be slurried with water used in the AFFF. The material will drain into the fuel surface and gel the JP-4 fuel surface. Some of these materials absorb and swell upon contact with JP-4, forming a fuel gel. These absorbents can be saturated with fire retardant materials, such as halon 2402, which will dissolve in the JP-4 and absorb the JP-4 forming a fuel gel.

While these materials are effective gelling materials, the question to be addressed is whether more effective results for fuel neutralization will result by some of the other methods outlined. This will require experimental evaluation in Phase II.

The objective of this study is to determine which concepts are the most feasible for fuel neutralization. The most promising concepts include fuel thickening and neutralization by: emulsification with water and/or halon; gelling with

gelling agents, solid absorbents and solid inorganic compounds; and use of chemical kinetic modifying additives. During the Phase II Program, these concepts will be experimentally developed, and the most promising concepts will be tested in a large-scale aircraft fire.

SECTION II

AQUEOUS FILM FORMING FOAM (AFFF)

A. BACKGROUND

A 1972 Advisory Group for Aerospace Research & Development (AGARD) paper by Dr. Richard Tuve, "Surface Active Considerations in Fuel Fires," (Reference 1) states that water, our most plentiful, efficient and useful agent, would be our best material for extinguishing fires in flammable fuels were it not for its greater density which causes it to sink below the burning fuel surface. Under certain circumstances, a water spray may be used to extinguish certain flammable liquids, even those which are water-miscible. Nash and Rashbash (Reference 2), noted that water sprays with droplet sizes from 0.28 to 0.49 mm were capable of quick extinguishment of kerosene fires.

The use of foams with gases held in the water-solids suspension or solution was an obvious and early (Reference 3) solution to the water-fuel density problem. The first practical chemical powder foam fuel firefighting agents utilizing the bicarbonate effervescing reaction, were difficult to employ and fortunately, mechanically formed foams were invented in the 1930s and were quickly and simply put into action.

In 1941, the U.S. Navy began an investigation to learn more about the basic action of foams on fuel fires. At the inception of this work, the popular explanation of a fuel fire extinguishment was that "the fire was smothered and access to air or oxygen was cut off by the foam." This would suggest that foam volume was very important to the extinguishment mechanism.

According to Tuve (Reference 1), an astonishingly simple explanation of the extinguishment mechanism was developed by the Navy team, employing fuels of all types from naphthas to bunker fuels and firefighting foams of all types, chemical and mechanical. Tuve states that it was the water in the foam which was needed for extinguishing the fire. The smothering action was a secondary and preventative action only (Reference 4). This meant that criticality existed in the number of gallons or liters of water in the foam applied to each square foot or square meter of burning fuel surface.

Tuve (Reference 1) states that dry chemical agents are the safest and most effective fuel flame-extinguishing agents on a weight basis. Their main drawback is their lack of reflash protection. The need for a vapor-sealing blanket of heat-dissipating foam will perhaps always continue to exist. When one compares the weight of foaming solutions to create this blanket, it is found that even the most effective protein foams require up to 3 lbs. / ft² (14.8 kg/m²) of water solution to accomplish extinguishment and vapor-sealing of a gasoline surface. Contrast this figure with the only 0.5 lbs./ft² of potassium bicarbonate dry chemical needed for flame extinction. Quite obviously, one can see why the Navy team began a search in 1960 for a new and better foaming material than the protein developed in the 1930s.

Two years of careful examination and testing were conducted, surveying all types of organic compounds having characteristics and structures which enabled them to lower the surface tension of water and form foams. Only one type of compound showed fire extinguishment efficiency superior to the protein and these new materials were expensive and were available in only small quantities. These effective materials were synthetic highly-fluorinated long chain carboxylic acid and sulforic acid derivatives. The following compound is a typical one: perfluoroalkylsulfonamide-N-alky-trimethylammonium iodide.

When these fluorinated foam-forming compounds were formulated with other synthetic high-molecular-weight materials to render the foam bubble wall more resistant to rupture from mechanical or heat action and the resultant mixture was foamed with air, Tuve states that a very interesting and new surface phenomenon on fuel surfaces was seen. As the water solution of the fluorinated compounds drained slowly away from a foam volume which had been placed on an open gasoline surface, it spread quickly over the surface of the fuel without sinking, as any water solution would normally be expected to do.

This was the first instance of water solutions of a surface active nature being capable of floating in significant thickness on a gasoline fuel, according to Tuve. When a burning match was passed over this water-layer-protected fuel surface, no ignition of vapors took place. After careful experimentation, it was found that the water solutions of these organic fluorocompounds could be introduced at the immediate surface of hydrocarbon fuels. Such manipulation produced floating surface layers of water up to 10 microns in thickness on the fuel before pendant drop formation occurred.

The surface tension of these solutions varies from 15 to 17 dynes per centimeter. This value is extremely low when one realizes that ordinary protein foam solutions lower the surface tension of water from 72 dynes per centimeter to only about 45 dynes per centimeter. The interfacial tension between various pairs of the new fluorocarbon surfactant solutions and various fuels vary from 0.5 to 6.3 dynes per centimeter.

The water solution film formed on flammable fuel surfaces by these new surfactants is not a completely impermeable film. On cyclohexane, for instance, measurements of the vapor concentration above a surface film show that cyclohexane vapors drop immediately to 2 to 5 percent of that exhibited by open unfilmed cyclohexane surfaces. In other words, this fuel will demonstrate vapor space mixtures of 0.2 to 0.5 of its lower limit of vapor flammability when covered with floating fluorocarbon surfactant films. No ignition of cyclohexane vapors in these ranges of concentration is possible.

This process can be utilized for fuel neutralization. If an emulsifier is added to the AFFF, the surface layer will emulsify with the JP-4 layer. If a hydrocarbon-in-water emulsifier is used, each JP-4 droplet will be encapsulated in a water film reducing the vapor concentration as occurred with the cyclohexane example. The JP-4/water emulsion may also thicken the fuel surface, reducing evaporation from the fuel pool.

The actual firefighting capabilities of air foams generated from AFFF surfactant solutions was found to be phenomenally efficient when compared to the old protein type foam solutions in laboratory tests. Using a measurement standard of volume of water solution required for extinguishment of a unit area of burning fuel, the AFFF fluorocarbon surface active agent materials required only 0.04 gal/ft² (or 1.6 liters/m², which is 0.33 lbs/ft², or 1.61 kg/m²); whereas the protein solutions require 0.23 gal/ft² (or 9.3 liters/m², which is 1.9 lbs/ft², or 9.3 kg/m²).

Going back to the weight per square foot figure of 0.5 pound of potassium bicarbonate needed to extinguish fuel flames, a similar figure of 0.4 pound per square foot of solution of the new fluorocarbon formulation was found to be sufficient to achieve permanent sealing and vapor protection of the fuel surface. These very nearly identical figures of efficiency were demonstrated time after time in large-scale fire tests, according to Tuve (Reference 1). From these results, an interesting concept arose; that being a "twinned" application

system whereby one firefighter can accomplish the work of two nozzle operators, applying potassium dry chemical and the fluorocarbon foaming solution,, simultaneously. The new foam was named "Light Water" by Tuve and Jablonski (Reference 5).

The simple substitution of the "Light Water" fluoro-carbon formulation's for the protein foam-forming concentrates has demonstrated a three-to-five times superiority in many tests and fuel fire conditions. The "twinned agent" application concept claims 15 times the efficiency of protein foam agents.

B. QUASI-TWO-DIMENSIONAL FIRES

For the extinguishment of quasi-two-dimensional fires, namely pool fires following a crash in the presence of reignition sources, extinguishing foams are the only adequate extinguishing agent today. The extinguishing mechanism of foams is mainly due to the separation of the reactive species fuel and oxygen by a closed foam blanket. Furthermore, the water released by the foam cools the fuel surface. The water vapor which is formed at the interface between the foam and the flame may also contribute to the extinguishment via a change in the fuel/oxygen ratio.

Extinguishing foams are described mostly by the foam-forming agent used, the mixing ratio of foam-forming agent and water, the expansion ratio and the drainage time (25 or 50 percent). Four different types of foams are in use today: protein foam, fluoroprotein foam, synthetic foam and aqueous film-forming foam (AFFF) depending on the nature of the foam-forming agent. All foams can be employed as low expansion foams; AFFF and synthetic as medium expansion and high expansion foams too. With the expansion ratio of a foam, the ratio of air to water is denoted. For the extinguishment of large fuel spill fires only low expansion foams are used. The tests described by Fiala (Reference 6) if not mentioned specifically - are all carried out with low expansion foams.

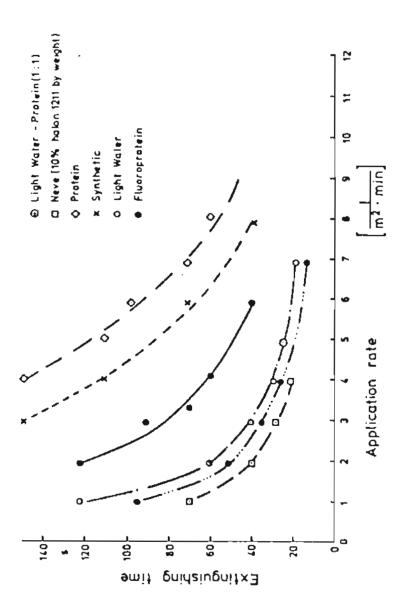
The extinguishing efficiency of the foams depends on the type of foam-forming agents. Comparing the relevant foams to a preselected application rate, the shortest extinguishing times were achieved with AFFF like Light Water. Fluoroprotein foam follows in efficiency. Synthetic foam proved to be less effective than fluoroprotein foam and Light Water. The worst results were obtained with protein foam. For fundamental studies, Fiala (Reference 6) used a foam from a mixture of Light Water and protein foaming agent.

Although this foam showed best results, it is believed to be of no importance for practical use. The high efficiency is only achieved under very specific conditions and Fiala indicates it is doubtful, if these conditions can always be obtained. Figure 2 shows Fiala's test results for a 0.1 m², pan and Figure 3 for the 200 m² pool. In these figures the extinguishing time is plotted against the application rate and as shown, the extinguishing time depends on the application rate of the foam. With increasing application rates the time needed for extinguishment decreases. Application rates greater than 7 to 10 1/m² min (depending on the type of foam forming agent) lead to no further decrease in extinguishing time, since the amount of foam applied per unit of time cannot spread in this time; hence an unnecessarily thick layer of foam is produced.

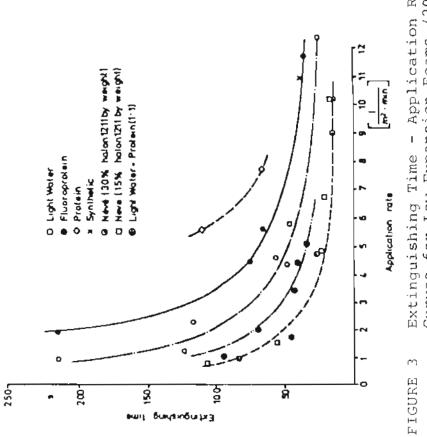
On the other hand, no extinguishment is achieved, if the application rate subsides below a critical value called the critical application rate. The critical application rate is different for each type of foam. An extrapolation of the curves in Figure 1 gives the following critical application rates for the four types of foams: Light Water $0.8\ 1/m^2 \cdot min$, fluoroprotein foam $1.3\ 1/m^2 \cdot min$, synthetic foam $2.6\ 1/m^2 \cdot min$ and protein foam about $4\ 1/m^2 \cdot min$. The critical application rate depends mainly on the foam-forming agent. The size of the burning fuel surface seems to be (if there is a dependence) of minor influence on the critical application rate, at least between burning areas from $0.1\ m^2$ to $500\ m^2$.

The critical application rate is of great practical importance, since the number and the capacity of crash tenders available are fixed and, with this, the maximum possible application rate. Under these conditions, the size of the fire which can be extinguished depends only on the foam-forming agent used. For example, Table 1 shows the results of tests in which the maximum size of burning fuel surface was evaluated which could be extinguished with a 200 1/min. foam nozzle.

Normally, the foam is applied locally to the fuel surface by hand branch pipes or monitors. From these points the foam must be spread under the action of the gravity force to form a closed foam blanket. Figure 4 shows the spreading behavior of the foams. In the figure, the flow-time is plotted versus the distance the foam has propagated during that time. The figure shows that Light Water, an AFFF foam, spreads most rapidly, followed by fluoroprotein foam and synthetic foam. Protein foam exhibits the worst spreading behavior.



Extinguishing Time - Application Rate Curves for Low-Expansion Foams (0,1 m² Pan). FIGURE 2



RE 3 Extinguishing Time - Application Rate Curves for Low-Expansion Foams (200 m² Pool)

TABLE I

MAXIMUM SIZE OF BURNING FUEL AREA WHICH COULD BE EXTINGUISHED WITH A 200 L/MIN. FOAM NOZZLE.

Foam forming area application rate agent 1/m² · min Light Water 250 0,8 Fluoroprotein 150 1,33 Synthetic 75 2,66 Protein 50 4,0		
	application rate 1/m ² · min	0,8 1,33 2,66
Foam forming agent Light Water Fluoroprotein Synthetic	Area	250 150 75 50
	Foam forming agent	Light Water Fluoroprotein Synthetic Protein

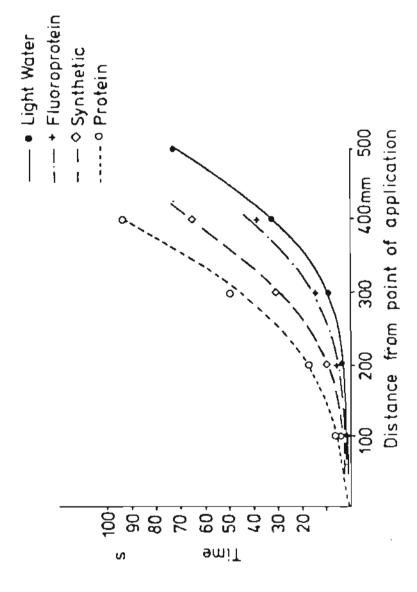


FIGURE 4 Flow Characteristics of Foams on Fuel

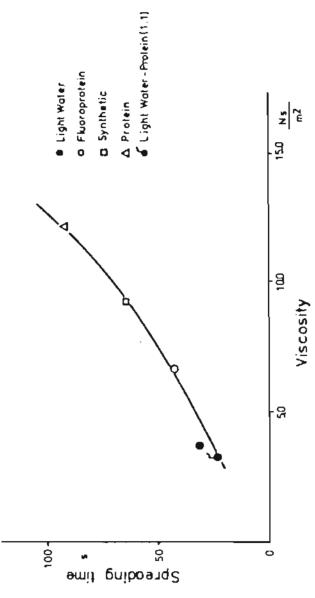
Foams in general are media of high viscosity; therefore, the spreading of the foam is governed by the foam viscosity. In Figure 5, the viscosity of the foam is plotted versus the time the foam needs to propagate a given distance. As could be expected, the foam with the lowest viscosity (Light Water) has the highest spreading velocity and vice versa (Protein foam). That means that Light Water will form a closed foam blanket in the shortest time, while protein foam needs the longest time to achieve the same results. As also can be seen in this figure, the different foaming agents lead to foams with different viscosities.

Since viscosities play a major role in the spreading of foams, one should expect, that there is a correlation between the viscosity of the foam and extinguishing time. In Figure 6 the extinguishing time is plotted against the viscosity of the foams used. The lower the viscosity of the foam, the higher its spreading velocity. Therefore, less time is needed to form a closed foam blanket (a requirement for the extinguishment).

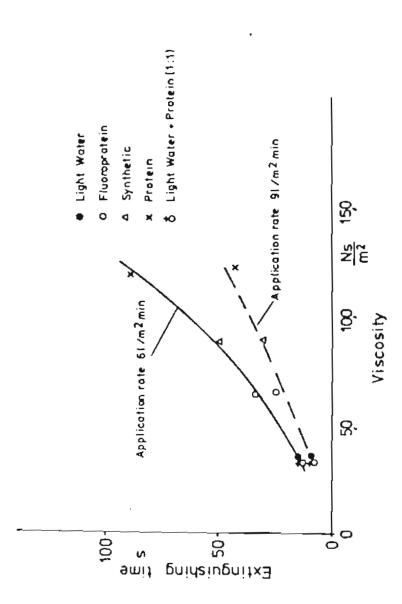
Besides the influence of the foam-forming agent on the foam viscosity, the viscosity (within certain limits) also depends on the energy used to form the foam from the water foaming-agent solution. The more energy put into the foam, the stiffer the foam becomes, increasing its viscosity. Beyond a certain amount of energy input, the viscosity of the foam remains constant. In Figure 7 the number of sieves in the mixing chamber is chosen as a measure for the energy The number of sieves is correlated to the energy input by the pressure loss caused by them. This foaming energy-dependence of the viscosity is reflected on the time needed for extinguishment. In Figure 8, the extinguishing time for AFFF is plotted against the viscosity of the foam. The viscosity is expressed by scale units. The time needed for extinguishment increased as more energy was used to foam the water-foaming agent solution. This energy dependence of the foam viscosity is one of the causes of different extinguishing efficiencies of foam monitors or branch pipes. Monitors and branch pipes of different manufacturers deliver foams with different viscosities depending upon the energy they impart to the foam.

It is also one of the reasons, why an AFFF has a higher extinguishing efficiency when applied with a non-air-aspirating nozzle. Other factors are discussed in detail later in this report.

The expansion ratio of the foam also influences the extinguishing efficiency of a foam. Test results, obtained



Dependence of the Spreading Time on Foam Viscosity. FIGURE 5



Influence of the Foam Viscosity on the Extinguishing Time. FIGURE 6

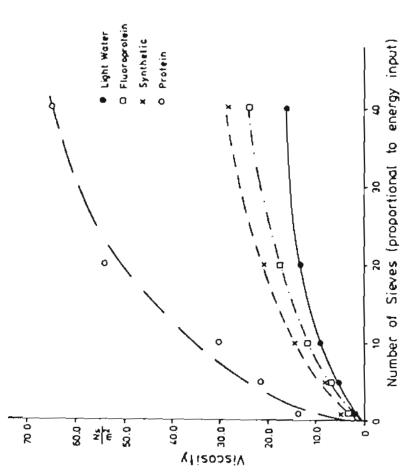
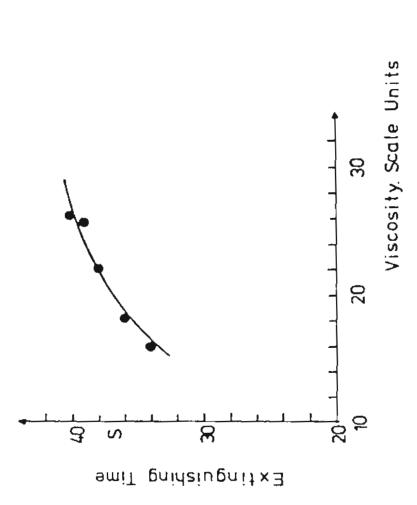


FIGURE 7 Influence of Energy Used to Produce the Foam On the Foam Viscosity.



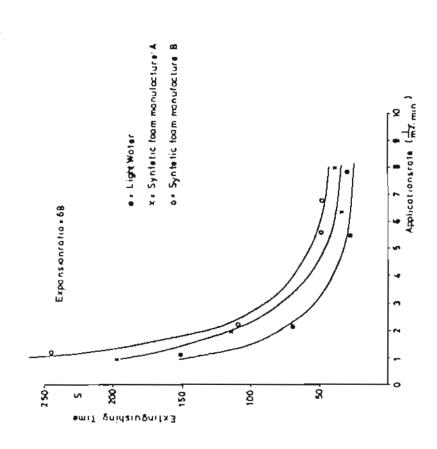
Dependence of the Extinguishing Time of AFFF on the Energy Used to Foam the Solution. ∞ FIGURE

with medium expansion foams (expansion ratio 68) on a 200 m² pool, give evidence that with these types of foams, shorter extinguishing times can be achieved (Figure 9). Although the fuel fire could be extinguished with the medium expansion foam in a shorter time, the use of medium expansion foam for postcrash firefighting cannot be recommended for two reasons. The throw range of medium expansion foam nozzles is too short (just a couple of meters). Wind velocities exceeding 6 to 8 m/sec make it impossible to cover the whole fuel surface with a foam blanket. The specific weight of the foam is too low, and as a consequence the foam is blown away by the wind. Wind velocities of this magnitude are possible at an airbase. Hence, only low-expansion foams can be used for crash firefighting. In Figure 10 the correlation between expansion ratio and extinguishing time in the range of an expansion ratio from 0.1 to 40 is shown for Light Water foam. With Light Water foams of an expansion ratio under 0.5 a fuel fire cannot be extinguished. extinguishing efficiency increases rapidly as the expansion ratio increases between 0.5 and approximately 1 to 1.5. Expansion ratios between 1.5 and 10 have minor influence on the extinguishing efficiency. With increasing expansion ratios over 10, the extinguishing time of the Light Water foam decreases. Most of the monitors and hand branch pipes for low expansion foam produce foams with expansion ratios between 4 and 8.

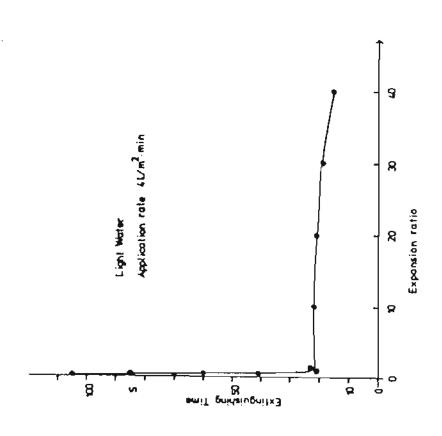
The concentration of the foam-forming agent also influences the extinguishing time. In Figure 11, the extinguishing time is plotted versus the concentration of an AFFF foam forming agent in the water-foam-forming agent solution. The extinguishing time decreases rapidly with increasing foam-forming agent concentration to a minimum value in a concentration range from 2 to 3 percent. For foamforming agent concentration from 2 to 4 percent this value is nearly independent of the concentration. This correlation is explainable, by considering that the surface tension of a water-foam-forming agent solution is a function of the concentration of the foam-forming agent. As can be seen from Figure 12, the surface tension of the solution is proportional to the extinguishing time, a result which could be expected because of the correlation between surface tension - foam viscosity spreading velocity and extinguishing time.

The concentration recommended by the manufacturer for this foam-forming agent is 3 percent. As shown in the figures, the concentration of the foam-forming agent can vary between 2 to at least 5 percent, without changing the extinguishing efficiency of the foam.

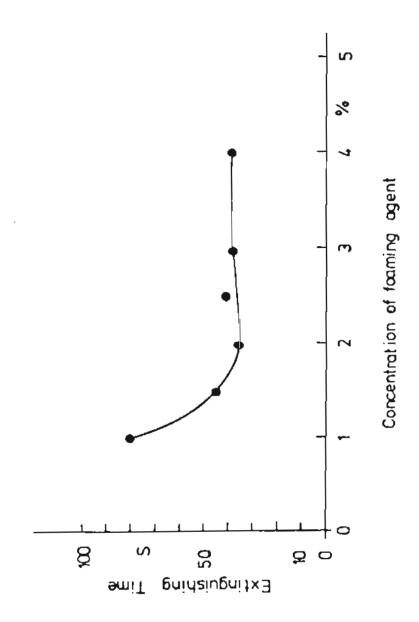
From the dependence of the extinguishing efficiency on the concentration of the foam-forming agent in the water-foam-



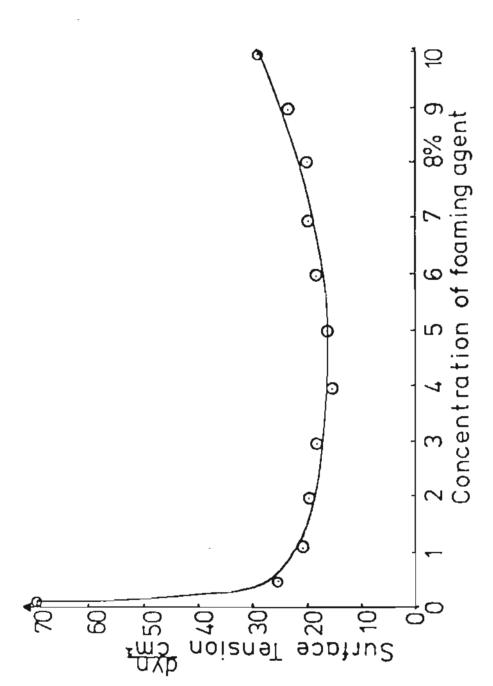
Extinguishing Efficiency of Foams with Medium Expansion Ratio . FIGURE 9



Influence of the Expansion Ratio of the Foam on the Extinguishing Time. FIGURE 10



Correlation Between Extinguishing Time and the Concentration of Foaming Agent (AFFF). FIGURE 11



Influence of the Concentration of Foaming Agent on the Surface Tension of the Solution. FIGURE 12

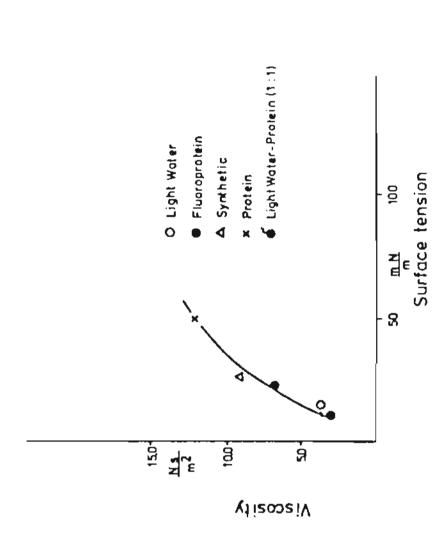
forming agent solution the requirements on the accuracy and reliability of mixing units can be determined.

The foaming agents differ in their ability to reduce the surface tension of the water-foaming agent solution. Surface tension reduction is a requirement for the formation of foam. With the exception of the Light Water protein mixture, Light Water shows the highest reduction of the surface tension, followed by fluoroprotein and synthetic foam agents. Protein-based foaming agents are less effective. The surface tension of the water-foaming agent solution influences the viscosity of the foams formed from the solution; from solutions with low surface tensions, low-viscosity foams are produced. The higher the surface tension, the higher the foam viscosity becomes. The correlation between surface tension of the solution and the foam viscosity is shown in Figure 13.

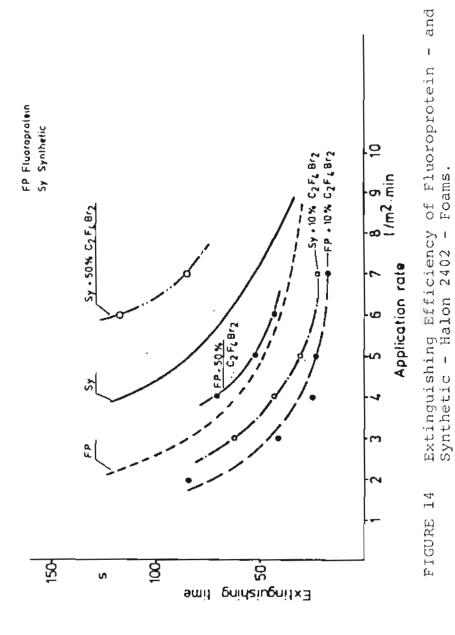
From Fiala's (Reference 6) test results one can assume, that the extinguishing efficiency of foams is proportional to the velocity with which a closed foam layer is achieved on the fuel surface. This velocity is a function of the foam viscosity. The foam viscosity itself depends on the surface tension of the water-foaming agent solution and can be influenced to a certain extent by the energy used to foam the water. From the correlations between surface-tension, foam viscosity and extinguishing time one may derive the conclusion, that the extinguishing efficiency of the presently used foams is near optimum.

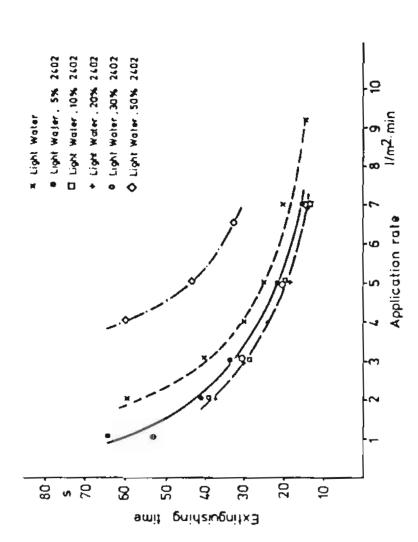
C. EXTINGUISHING EFFICIENCY OF HALON FOAMS

The extinguishing efficiency of water-air foams can be increased by an addition of halons to the water. When a liquid halon such as halon 1202, 2402 and halon 1211 (although the boiling point of 1211 is -4C) is mixed with the waterfoaming agent solution, and the solution is foamed in the usual manner with air, an increase in extinguishing efficiency can be obtained in a limited range of halon concentration. Fiala's (Reference 6) results of extinguishing tests with synthetic foaming agent and fluoroprotein foaming agent are shown in Figure 14 and in Figure 15 for Light Water foaming agent. The sequence of effectiveness of halon foams is again Light Water, fluoroprotein foam and synthetic foam. Figure 16 the extinguishing efficiency of Light Water-halon 1211 foams with various halon concentrations in the solution is shown. The extinguishing time decreases with increasing halon concentration, with a minimum between 10 to 30 percent of halon in the solution. Halon concentrations over 30 percent, increase extinguishing times again and halon foams with a concentration of 50 percent halon and more in the

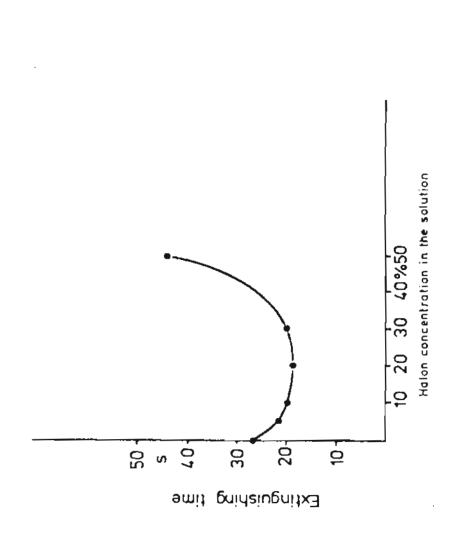


Dependence of Foam Viscosity on the Surface Tension of the Solution. FIGURE 13





Extinguishing Efficiency of Light Water - Water Air Halon Foam. FIGURE 15



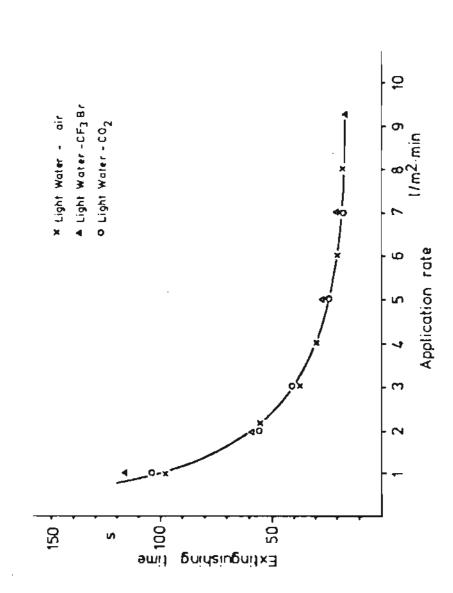
Influence of the Halon 1211 Concentration on the Extinguishing Time of a Light Water Foam. FIGURE 16

solution have no extinguishing effect at all, since the specific weight of the foam is greater than that of the fuel. As a consequence, the foam submerges under the fuel surface. Fiala showed that the extinguishing efficiencies of halon 1202 and 2402 Light-Water foams are of the same order.

Fiala states that from the point of view of extinguishing efficiencies, only Light-Water-halon foams can be recommended for practical use, and, from the toxicological point of view, halon 1211 should be preferred. The halon 1211-Light-Water foam is known under the name Neve. The extinguishing efficiency of Neve with respect to the other foams is shown in Figures 2 and 3. Although the extinguishing mechanism of the halon foams is not yet completely understood, it can be assumed that a chemical interaction of the halons with the burning reactions may be of importance. Halons are known as very effective inhibitors of the hydrocarbon-oxygen reaction. If this is the main reason for the increase in efficiency, Neve and the halon 1202 and 2402-Light-Water foams would be the halon foams with the highest efficiency that could be expected. It might be possible to generate more efficient foams using superkinetic modifiers discussed in later sections.

For the formation of foam from the foam-forming agent water solution usually air is used. The use of other gaseous medias instead of air were under discussion in order to increase the extinguishing efficiency. From Fiala's tests, the nature of the gas contained in the foam bubbles has no influence on the extinguishing efficiency. Figure 17 shows the test results with Light Water foams. The water-Light Water solution was foamed with gaseous halon 1301 and carbon dioxide, respectively. For comparison, the results for Light Water-air foam are also plotted. The limited effect of the gas may be attributed to the fact that the halon concentration, in those foams containing a liquid halon, is four times greater than in the results described in Figure 17. To increase throw range, it was proposed that the foaming of the solution should take place on the fuel surface, under the influence of the heat produced by the flame. By choosing halons with adequate boiling points, this is possible; however, Fiala found all tested mixtures were less effective than Neve.

Attallah and Buccigross (Reference 7) experimented with halon foams for the development of halogenated hydrocarbon foam extinguishants. Tests were conducted using halon 1211 foam and results showed that it is possible to foam halon liquids (and mixtures thereof) with commercially available surfactants. A mixture of halon 1301 and nitrogen is a suitable propellant gas and the addition of small amounts of fumed silica improves the quality of certain foam formulations. Results showed that halon foams were able to suppress JP-4



Extinguishing Time/Application Rate Curve for Light-Water - Water - Air, ${\rm CF_3Br}$ and ${\rm CO_2}$ - Foams. FIGURE 17

pool fires seven times faster than bromochloromethane with approximately seven times less quantity of extinguisher.

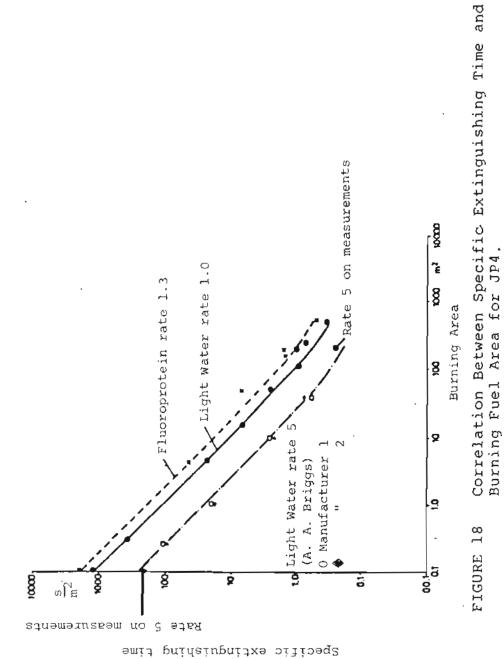
Their work did not note the sinking of the foam on the surface of the pool fire, which was reported by Fiala (Reference 6). It would be interesting to repeat these experiments since the sinking foam limited the effective halon concentration to 50 percent in Fiala's experiments, while Attallah and Buccigross used pure halon foam and still found extinguishment for JP-4 pool fires. Also, due to the high effectiveness of the halon materials they represent a likely choice for neutralizing the JP-4 fuel, when used on combination with AFFF. Further, halons are known to hydrolyze in the presence of moisture and water. Any system must consider the possibility of stability and corrosion.

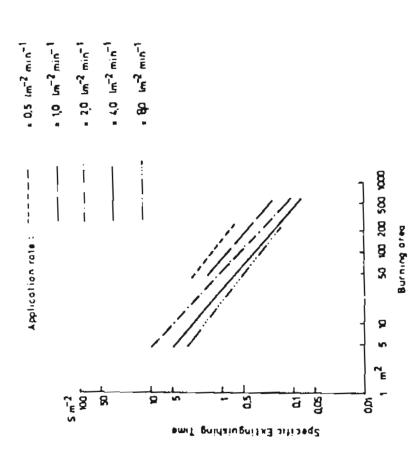
D. INFLUENCE OF THE SIZE OF THE BURNING FUEL SURFACE ON THE EXTINGUISHING TIME

The extinguishing tests, described by Fiala (Reference 6) were carried out on fuel surfaces ranging from 0.1 m² to 500 m². If one relates the time needed to extinguish the burning fuel surface to the size of the surface, that is, the specific extinguishing time or the time needed to extinguish a unit of burning area (sec $/m^2$), one gets a correlation between the specific extinguishing time and the size of the burning fuel area for a given application rate. This is shown in Figure 18 for Light Water (application rate 1 and 5 $L/m^2 \cdot min$) and for fluoroprotein foam (application rate 1.3 $L/m^2 \cdot min$). Results in the figure are plotted on a logarithmical scale.

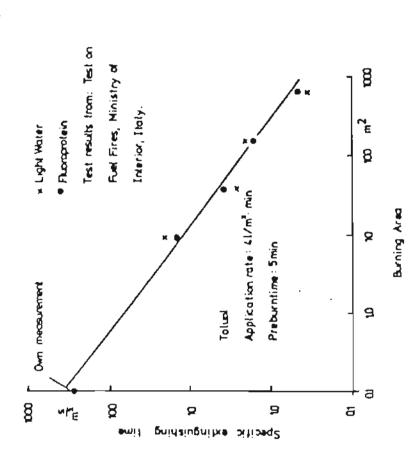
In the range of burning areas between 0.1 m² and 100-200 m², the specific extinguishment time decreases linearly with the burning rate when plotted on a log scale. In Figure 19, the correlation between specific extinguishing time and burning fuel area for different application rates of AFFF foam is shown. Tests carried out with toluene lead to a similar correlation in Figure 20.

For larger burning areas the linear correlation when plotted on a log scale, must change, otherwise the extinguishing time would approach zero at very large burning areas. Fiala states, that in the literature only four tests on larger areas than $500~\text{m}^2$ were found on which results could be utilized. Unfortunately, the burning areas differed only by a factor of four and five, hence a reliable extrapolation to larger fire surfaces is not presently possible. Fiala states that it is intended to carry out extinguishing tests on 5000~and $10,000~\text{m}^2$ pools in order to complete the correlation.





Correlation Between Specific Extinguishing Time and Burning Fuel Area for Different Application Rates of AFFF Foam. FIGURE 19



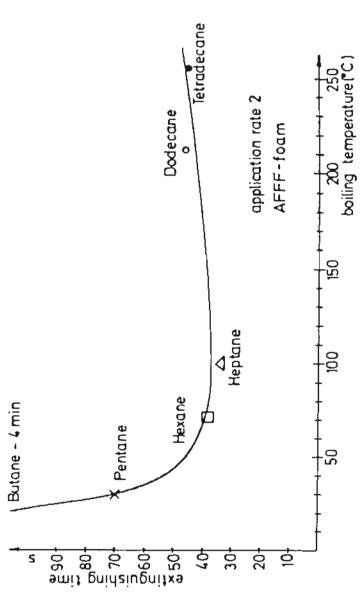
Correlation Between Specific Extinguishing Time and Burning Fuel Area for Toluene. FIGURE 20

E. INFLUENCE OF THE FUEL ON THE EXTINGUISHING EFFICIENCY OF FOAMS

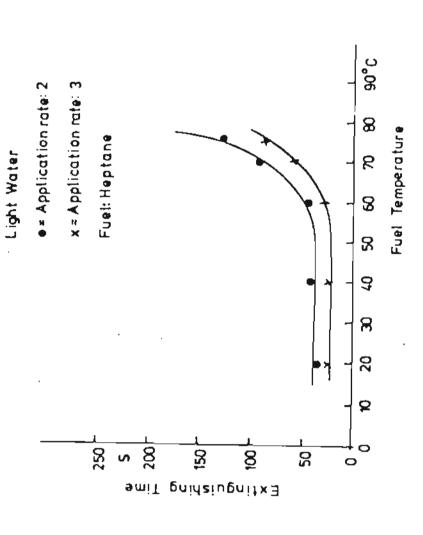
The fuel which is to be extinguished has also an influence on the extinguishing time. From the test data presented by Fiala, one can conclude that the boiling temperature and the viscosity of the fuel influences the extinguishing time. Figure 21 shows the dependence of the extinguishing time on the boiling temperature or vapor pressure of the fuel. For these tests Butane, Pentane, Hexane, Heptane, Dodecane and Tetradecane were used as fuels. From that figure, it can be seen that the lower the boiling temperature or the higher the vapor pressure of the burning fuel, the more time is needed to extinguish the From this correlation, follows that the fuel temperature must also have an influence on the extinguishing time. It is interesting to note that the JP-4 boiling range is approximately 50-250C. Therefore, AFFF is an effective extinguishant for JP-4 fuel fires. In Figure 22 the extinguishing time is plotted against the fuel temperature before ignition. these tests Heptane was used and as expected, the extinguishing time increased with the fuel temperature.

The spreading velocity of a fluid, not only depends on the viscosity of the fluid itself, but also on the friction between the fluid and the surface on which it flows or spreads. Foams are high viscosity media, thus their viscosity is normally higher than that of the fuel which is to be extinguished. Therefore, velocity with which the foam spreads on the fuel surface, also depends on the viscosity of fuel. Due to the friction forces, secondary flows in the fuel are induced. The higher the spreading velocities resulting from the lower viscosity of the fuel, the faster the foam spreads on the surface of the fuel. In Figure 23 the extinguishing time for Diesel fuel is shown as a function of the viscosity of the fuel. The viscosity of the fuel was changed by adding different amounts of an inert fuel thickener, in this case SiO2. The maximum amount of thickener added was about 1 percent by weight.

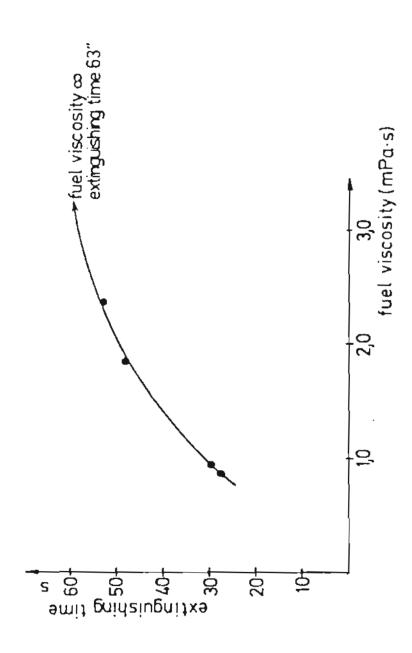
From Figure 23, it is shown that the extinguishing time increased with the viscosity of the fuel and for the solid Diesel fuel, reached a value which is nearly three times higher than that of the unthickened fuel. These results are very important to the Fuel Neutralization Program since one of the concepts being evaluated is to thicken or gel the fuel to reduce vaporization from the fuel surface. These results indicate that methods which thicken the fuel spill before the AFFF is applied may be counterproductive. Materials added to the AFFF, which gel or thicken the fuel surface, may be satisfactory since thickening would not result until



Dependence of the Extinguishing Time on the Boiling Temperature of the Fuel. FIGURE 21



Influence of the Fuel Temperature Prior Ignition on the Extinguishing Time. FIGURE 22



Dependence of the Extinguishing Time on the Viscosity of the Fuel (Diesel Fuel). FIGURE 23

after the AFFF has covered the surface.

Fiala, states that for foam, the dependence of the extinguishing time on the fuel viscosity may affect the extinguishment of thickened, gelled or antimisting fuels being proposed to enhance aircraft safety. While these fuels may reduce the initial mist fire ball, if they ignite, they may produce a pool fire which is difficult to extinguish.

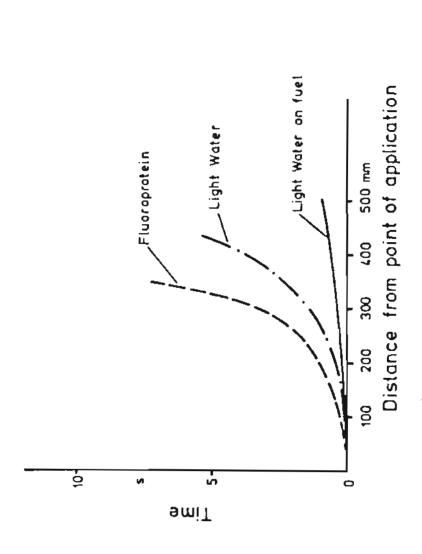
Results of experiments by Fiala (Reference 6), for fuel-soaked sand are presented in Figures 24 and 25. Fuel was spilled on sand so that it was absorbed into the sand, without forming a liquid surface, but a surface similar to a solid fuel. It was found that on such a surface, the foam spreads considerably slower on fuel soaked sand than on a liquid fuel surface as shown in Figure 24. As expected, Figure 25 shows a considerable increase in extinguishing time, with Light Water, on a fuel soaked sand surface than a liquid fuel surface.

Again, these results indicate that thickening or gelling the fuel with absorbents, prior to extinguishing the fuel with AFFF may be counterproductive. It is expected that the fuel surface will be stabilized so it would not flow from under the AFFF blanket and evaporation would be reduced, but the foam will take longer to cover the surface. If the fuel is thickened or gelled after it is covered with foam, the results will probably be more satisfactory. There are few data on these questions and, therefore, this will have to be studied in a Phase II program.

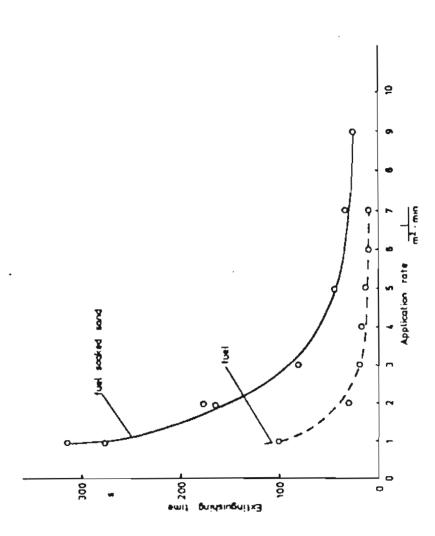
F. AFFF EXTINGUISHING TACTICS

As shown in Figure 26, the distance the foam has to spread under gravity forces influences the extinguishing time. In this figure, the extinguishing time versus foam application rate is shown for a circular and a rectangular pan. The foam has to spread on the fuel surface in order to form a closed foam blanket. Fiala also states the results of tests conducted with Light Water on a 50 m² pool fire. Four minutes was necessary to extinguish the fire when the foam monitor turned during extinguishment without changing position. Further, the extinguishing time decreased by a factor of two, when the foam was placed on the fuel surface in the vicinity of the interface between the flame and the already extinguished fuel surface. This technique requires that the foam monitor follows the retreating flame and sweeps at the same time.

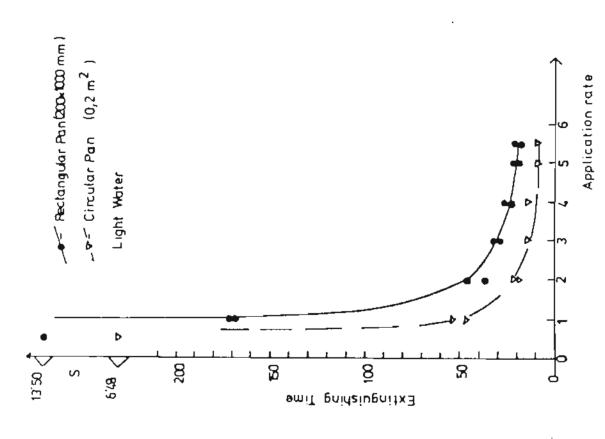
The shortest extinguishment times are achieved with a technique whereby the distance the foam has to spread under gravity forces is the shortest. Basically, that requires placement of the foam on the total fuel surface without depending on the foam to spread across the fuel surface. This requires foam monitors which have adequate throw range to reach the



Flow Characteristics of Foams on Fuel-Soaked Sand. FIGURE 24



Extinguishing Time - Application Rate Curve for Light Water for Fuel-Soaked Sand. FIGURE 25



Influence of the Geometry of the Burning Fuel Surface on the Extinguishing Time. FIGURE 26

total surface of the fuel pool.

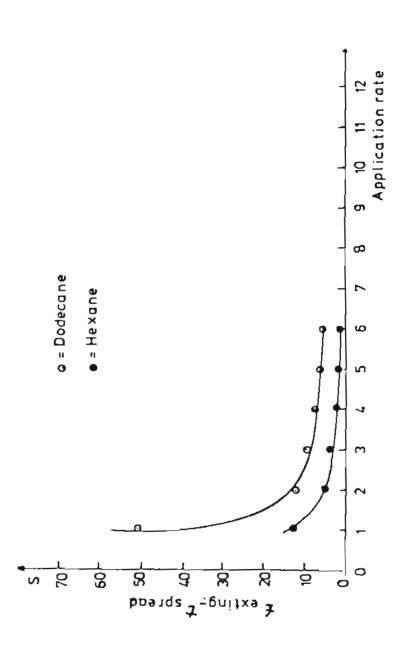
Figures 27 shows the difference of extinguishing time and spreading time of AFFF on a fuel surface for Dodecane and Hexane fuel.

Since reaching the total pool surface with foam is important to reduce extinguishing time, Fiala (Reference 6) tested air and non-air-aspirating nozzles. Water nozzles display higher throw ranges than comparable air-aspirating nozzles. Jablonski (Reference 8) of NRL in a comparative nozzle study for applying AFFF on large-scale fires found that by use of non-air-aspirating nozzles the extinguishing time could be reduced about 20 percent, under the conditions of the same application rate.

G. EXTINGUISHING EFFICIENCY OF DRY POWDER-HALON-FOAM COMBINATIONS

In a postcrash fire, quasi-two and three-dimensional fuel fires may occur and have to be extinguished. Optimum fighting of these fires is usually only possible when using a combination of three-dimensional acting agents like halons or dry powders and AFFF. Fiala (Reference 6) states that the extinguishing efficiency of halon or dry powder-foam combinations has not been sufficiently documented. Also the same is true for problems arising from the use of these combined agents. For instance, the U.S. Air Force does not use dry powder, partly because of its corrosion potential to aircraft engines and maintenance required to the jet engines after the fire is extinguished. Ideally, the fuel-neutralization additive would also give the AFFF three-dimensional extinguishing properties, and be compatible with aircraft and human requirements. Halon has these properties; however, problems of dispersion and liquid density have so far prevented its effective use on open crash fires. The Fuel Neutralization Program proposes to use halon materials with AFFF foam, as one of the possible additives.

Fiala (Reference 6) states that from the few test results that could be evaluated, one may conclude that the time for extinguishment will be decreased when using a combination of dry powder, halon and foam. The extinguishing efficiency of a combination seems to depend on the efficiency of the different agents used. The more effective both are, the shorter extinguishing time is achieved in combined use. Fiala found that the shortest extinguishing times were obtained when a halon 1211 - AFFF combination was used for extinguishment, followed by potassium sulfate - AFFF. The longest extinguishing times were needed, when the extinguishment was carried out with NaHCO₃ based powder and protein foam. The extinguishing times differed by a factor of approximately three. Fiala states



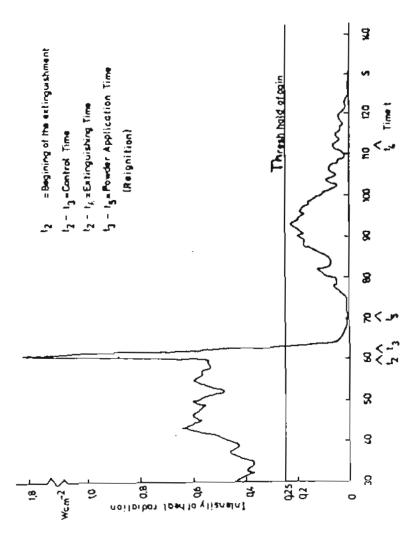
Difference of Extinguishing Time and Spreading Time of AFFF Foam on a Fuel Surface. FIGURE 27

that the results may be slightly inexact because different equipment was used for the extinguishing tests.

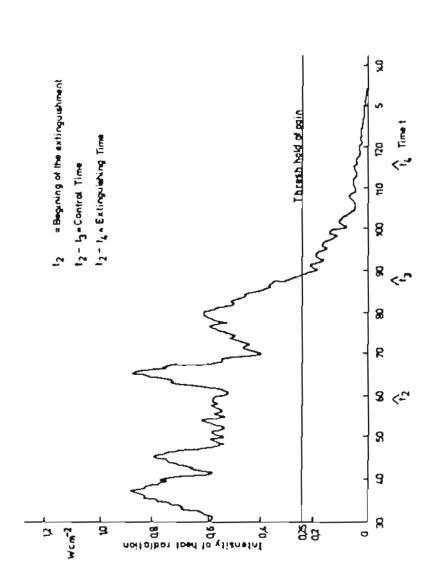
A combined use of dry powder and foam is efficiently utilized in a pool fire with reignition sources, as can be seen from Figure 28 and 29. In these figures the heat radiation from the flame is plotted versus the extinguishing time. Using a dry powder with the foam (Figure 28) the heat radiation is reduced immediately nearly to zero with the onset of the dry powder application, except for the first seconds of powder application. This decrease in heat flux may be important to the survival of the crew and passengers of the aircraft. Measurements taken of the conditions in a cockpit of a combat aircraft during extinguishment, lead to this conclusion. If the fire is extinguished with foam only (Figure 29), the heat radiation decreases more slowly with time over the period required for extinguishment.

The use of dry powder with foam may lead to shorter extinguishing times, since the time needed to cover a fuel surface with foam is shorter without the presence of fire. During the time needed for generating a closed foam blanket, the foam is destroyed by heat from the flames. Therefore, the closed foam blanket will be formed faster without a fire or after flame extinguishment. When a dry powder is used in combination with a foam, the fire is at least partly extinguished for some time by the dry chemical, so that the closed blanket of foam will be formed faster.

Dr. Tuve (Reference 9) in a 1964 paper states enthusiastically, that the discovery of Light Water and dry chemical, and its twin-quantity, dual-agent application constitutes the beginning of what is believed to be a radically new departure in the control and extinguishment of flammable liquid fuel fires. It combines the superior flame extinction qualities of potassium bicarbonate dry chemical (which, proved by test is the most potent, nontoxic, free radical quenching agent available in 1964) with a superior film-spreading agent. This combination removes the basic problem of all free radical quenching agents, namely, their temporary action because of reignition potential.



Heat Radiation from a Flame During Extinguishment with Dry Powder and Foam. FIGURE 28



Heat Radiation from a Flame During Extinguishment with Foam. FIGURE 29

SECTION III

GELLING AND EMULSIFICATION OF FUEL SPILLS

A. BACKGROUND

To reduce aircraft crash fires the use of gelled or emulsified fuels has been evaluated. Primarily the thickened fuels reduce the risk of mist fires and explosions because the gel will not atomize as does liquid fuel. Furthermore, many types of gel will reduce the rate of evaporation of fuel by rapidly producing a skin over the fuel surface, thus reducing the burning rate. Since the problem of fuel neutralization is related to thickening the fuel after the spill and fire has started, the latter property of producing a skin over the surface would be of greatest interest rather than reducing atomization. Further, the thickened fuel will be more stable and prevent the continuous flow of fuel under the AFFF blanket.

The history of gelled fuels, extending back to the use of Greek Fire, a natural petroleum gelled by lime and pitch, in the seventh century B.C., has been reviewed by Beerbower and Philipoff (Reference 10). Between World Wars I and II, gelled alcohol was developed as a safety fuel, and in World War II naphtha gelled with a sodium soap was used as a safety fuel to distill water in lifeboats. Wartime requirements produced a greater research effort towards fuel gelling, but most successful of these resulted in the development of Napalm MI, which has found peaceful use in gelling diesel fuel for lighting up standby coal fired boilers in power plants. Paraffinic fuels gelled with super absorbent silica gel have found a similar use in lighting charcoal barbecue stoves.

Losev (Reference 11) has described the use of packaged gasoline to solve transport difficulties in the USSR. Stabilized highly concentrated emulsions of hydrocarbon dispersed in water were treated with a plasticizer and a hardener. Briquettes could be produced containing 95-8 percent of liquid hydrocarbon. Screw presses lead to recovery of this fuel in 97-8 percent yield. It was claimed that transportation of petroleum products was made "considerably easier and cheaper." The danger of fires caused by static electricity was eliminated, there was no longer any hazard associated with the fluidity and evaporation of the liquid fuel, and even if ignition did take place at any point it was easily extinguished.

Beerbower and Philipoff (Reference 10) considered five

different types of fuel "gels" classified according to their structure:

- (a) Soap gels have as their basic unit a long molecule with a polar "head" and inert "tail." These molecules are attached head-to-head in sheets which, in turn, stack into ribbons. Gelation is due to a structure of interwoven ribbons, liquid fuel being loosely bonded by surface tension within the capillaries.
- (b) Elastomer-thickened gels contain long polymer molecules which are loosely coiled. Vulcanization produces occasional cross linking.
- (c) Napalm type gels have properties similar to those of elastomeric gels, but are based on aluminum soaps. No catalyst is involved in their production and any damage due to shearing is readily repaired. Many molecules can act as terminators for Al-OH chains so that these gels are rather sensitive to contamination.
- (d) Solid thickeners include silica gel and ureaformaldehyde. These give rise to absorption type gels consisting of three-dimensional sponges with liquid fuel contained in the interstices.
- (e) Emulsions are classified as the fifth type of "gel." Here two mobile liquids emulsify to produce a solid of considerable rigidity. The continuous phase, which must contain a surfactant to stabilize the emulsion, may be very considerably stretched and the disperse phase subjected to considerable distortion. Emulsions may be produced in which the continuous phase constitutes as little as 2 or 3 percent of the mixture.

Clearly there is a considerable technology of thickened fuels, but application of this technique to aircraft crash fires has only been studied in the last two decades. At high rates of shear, thickened fuels behave similarly to unthickened fuels; however, it has been claimed that forces involved in aircraft crashes are lower than those necessary to produce this type of behavior, so that atomization will not occur.

The first attempt to apply fuel thickening to aircraft lay in attempts to gel all the remaining fuel when a crash became unavoidable. Because of the danger of inadvertent operation a two-shot system was favored. When a crash appeared imminent, one reactant would be injected into the fuel which would not affect its burning properties. Should the difficulty

be overcome the plane would continue to fly. If the crash became inevitable a second reactant could be injected which would solidify the fuel (Reference 12). Methods of rapidly gelling aircraft fuels were studied at Southwest Research Institute (References 12 and 13). Two systems, each having very high reaction rates, appeared promising. The first involved reaction of dibasic acid chlorides with amines to form amides or polyamides; the second involved the reaction of amines with isocyanates.

It was shown that gels, formed by the reaction of a primary monomine with various dibasic acid chlorides in JP-4, were due to formation of the amine hydrochloride and not to polyamide formation. The larger part of the work was devoted, however, to the amine-isocyanate reaction. The properties of the gel could be controlled by the structure of both the amine and the isocyanate used, and gelling times as low as 0.04 second were noted. The most rapid reactions were produced with certain aromatic di-isocyanates and either aliphatic amines or alkoxyamines.

Aliphatic di-isocyanates and an alkoxyamine converted JP-4 to a tough visco-elastic gel which would contain the fuel well under impact conditions. The gels produced by aliphatic, aromatic and alicyclic amines, or diamines together with the corresponding isocyanates and di-isocyanates showed little flow while burning. Aromatic tri-isocyanates with aliphatic amines or alkoxyamines converted JP-4 into a tough gel in which the rate of burning was significantly decreased and which showed no tendency to flow.

Some gels burned for 15-16 minutes without melting under conditions where an equivalent amount of JP-4 would have burned within one minute. Gels containing a high concentration of aromatic rings and of halogen substituted aromatic rings significantly retarded the burning rate.

Tests were made to determine evaporation rates of gelled fuels. It was found that, with certain gels, the air flow required to reduce the vapor concentration of JP-4 to a condition below the lower flammable limit could be reduced by a factor of eight without producing a hazardous condition. No additive system was developed which excelled in impact properties, burning properties, rapidity of gelation and temperature properties. Several systems were found which gave good results in two or more of the tests.

Rapid solidification of aircraft fuels is thus seen to be perfectly feasible. For aircraft use, however, rapid gelling might prove difficult because of the complex shape of fuel tanks. The view has been expressed that the mechanical and hydraulic forces needed for injection of the gelling agents

are not compatible with current and foreseen aircraft fuel systems (Reference 14). Therefore, interest switched to advances in fuel emulsions or viscous gels.

Use of fuel gelling for the Fuel Neutralization Program, will require injecting and mixing the gelling agent with the minimum of energy. Since, it was found that the mechanical and hydraulic forces needed to gel the fuel in aircraft fuel tanks were too high, it seems unlikely that gelling could be achieved easily in a pool of fuel. For this reason, it is felt that emulsions would have a greater application to fuel neutralization.

Work on controlled flammability fuel emulsions and gels was discussed at the Aircraft Fluids Fire Hazard Symposium held at Ft. Monroe, Virginia, in 1966; this has been reveiwed by Yaffee (Reference 15). It was claimed that these fuel modifications resulted in significant reduction in aircraft fire hazards, although the emulsions or gels could be burned directly in gas turbine engines. The prime sponsors of the work were the FAA who were interested mainly in gelled fuels, and the U.S. Army Aviation Material Laboratories, concerned primarily with fuel emulsions.

Work at the Western Company (Reference 15), was originally concerned with gelling aircraft fuel inside the fuel system and a gelling agent "Jet Gel" was developed for this purpose. Because of the above-mentioned limitations of this method, emphasis shifted towards the development of gels and emulsions of a fairly light consistency which could be pumped into the aircraft and which could be burned in the combustion chamber; FAA sponsored work was directed towards gelling agents which would be present with the fuel at all times. The most promising of these gelling agents was N coco hydroxybutyramide (CHBA) at a concentration of 1.5 percent by weight. The splash, flow and vaporization tendencies of the fuel were substantially reduced and surface flame propagation was cut by 96.7 percent. The gelled fuel is liquified at 130°F (57°C) and is satisfactory as a fuel in all respects except freezing point. Rocking and vibration tests carried out by FAA caused very small amounts of liquid fuel to separate from the gel.

FAA conducted tests of CHBA gelled fuel on a J47 turbojet engine. In one test a heat exchanger was used to raise fuel temperatures to 130°F. In the other, gelled fuel was forced into the engine to see whether the normal heat of the fuel system can be used to liquify fuel (Reference 16). Present work is concerned with the possibilities of rheopectic gels

or antimisting Euels, which are normally liquid but change to solid under impact loads. Considerable effort was devoted to a study of the compatibility of CHBA gelled fuel with aircraft fuel systems.

The Fuel Neutralization Program is concerned with reducing vaporization rate and increasing fuel viscosity at very low shear rates, therefore, the antimisting work of the FAA is not applicable.

U.S. Army Aviation Material Laboratories stated that their efforts have not yet produced a gel which does not start to separate liquid fuel before reaching the combustion chamber, whereas, this separation is not shown by emulsified fuels. Accordingly, a contract was awarded to Esso Research and Engineering Corporation to develop an emulsified JP-4 fuel. Two requirements were envisaged. The first was for a fuel which can be transported relatively safely. After transportation the fuel would be deemulsified and used in conventional vehicles. The second application would be in an aircraft with a fuel system designed to take emulsified fuel right up to the combustion chamber.

The Western Company and Petrolite Corporation have also supplied fuel emulsions. Petrolite's emulsified fuel contains 2 percent by volume of water in JP-4. It is stable between -40°F and +130°F and can be pumped with standard equipment. It has been burned in diesel and gas turbine engines. Qualitative tests indicate that the emulsion is less easily ignited, has a lower evaporation rate and flame propagation rate, and is more resistant to spillage than JP-4.

Simulated crash impact tests have been carried out by the Western Company on several emulsions and gels. Compared with JP-4, flame duration was reduced by as much as $76 \cdot 7$ percent for one emulsion and 85 percent for a gel. Flame propagation rates were also reduced (by 91 percent for one emulsion and $96 \cdot 7$ percent for a gel) (Reference 15).

Various engine tests, made with emulsified fuels, have demonstrated that emulsified fuels can be pumped, metered, atomized and burned satisfactorily in an Allison T63 engine (Reference 15).

The use of gelled and emulsified fuels to lessen the fire hazard in aircraft crashes appears to be promising; however, much remains to be done. Basic work is still needed on evaporation rates, and on ignitability and subsequent

flame spread for such fuels. Temperature stability remains a problem, particularly where fuel is to be used as a heat sink. Squeezing JP-4 from gelled fuel by small pore filters has given rise to problems, such as removal of dirt and contaminants which tend to be held in suspension by gelled fuels more than by JP-4. Expulsion of the last traces of fuel from tanks is also difficult.

For civil use a major question centers on the economics of such fuels and their supply. Estimates of the additional cost vary widely, from 0.5 cents per gallon of fuel to a doubling of present fuel costs. Clearly this situation needs to be clarified.

Fortunately, the application of gelled or emulsification processes to the Fuel Neutralization Program is considerably easier than required to prethicken the fuel used in the aircraft engine. Primarily, fuel stability is not a question. It is necessary to inert the fuel spill for a relatively short period of time compared to that required for the fuel to be used in the aircraft. Further, we would like to completely inert the fuel, rather than in the case of aircraft fuel, which requires that the fuel is stable and inert in the tank and in case of a crash, but readily burns once injected into the jet engine. Also, all the problems of handling, storage and fuel system compatibility, are of no concern for fuel neutralization. Since so much work was conducted on gelling and emulsification, it is worthwhile to review, as it may apply to the Fuel Neutralization Program.

In one aspect, the fuel neutralization requirement is more demanding than that of the fuels program, in that the spilled and burning fuel must be thickened while on the open ground. Therefore, mixing of the thickening agent must occur with a minimum of energy. Ideally, if the agent was contained in the AFFF, it could drain as the foam collapses and thicken the fuel. Again, the agent must mix with the fuel without the aid of mechanical agitation. The prime purpose of thickening the fuel is to reduce vaporization and stabilize the fuel spill, so the fuel does not spread under the AFFF blanket. To accomplish this, it may be possible only to thicken the fuel surface rather than the total fuel spill. If this is the case, the amount of agent needed and its mixing with the fuel could be greatly reduced.

B. CHEMISTRY OF GELLED AND EMULSIFIED FUELS

Gels and emulsions have been studied in the development of safety fuels for aircraft. Both gelled fuels and emulsified

fuels show greatly reduced rates of vaporization, a much lower tendency to flow and effective control of splash, as compared with liquid fuels.

Gels are formed when solid particles of colloidal size are placed in a liquid medium. All solids in liquid colloidal suspensions, however, are not gels. For gellation to occur, there must be an interaction of the particles with one another and with the medium in which the particles are suspended. Whether a gel is formed, therefore, depends upon the nature of the particle surface and the nature of the suspension medium. The forces of particle interaction are short-ranged. Thus, particle concentration is also important for gellation. It is the particle interaction that provides gelled fuel the desired properties of reduced splash, flow and vaporization at low additives concentrations.

The conditions for gellation can be established in several ways. Colloidal particles with the necessary surface properties may be suspended directly in a liquid medium. This is the procedure for thickening liquids with silicone flour and acetylene black. Gellation can also be brought about when colloidal particles are grown from dissolved molecules by the process of precipitation. Precipitation can occur either as the result of a chemical reaction or as the result of a change in solution properties such as temperature, concentration or pH.

Emulsions are formed when liquid droplets of colloidal size are suspended in a second liquid. It is commonly known that a suspension of oil-in-water soon separates. There is also a familiar thermodynamic explanation for this phenomenon. A reaction is spontaneous when it reduces the free energy of a thermodynamic system. Lowering the interfacial area between two immiscible liquids lowers the total interfacial forces which lowers the free energy of the system. The coalescing of oil droplets reduces interfacial area and the free energy, and is therefore a spontaneous process.

To produce a stable emulsion, it is necessary to use an emulsifying agent. Because these materials are capable of reducing interfacial tension, they concentrate at the interface between the two liquids. Because they reduce the interfacial tension of the system, they also stabilize the emulsion.

As with gelled fuels, the reduced hazard properties of emulsified fuels are the result of interactions between particles or droplets. When the internal or droplet phase of an emulsion is increased, the droplet concentration is

increased, resulting in increased droplet interaction. This is evidenced by an increase in emulsion viscosity. The concentration of the internal phase may be increased until the continuous phase can no longer envelop the internal phase and the internal phase material will coalesce into large particles or separate entirely.

A fuel emulsion should be as rich as possible in fuel. For the emulsion to also have reduced hazard properties the fuel must be the internal phase. For fuel neutralization it is also important that the emulsion be rich in fuel since this would reduce the amount of additive required to emulsify the JP-4. For instance, if water was used to gel the fuel, it would be necessary to have a system with the least water required.

Emulsification is often accomplished by dispersing one liquid in a second liquid in the presence of an emulsifying agent. Dispersion can be achieved, for example, by mechanical agitation, shearing with pumps, ultrasonic agitation, etc. Emulsions are also made when one liquid is forced rapidly into another through a small orifice in the presence of an emulsifying agent. In a third method of making emulsions, the solubility of one liquid in a second liquid is decreased by the addition of a third material in the presence of an emulsifying agent. The separation of the now immiscible liquid occurs in the form of an emulsion. For fuel neutralization, it is necessary to find a method which will require the minimum mixing energy.

Both the gel and emulsion processes for safety fuel are in effect a protective packaging process on a very minute scale. In the gel, the molecules of fuel are bound into a matrix formed by the gelling agent. This structure provides rigidity which prevents splash and spreading of fuel, and also reduces the rate of vapor release. The emulsion consists of minute droplets of fuel surrounded by an extremely thin but very resistant film of immiscible, low flammability fluid. The droplets are essentially in contact with each other and because of their small droplet size with inherent high-surface curvature, they strongly resist deformation and behave more like a solid than a riquid. This stiff emulsion prevents fuel splash and spreading, and the immiscible film of low flammability material surrounding the fuel droplets effectively reduces the rate of vapor release.

Droplet size is important because the rigidity of the emulsion arises from their resistance to deformation. Thinner, more mobile emulsions splash, spray, spread and burn almost as readily as unmodified fuels.

C. GELLED FUELS

The chemistry of gelled fuels would be extremely complex if one attempted to discuss it by individual formulations. Fortunately, there are only five classes, and each can be covered in a general sort of way.

1. Soap Gels

The oldest and most versatile is the ordinary soap gel. The study of these has been greatly benefited by their intimate relation to the lubricating greases. It also applies in a general way to the CHBA gels.

The basic unit in a soap gel is the long molecule with a very polar "head" group at one end and an essentially inert "tail." The nature of these molecules directs them into an unusual ribbon-like crystal form, in which the heads cohere strongly to form a double sheet of soap with the tails extended as in Figure 30a. These sheets adhere to each other to form a stack as shown in Figure 30b. The strength is nearly all in the polar-end bond; this is usually augmented by considerable hydrogen bonding, as these soaps work properly only in the presence of water of hydration. These ribbons may be quite small in a calcium soap gel; in some sodium soap gels where their growth has been encouraged by suitable techniques, they may reach a few millimeters in length.

The gellation is due to the formation of a "brush-pile" structure, as in Figure 30c, in which the ribbons mat together. Enough excess surface-energy exists to make loose bonds between ribbons, and the structure becomes rigid enough to be self-supporting under normal gravity, in mounds up to cylinders whose height exceeds their diameter. The liquid is, however, mostly very loosely bound by surface tension effects in these "capillaries" and can be removed with no special energy input until the last portion (roughly equal in volume to the soap) which requires some additional energy to detach it from the hydrocarbon tails.

2. Elastomer Thickeners

The elastomer or polymer thickened fuels consist of the individual molecules of polymer as in Figure 3la, so that their diameter is the same as that of a molecule of monomer. The length is proportional to the molecular weight, and will frequently run from 100,000 to a million diameters. They show considerable tendency to coil loosely, and are seldom found fully extended except under conditions

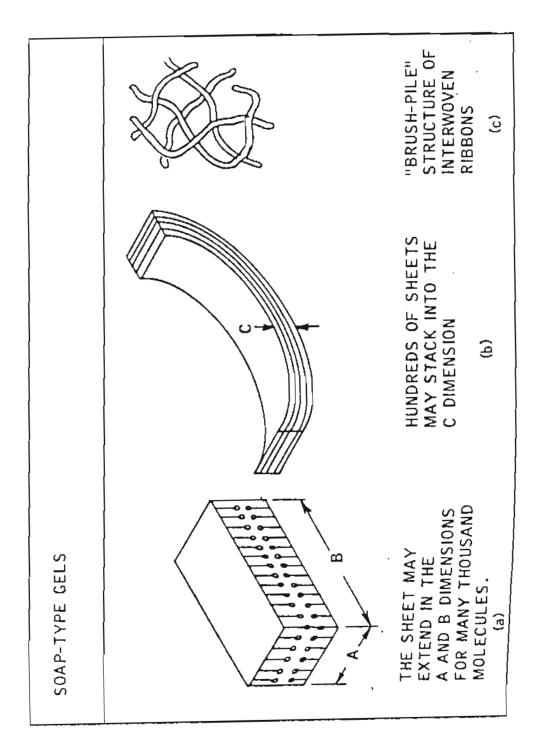


FIGURE 30 Soap-Type Gels

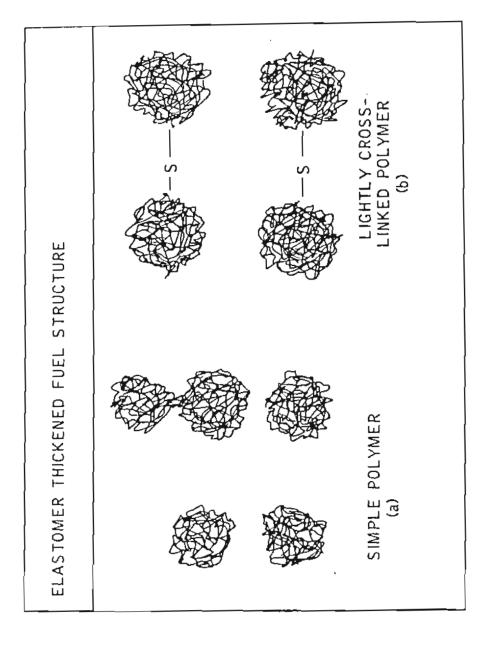


FIGURE 31 Elastomer Thickened Fuel Structure.

of flow.

In the special case of vulcanized elastomers, there is an occasional cross-link as in Figure 3lb. When done in moderation, this produces aggregate units with several times the molecular weight and effective length of the original polymer. Excessive vulcanization destroys the freedom to uncoil and recoil, and the aggregates coalesce into lumps with no thickening power.

Napalm Thickeners

The aluminum soap gels are very similar to the elastomer ones, with a few important differences. The reason for this is shown in Figure 32, which illustrates a portion of the chain. Unlike polymers, however, the bonds form (and break) with great ease. No catalyst is required, and damage due to mechanical shearing is readily healed. However, because many chemicals act as chainterminators, most of these soaps are very sensitive to contamination.

The length is, of course, variable; but the "molecular weight" of a typical Napalm gel appears to be in the millions. Some cross-linking may take place, especially if the Napalm has been allowed to oxidize. The gel then becomes "short," and may coagulate to ineffective lumps.

4. Solid Thickeners

The absorption-type gels include those from silica gel and also the urea-formaldehyde type. Both are based on a three-dimensional structure resembling that of a sponge, with the liquid in little "boxes" surrounded by solid (though very thin) walls. In the case of the silica gel, a number of these cells constitutes a particle, so that the gel is plastic and resembles a soap-base product. The urea-formaldehyde structure, on the other hand, extends to the outer edges of the piece and no flow is possible until the integrity of the lattice is destroyed.

D. EMULSIONS

The latest class of gelled fuels is quite baffling because two liquids, neither of which has much viscosity, are combined to form a pasty solid which exhibits considerable rigidity. The secret lies in the extreme stretching of the continuous phase, and the distortion of the dispersed phase from the spherical shape usually found in emulsions. The nature of the phenomenon is much more easily seen in

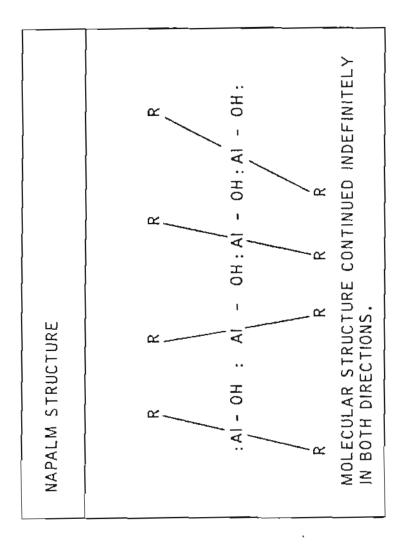


FIGURE 32 Napalm Structure

foams, where the dispersed phase is air. Careful examination of a foam reveals that the bubbles tend to have flat dodeca-hedra faces. (Due to the circumstances, few if any are perfect.) The ability of an emulsion to stand in a mound is really less surprising than that of a foam.

The film separating these dodecahedra is not a simple liquid. Were it not for the surfactant in it, the liquid would rapidly drain out and flow down the lattice so that the walls would puncture. The surfactant is generally a soap-like molecule, but here its action is the opposite that of Figure 30. An idealized situation is shown in Figure 33; the water layer is actually somewhat thinner, so that its draining rate is slowed to negligible values.

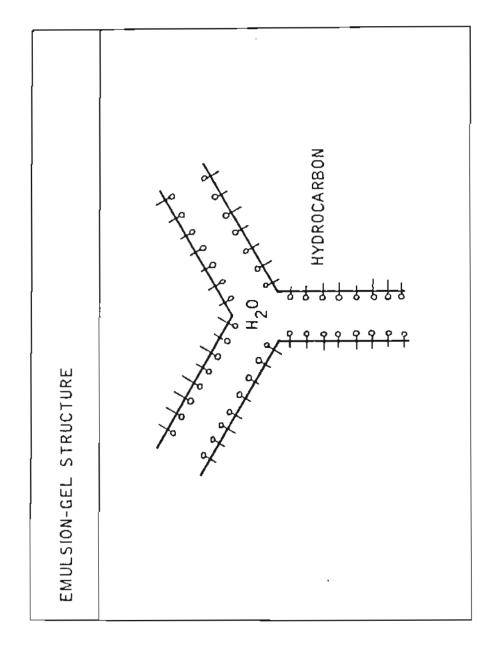
E. EMULSION FUNDAMENTALS

Emulsion theory, like all other specialized fields, has developed its own vocabulary. An emulsion consists of a dispersion of one liquid phase in a second immiscible liquid phase. Figure 34 is a diagram of a simplified classification for emulsions. Emulsions are usually classified broadly into two groups: oil-in-water (O/W) and water-in-oil (W/O), where the terms "oil" and "water" are used quite loosely. Emulsions may be further subdivided in terms of the volume percent of internal phase into three broad categories: low-internal-phase-ratio, medium-internal-phase-ratio, and high-internal-phase-ratio emulsions.

Low-internal-phase-ratio emulsions contain up to about 20 percent of internal phase. Their physical properties are controlled primarily by the nature of the external phase, and their viscosity is essentially the same as that of the external phase. Examples of L.I.P.R. emulsions are such things as ordinary floor polish emulsions or agricultural insecticide emulsions.

Medium-internal-phase-ratio emulsions contain from about 20 percent to about 70 percent internal phase. They become increasingly "viscous" as the interal-phase ratio increases. Examples of M.I.P.R. emulsions are such things as mayonnaise and certain road asphalt emulsions.

High-internal-phase-ratio emulsions are those which contain more than about 70 percent internal phase. Until the last 20 years emulsions of this type were laboratory curiosities. Some textbooks still create the impression that when the percent of internal phase exceeds about 74 percent (the volume of closely-packed spheres), inversion occurs. While a few examples of emulsions containing more than 95 percent internal phase are cited in the literature as early as 1912, it has only been within the last few decades that commercial production of such emulsions was practical.



Volume Percent Internal Phase

High	O/W, H.I.P.R.	W/O, H.I.P.R.
Medium	O/W, M.I.P.R.	W/O, M.I.P.R.
Low	O/w, L.I.P.R.	w/o, L.I.P.R.
	Oil in Water	Water in Oil

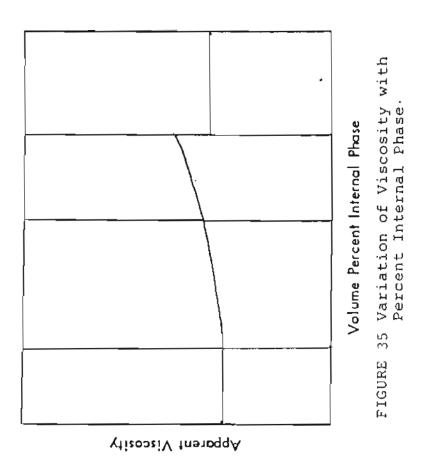
FIGURE 34 Emulsion Types

It is now possible to produce high-internal-phase-ratio emulsions containing less than 1 percent external phase. However, compositions in this extreme range require considerable care in manufacture and are less stable.

Figure 35 is a typical graph which can be found in many elementary textbooks showing the increase in apparent viscosity as the volume percent internal phase is increased. Until the volume percent internal phase reaches somewhere between 20 and 30 percent, no appreciable increase in viscosity is noted above the viscosity of the external phase. When the volume percent internal phase reaches approximately 52 percent, the viscosity begins to increase more rapidly and continues to increase until the percent internal phase reaches above 74 percent. In this region, most emulsions then invert, and their viscosity then approximates the viscosity of the new external phase.

The geometry of high-internal-phase-ratio emulsions have unique properties. If uniform spheres are packed in a cubic packing, they occupy approximately 52 percent of the total volume. If they are packed in a tetrakaidecahedral configuration, they occupy approximately 68 percent of the total volume; and when packed in a dodecahedral packing, they occupy slightly over 74 percent of the total volume. This packing is, therefore, referred to as the "closest packing of spheres." One of the probable reasons why medium-internal-phase-ratio emulsions exhibit increased viscosity is because portions of the system are organized into one of these three packings.

Above 74 percent internal phase either the spheres must be distorted or the emulsion must be extremely polydisperse. It can be shown mathematically that polydispersity probably requires more energy than would be required by distorted spheres. Above about 96 percent internal phase the droplets of dispersed internal phase must assume a polyhedral configuration. A study of the geometry of the tetrakaidecahedral and rhomboidal dodecahedral tessellations shows these to be the most likely arrangements. Neither of these tessellations has planar cleavage. Planar cleavage can only be achieved by a conversion of the tessellation to a prismatic tessellation. Prismatic tessellations have higher surface areas and therefore represent a higher energy state. This is probably why H.I.P.R. emulsions exhibit a phenomena known as yield value. Under very low shearing forces these emulsions behave like elastic solids. However, when the shearing force is large enough to locally produce prismatic configurations, shearing planes can develop, and the material begins to flow. As higher stresses are applied, more shear planes can develop and the "apparent viscosity" of the formulation decreases.

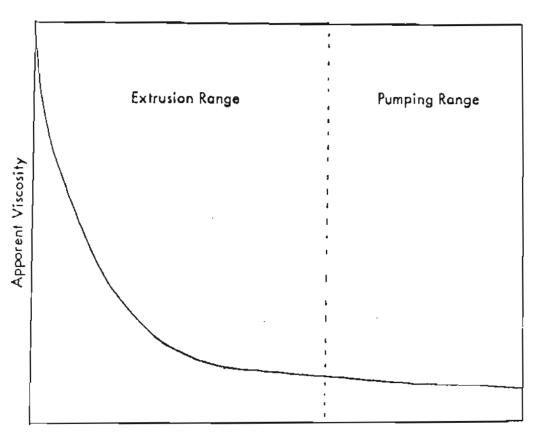


There is a fundamental topological difference between true gels and H.I.P.R. emulsions. A gel consists of a solid three-dimensional network intertwined with a similar liquid Topologically, neither network is really "inside" network. the other. In order for a gel to flow, the order of connectivity of the solid network must be reduced. When a gel ceases to flow and begins to "reset," the higher order of connectivity is being reestablished. In the case of the H.I.P.R. emulsions, however, each droplet of internal phase is topologically "inside" the continuous external phase, and while the geometric configuration may change under flow conditions, the order of connectivity of the external phase need not undergo change. For this reason, H.I.P.R. emulsions do not show the broad hysteresis loops in their stress strain diagrams which are typical of the gels. Gels are thixotropic materials. H.I.P.R. emulsions are not truly thixotropic, but may better be characterized as "pseudoplastic."

In actual fact, the viscosity curve shown in Figure 35 is meaningless over a large part of its range unless the means of determining viscosity are carefully specified, because medium-and high-internal-phase-ratio emulsions do not behave as Newtonian systems. In contrast to true Newtonian fluids, whose viscosity is independent of the rate of shear, viscous emulsions behave in the manner shown in Figure 36; at low rates of applied force their viscosity is either meaningless or infinite. Once the yield value is exceeded, they begin to flow; and as the applied forces increase, the apparent viscosity decreases at first and finally approaches a value close to the true viscosity of the external phase. It is this very property which makes them of interest in fuel systems, since, when they are at rest, they exhibit the properties of elastic solids while still being readily pumpable.

For fuel neutralization, the greatest concern is thickening the fuel while it is stationary or flowing from the spill. The thickened fuel must vaporize more slowly and also produce a more stable spill which can be covered by the AFFF. Further, if the drained water from the AFFF form the external phase with the JP-4 the internal phase, each fuel droplet will be encapsulated in a water film. Probably this would only occur at the fuel surface due to the limited amount of water available and mixing energy to form the emulsion in a short period of time.

There are two different techniques for producing stable H.I.P.R. emulsions. The first consists of increasing the viscosity of the external phase by the addition of polymeric materials to the point where coalescence of the internal phase is sufficiently retarded. This is the technique used as long ago as 1910 by Pickering and others to produce "emulsions" of



Applied Force

FIGURE 36 Variation of Apparent Viscosity with Applied Force.

benzene in concentrated soap solutions. Emulsions made by this technique have fairly high yield values but also level out at a much higher viscosity in the pumping range. They also tend to be more adhesive, sharing this property with true gels.

The second technique for producing H.I.P.R. emulsions uses a more fluid external phase, containing as an emulsifier an extremely efficient film-former which effectively prevents coalescence of the dispersed droplets. Emulsions made by this technique allow control of the yield value, by adjustment of the phase ratio or the composition of the external phase, and exhibit appreciably lower apparent viscosities in the pumping range. It is this technique which has been employed in producing various fuel compositions.

F. RHEOLOGY

At the outbreak of World War II, the only instrument recognized as applicable to the rubber-thickened fuel was the falling ball viscometer. The results were often converted, by a misapplication of Stokes' Law, to "absolute viscosity." As supply problems arose and other thickeners were introduced, each brought with it an instrument which seemed applicable. A considerable effort was made by the Eastman Kodak NDRC 11 group to correlate this haphazard collection, but the present real understanding of the problem is largely due to a peacetime program during the 1950s at the Franklin Institute.

The naive concept of "viscosity" was soon replaced by the "apparent viscosity," a term now deservedly in disrepute but at least recognizing that all these materials are non-Newtonian. By this it is meant that the flow (usually expressed as Shear Rate or the equivalent Velocity Gradient) is not directly proportional to the applied force. The latter is usually expressed as Shearing Stress.

The first stage of rationalizing the various measurements was to establish complete diagrams of shear rate versus stress under kinematic conditions. The kinds of plot obtained are shown in Figure 37, which is typical of those resulting from the ASTM D 1092 Pressure Viscometer. This clearly distinguishes the Formula 122 soap gel and emulsion from the other fuels, in that the former exhibit a yield stress. (The terminology here is based on ASTM D 2507-66T, Definitions of Terms Relating to the Rheological Properties of Gelled Rocket Propellants.) This property is the virtue of these gels; it describes the property which controls the ability to resist spilling and spreading, and also resist the atomization effect. This

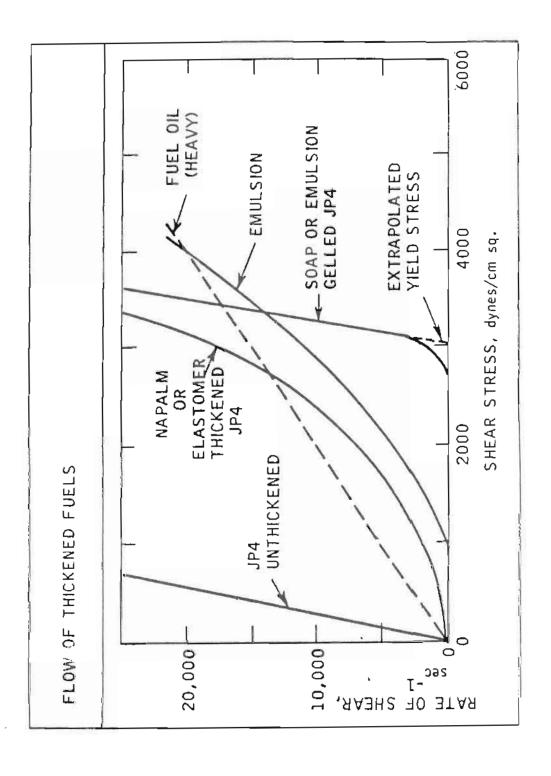


FIGURE 37 Flow of Thickened Fuels

contrasts with the true viscosity of a thick Newtonian fluid, which merely delays these effects. On the other hand, the yield stress is the factor which prevents complete discharge from tanks. Emulsions are less subject to this problem, due to the continuous phase acting to lubricate the wall but both types require a starting pressure to initiate flow in a pipe which must be added to the frictional pressure drop. grease industry has long since learned to live with these problems of soap gels; by using follower plates, etc., it has been possible to deliver greases of quite high yield stress from packages and even tank trucks to systems where highpressure pumps distribute them to bearings 1,000 feet or more away. However, in the fuel business the volumes and rates handled preclude many such niceties as are tolerated with the lubricants. In the portable flamethrower, SOD Formula 122 would often show only 15 percent discharge while a heavy fuel oil would give over 90 percent discharge.

At high rates of shear, gels like SOD Formula 122 become almost indistinguishable from the unthickened fuel. Hence, a high velocity nozzle or the violent burster of the M-47 bomb will produce a very high flash burn. This property, a drawback to the weapons designer, can become a blessing to those who wish to burn these fuels in engines. The evidence is that aircraft crash forces are low enough to avoid this region of atomizing velocity gradients.

The failure of the stress-shear rate diagram to explain dynamic flow behavior soon became evident. Nothing on Figure 37 can be used to predict that the rubber-thickened fuel will work in the M-47 bomb, so a number of simulative tests were set up to measure this elusive property called "cohesion." The oldest, and still one of the best of these tests was the behavior when the fuel was cut with a spatula and a sample withdrawn. The Torsiometer was the first tool to give anything approaching a fundamental measure of it; various "extensiometers" for measuring the length of thread which could be drawn out, and impact devices which measured the energy absorbed from a pendulum or a fast-starting rotary viscometer were the intermediate steps. The first really scientific instrument was the Weissenberg Rheogoniometer. This makes a quantitative measurement of the "Normal Force," which causes some gels to climb the stirrer during their preparation. "Normal" is used in the sense of perpendicular to the plane of rotation. This can be shown to be fundamentally related to the elasticity of the gel. Unlike the yield stress, it cannot be measured separately and must be expressed as a function of viscous force. Figure 38 plots the typical fuels in such a fashion. The "Elastic Elongation" can be expressed by various ratios: Elastic Force/Viscous Force and Normal Force/ Shear Stress are roughly equivalent.

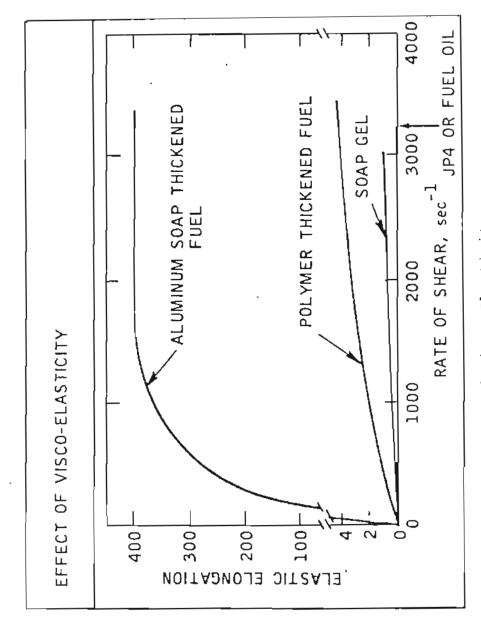


FIGURE 38 Effect of Visco-Elasticity.

G. COMBUSTION OF JP-4 THICKENED FUELS

The evaporation rate of a fuel affects its combustion or burning rate, since fuel combusts in the vapor phase. Evaporation is far more dependent on diffusion than on vapor pressure; in fact, it can be readily demonstrated that all gels have the same equilibrium vapor pressure as the unthickened fuel they contain. The need for the molecules of fuel to pass through a partly dried layer of gel causes the rate of evaporation to be highly variable in the Napalm, elastomer and soap gels. All start as if unthickened, but the elastic systems rapidly skin over with a drastic reduction in rate. The soap acts as a wick for a time, then forms a Not enough has been done on emulsions yet to describe the complete action, but it appears similar to soap gel evaporation. The burning rate follows the evaporation rate, except when a thinning causes a change in lump configuration; this tends to speed up the rate. In general, such tests have shown flame spread rates of 60 to 150 times lower than for the unthickened fuel.

Therefore, it appears that thickening the JP-4 fuel spill will reduce its evaporation, and thereby, its combustion or burning rate. This will enable the AFFF to more easily cover the surface and extinguish the fire since the spill will be stabilized and the vaporization rate will be reduced.

While the equilibrium vapor pressure is the same for thickened and unthickened fuels, the thickened fuels vaporizes at a much slower rate, giving time for the fire to be extinguished in the critical minutes (or seconds) after the fire starts.

Western Company (Reference 14) conducted experiments to determine the reduction in fuel fire hazards by gelling the JP-4 fuel. The gelling was reported to reduce crash fire hazards in three ways: (1) reducing the vaporization rate of fuel; (2) reducing the intensity of burning; and (3) limiting dispersion of the fuel into a finely divided state and area covered by the fuel spill.

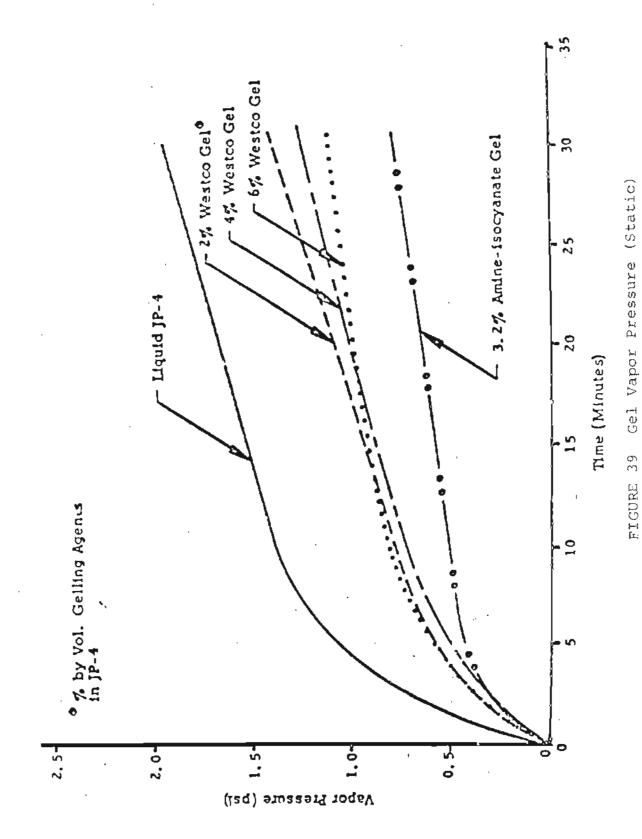
Tests comparing vaporization rates (Reference 14) of gelled and ungelled fuel confirmed that gelled fuel vaporizes much slower than liquid fuel. An apparatus for obtaining consistent gelled fuel vaporization measurements was constructed. The apparatus was based on a modification of the Reid Vapor Pressure Test. The standard Reid test did not give accurate results due to variable surface effects when trying to compare liquid and gelled fuel. For crash fire tests measurement of the effects of atomization are important. This would not be the case in the Fuel Neutralization Program, since the fuel will be relatively static when the extinguishant would be applied.

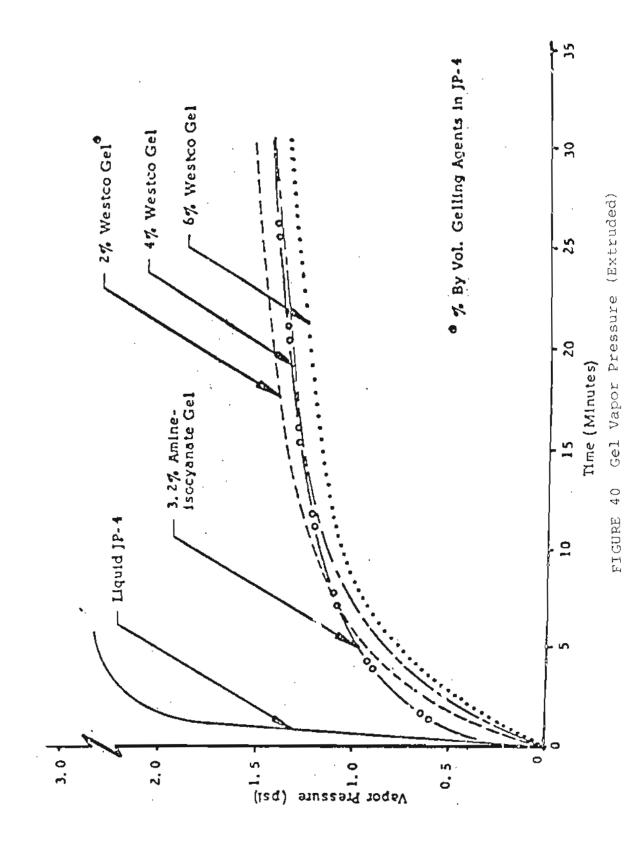
Figure 39 shows pressure versus time curves for undisturbed JP-4 and JP-4 gelled with several concentrations of G-5 + Solution G system and an amine-isocyanate system. Figure 40 shows the pressure comparing liquid fuel and gelled fuel after being forced violently through small diameter holes, more closely simulating a crash condition where the fuel would be sheared. Figure 39 for the undisturbed fuel would probably be more representative for the fuel neutralization case. In both figures, it can be seen that there is much slower vapor release by the gelled fuels. From Figure 40, it can be seen that agitation or splattering does not cause as sharp an increase in vaporization rates of the gels as it does with the liquid JP-4. The curves shown in Figures 39 and 40 also indicate that increasing the gelling agent concentration does not produce a corresponding reduction in vaporization rate.

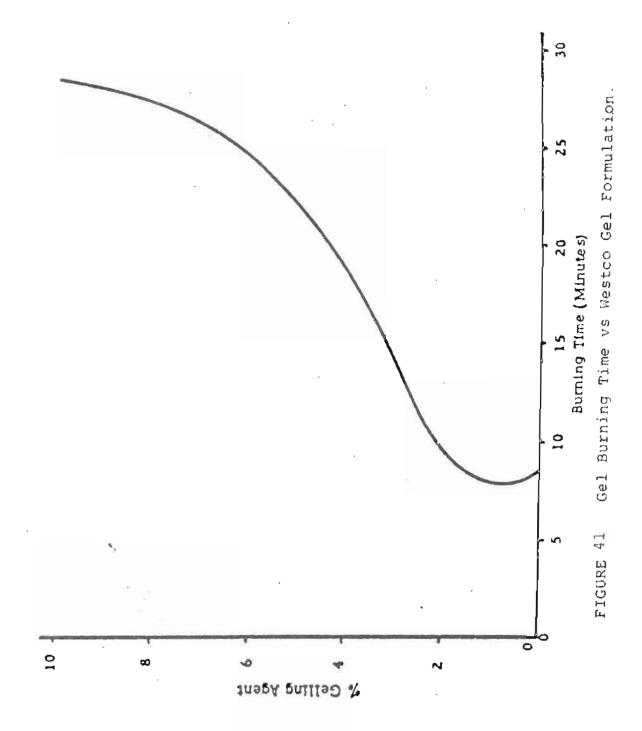
The time range which the vaporizing fuels would reach their explosive limit is of particular interest. The explosive range of JP-4 vapor pressures is very narrow. The lower limit is about 0.2 psi (to allow a slight safety margin 0.18 psi is used) while the upper limit is about 1.5 psi (to allow a safety margin, 1.8 psi is used). For this discussion, only the lower limit can be considered a boundary, because in an open spill there is always a chance that air will mix with the vaporized JP-4 and prevent extinguishment by the upper limit of the explosive range, as would occur in a closed tank. From Figure 39 for the static case, liquid JP-4 reaches the lower explosive limit in approximately 30 seconds. The gelled fuel reaches this vapor pressure in 60-90 seconds; therefore, ignition of the fuel vapors could be delayed 30-60 seconds by gelling the fuel spill.

Burning rate tests were made to obtain comparisons of liquid and gelled JP-4. Figure 41 shows a graph of burning times of 160-cc samples of fuel with different concentrations of Westco gelling agents. This figure shows a slight decrease in burning time for the percent gel, compared to the liquid fuel; this variation is within experimental error. Note that this gel is actually a viscous liquid at 1 percent concentration, while the higher concentrations give more or less rigid gels.

The Western Company (Reference 14) test showed that gelling the fuel can reduce the vaporization rate and burning rate by factors of 2 to 6. The properties of the fuel vapors are the same, whether the fuel is gelled or not. This means that the vapor pressure of a fuel gel will eventually reach the vapor pressure of the fuel liquid; however, the time required for vaporization is much greater with the gel. This increase in vaporization time can give the valuable seconds needed to extinguish the fire.







The chemical properties of the vapors from a gel are the same (with nonvolatile gelling agents) as those from the liquid fuel. As a result, the flash points, flammable limits, ignition temperatures, ignition threshold energies, etc., are the same for vapors from gelled or liquid fuel. This may not be the case for emulsions, where the water may retard combustion. Any variations in the behavior of the two states of the fuel related to burning is purely a rate factor due to retardation of vaporization by the gel. Liquid and solid fuels do not burn as such. All fuels must be vaporized or gasified before combustion can occur.

Further work performed by Brown (Reference 17) of Western Company, presents the results of impact tests for FAA 1069-1 gel and several JD-1 emulsions of different consistencies compared to liquid JP-4 are shown in Figures 42 and 43. As noted in these figures, both of the modified fuels offer a substantial reduction to the flame duration time. It is important to note that when the rigidity of the emulsion is increased, the flame duration decreases substantially. This is expected since the thinner the emulsion, the more its properties approach those of untreated fuel.

Once a fuel is ignited, the speed with which the flame advances is an important indication of its safety features. Slower flame propagation rates allow time for evacuation of a fire area or the effective application of a blanket of AFFF. In gels and emulsions, fuel vaporization is restrained to such an extent that disruption of the surface by the advancing flame is required to sustain burning. Brown (Reference 17) determined flame propagation rates of the various fuels by measuring the time required for a flame to spread over the length of a test trough of the material. Figures 44 and 45 show a comparison of the flame propagation rate of the FAA 1069-1 gel and the JD-1 emulsion with that of liquid JP-4. As shown in the figures, both of these modified fuels show a marked reduction in the flame spread rate.

Weatherford and Schaekel (Reference 18) report on measurements of relative flame velocities across liquid and emulsified fuel surfaces at 25°C conducted in a miniature trough, 46cm long by 3.8 cm wide and 0.48 cm deep. Although it was recognized that the trough size can influence flame speeds, such miniaturization was deemed necessary for two reasons. First, with the available facility, personnel safety dictated the use of only small quantities of JP-4 fuel for such measurements, and second, the small device facilitated rapid filling with emulsified fuel and subsequent rapid removal of excess emulsion to expose a fresh surface just prior to ignition. They report (Reference 18) that weathering effects

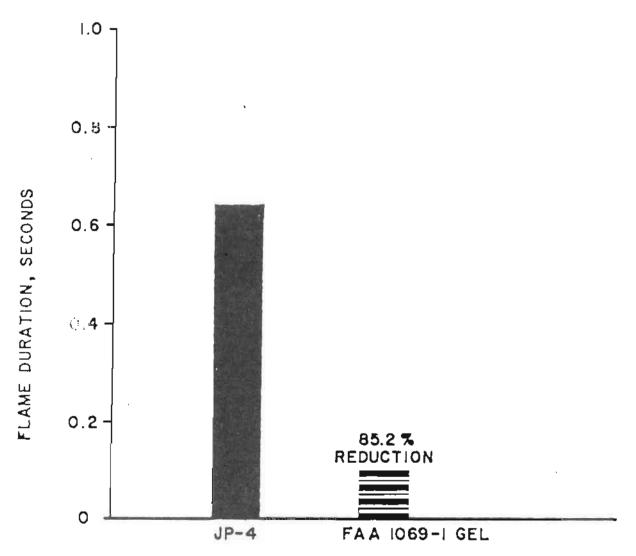


FIGURE 42 Flame Duration JP-4 versus FAA 1069-1 Gel.

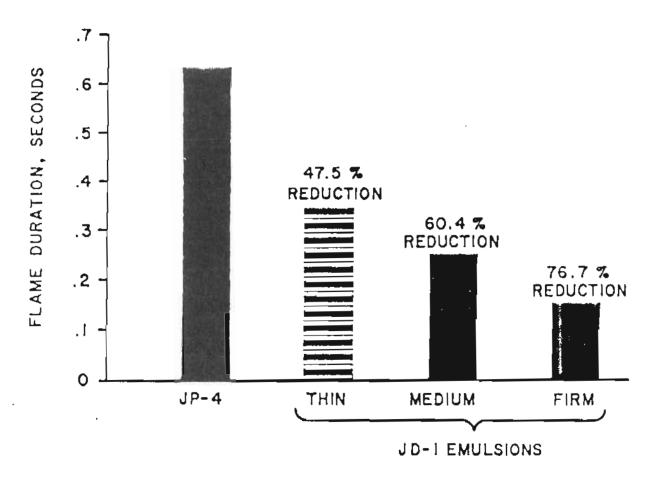


FIGURE 43 Flame Duration JP-4 versus JD-1 Emulsion.

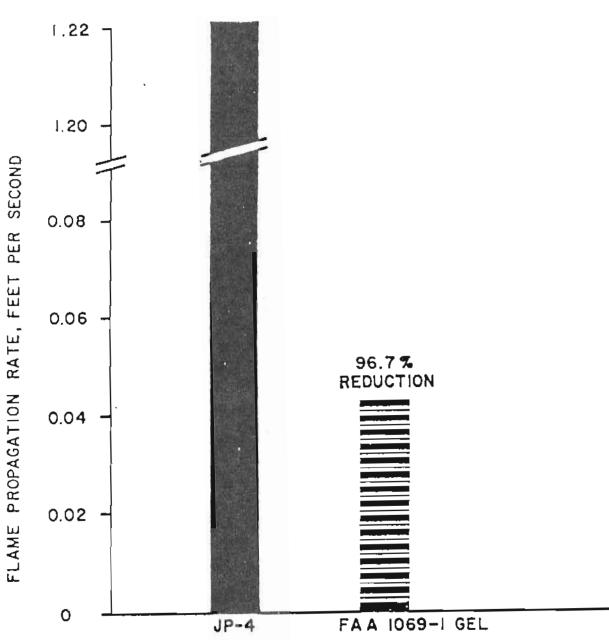


FIGURE 44 Flame Propagation Rate JP-4 versus FAA 1069-1 Gel.

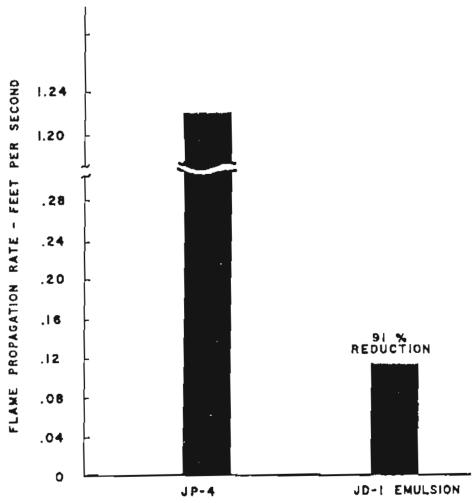


FIGURE 45 Flame Propagation Rate JP-4 versus JD-1 Emulsion,

can lead to spuriously low flame speeds unless fresh fuel surfaces are employed. With this device and procedures, no difference could be detected between the surface flame velocities across liquid and emulsified JP-4 fuel. It may be that reduction in flame velocity measured by other investigators may have been caused by formation of a skin on the surface of the JP-4 vapors to the surface. The validity of the relative flame speeds obtained (Reference 18) with the miniature trough was confirmed by limited experiments conducted with liquid JP-8 fuel and emulsified JP-8 fuel in a substantially larger device.

Kuchta et al. (Reference 19) performed a fire hazard evaluation of thickened aircraft fuels at the Bureau of Mines. They determined the ease of formation of flammable mixtures by measuring the relative volatility rates of the fuels. For this purpose, the ASTM Reid Vapor Pressure Test was modified to obtain continuous pressure measurements with a precooled fuel (32°F) under quiescent conditions. The time required for the fuel to attain a pressure of 0.5 psig at 100°F was selected by the investigators as the basis of comparison, since the corresponding fuel concentration would fall well within the flammable range for aircraft fuels.

Kuchta et al. (Reference 19) measured the rates of horizontal flame travel by burning the fuels in 4-foot long, V-shaped metal troughs (3-inch angle). Variations in the rates for thickened and unthickened hydrocarbon fuels are due primarily to differences in their volatility and thermal conductivity. Maximum rates occur when the temperature is increased above the flash point of the fuel, in which case flash propagation is possible. The flame spread rate under static conditions provides a measure of the flash propagation hazard that would exist in a postcrash fire with the spilled fuel at rest. It is expected that flame spread rate under static conditions would give a representative estimate of the reduction in vaporization to thickening the fuel under conditions of fuel neutralization.

A summary of the bench-scale test data for JP-4 base fuel and emulsified or gelled fuels is presented from (Reference 19):

JP-4 Fuel	Time To Obtain Vapor Pressure of 0.50 psi At 100 F, Min.	Flame Spread Rate, Ft/Sec.
Liquid	2.5	7.3
Gel A, 3%	23.0	4.8
Emulsion A-1, 2%	15.0	< 3.5
Emulsion A-2, 2.7	% 28.0	⁻ 0.05
Emulsion A-3, 3%	11.0	0.06
Emulsion B, 3%	24.0	<2.0

Figure 46 compares the vapor pressure time curves for two emulsified fuels and their base fuels, of vapor formation for JP-4 is reduced substantially by the addition of the emulsifying agent, which increases the viscosity. Results for JP-4 presented in Figure 46 indicate an increase from 30 seconds for liquid JP-4 to 60 seconds for emulsified JP-4, to reach the lower explosive limit at 0.2 psi vapor pressure. This is in approximate agreement with the results of (Reference 14), and indicates that the time for generating conditions suitable for fire on the fuel surface could be at least doubled by thickening the fuel, providing the firefighters valuable time to neutralize the fuel surface with foam.

Lissant (Reference 20) conducted similar tests with JP-4 and a JP-4 emulsion EF4-101, which contained 2.8 percent water by weight as the external phase. Tests were conducted measuring burning rate and flame propagation velocity. The apparatus consisted of a series of 1-5 inch by 20-foot long angle irons arrayed with the point of the Vee down and set level. The fuel composition to be tested was spread evenly along the bottom of the trough. Lissant found that the rate of propagation of flame along the trough containing the JP-4 was approximately 5 ft/sec and containing EF4-101 was approximately 5 ft/sec. These results approximately agree with those measured in (Reference 19) and indicate that JP-4 emulsions with 2.7 - 3 percent water as the external phase have flame propagation velocities approximately 60 to 150 times slower than JP-4 liquid.

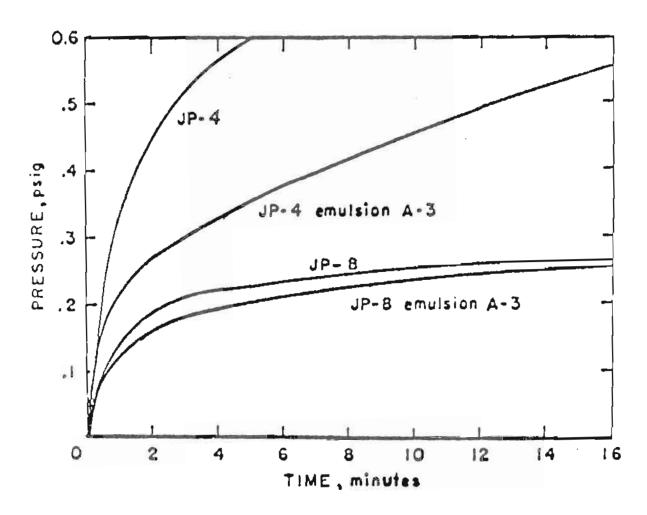


FIGURE 46 Vapor Pressure Versus Time for Liquid and Emulsified Fuels by Modified Reid Vapor Pressure Method.

SECTION IV

EMULSIFIERS

A. BACKGROUND

As discussed in previous sections, thickening of JP-4 can reduce evaporation and burning rates. However, the greatest problem to be overcome for fuel neutralization is how to mix the water and emulsifier with the JP-4 fuel. The water and emulsifier can be mixed by adding the two materials together in the water tank on the fire truck or mixing the two materials as the water is pumped from the tank. The emulsifier can be added to the water - AFFF mixture, so that the emulsifier drains with the water from the foam bubbles. In that case, the emulsifier must be compatible with the surfactant in the AFFF.

The difficult part is mixing the water, emulsifier and JP-4 together, since there will be limited energy and turbulence available as the liquids flow together. Considerable work has been conducted on emulsifiers for dispersants of oil spills at sea. Dispersants have been in existence for sometime, under various names; dispersants, emulsifiers, detergents, and degreasers are all names for the same thing.

Dispersing agents are those compounds which emulsify, disperse, or solubilize oil into the water column or act to further the surface spreading of oil slicks in order to facilitate dispersal of oil in the water column. Whatever they are called, dispersants consist of three primary components surfactants, solvents, and stabilizers. The surfactants alter the interaction between oil and water so that oil spreads can be more easily dispersed into small globules. Surfactants are either hydrophilic (water-compatible) or lipophilic (oil-compatible). They can be divided also according to atomic structure, being either anionic, cationic, or The anionic surfactants compose the largest group nonionic. in use since the anion is quite surface-active. Usually these dispersants are alkalai salts of sulphates or sulphonates. Cationic surfactants have a low surface activity as do the nonionic ones. However, the nonionic ones have been found to be the most effective in saline water oil spills, being composed of fatty alcohol condensates with ethylene oxide the most common.

The second primary component of a dispersant, the solvent, comprises the bulk of the product. The solvents enable the active agent (surfactant) to mix and penetrate

into the oil and form an emulsion. The solvents range in base from petroleum to water, petroleum solvents being the ones which dissipate most rapidly in a water environment.

A certain amount of mechanical mixing energy is generally required in order to get the dispersant into the water. In the past, helicopters and tugboats or other large powerful boats were flown over or driven through the spill in an effort to cause dispersion. In the U.K. the use of batter boards towed behind boats have proved very effective. Obviously, in high-sea conditions the mixing energy is no problem. Under such high-sea conditions, dispersants have found to be very effective.

For application to JP-4 fuel spills, it would be necessary to find a system where minimum energy was required to form the JP-4/water emulsion. G.P. Canevari, in Reference 21, an article in the proceedings from the 1975 Conference on The Prevention and Control of Oil Pollution wrote about the feasibility of self-mixing dispersants which, if perfected, could reduce the problem of supplying mechanical energy. A self-mix dispersant is oil-compatible and is applied directly to the oil. It utilizes the diffusion energy of the surfactant, acting where the oil-water interface contacts the water. self-mix formulation contains a particular surfactant component which enables the interfacial area, the most critical area in the dispersant process, to be more readily broken down. Thus, mechanical mixing energy is not needed. Canevari points to the formation of uniformly-sized droplets due to a constant energy source as another major advantage of the self-mix system. These small uniform droplets enhance the behavior, movement, and stability of dispersants as well as minimizing ecological and toxicological effects by getting the oil into the water column and dispersed more rapidly. Canevari concludes, "The ability of self-mixing has been well established and documented during the past several years."

Discussions with Canevari at Exxon indicated that finding the proper self-mixing emulsifier was a trial and error process. If a self-mixing emulsifier can be found which will form a water/JP-4 emulsion, it will enable the surface of the fuel to be neutralized. The emulsifier can be found which will form a water/JP-4 emulsion, it will enable the surface of the fuel to be neutralized. The emulsifier can be mixed with the AFFF. It will also be possible to emulsify halon materials into the water of the AFFF, as well.

B. DISPERSING OIL BY CHEMICAL DISPERSANTS

It is worth discussing the mechanism of dispersing surface oil slicks by chemical dispersants to see how it can

apply to the Fuel Neutralization Program. The dispersion of surface oil films as fine oil droplets into the water column is promoted by the use of a chemical dispersants. This oil spill dispersant consists primarily of a surface active agent (surfactant) and a solvent. The solvent is added as a diluent or vehicle for the surfactant. It also reduces the viscosity and aids in the uniform distribution of the surfactant to the oil film.

A surfactant is a compound that actually contains both water-compatible (hydrophilic) and oil-compatible (lipophilic) groups. Due to this amphiphatic nature, a surfactant locates and arranges itself at an oil-water interface, as schematically shown in Figure 47. The surfactant's molecular structure, e.g., ratio of hydrophilic to lipophilic portion, determines the type of dispersion (oil droplets dispersed in water phase or water droplets dispersed in oil phase), as well as stability of the dispersion. In essence, a surfactant that is principally water-soluble disperses oil-in-water and establishes water as the continuous phase; a surfactant that is principally oil-soluble, the converse. This is Bancroft's Law (Reference 22), which has been tested and proven empirically true over the years.

For fuel neutralization, it would be most desirable to form an oil-in-water emulsion, or specifically, a JP-4-in-water emulsion. In this way, the least amount of water would be required to thicken the fuel, and the evaporation of the JP-4 would be reduced, since each JP-4 droplet would be surrounded by a continuous water film.

A convenient classification for surfactants is based on the ratio or balance of the water compatible portion to the oil-compatible portion - sometimes referred to as HLB (Hydrophilic - Lipophilic Balance) by Becker (Reference 23). This relationship between the molecular structure of the surfactant and the emulsion type is also shown in Figure 48 and the physical concept behind Bancroft's Law may be appreciated. For example, it can be visualized that for a more water-compatible surfactant, the physical location of the larger hydrophilic group on the outside of the dispersed oil droplets results in a more effective "fender" to parry droplet collisions and prevent droplet coalescence.

The converse, locating the larger portion of the surfactant in the dispersed rather than continuous phase, would be geometrically awkward and unstable (Reference 24).

The mechanism of oil slick dispersion by the application of chemical dispersants has been covered in some detail by Poliakoff (Reference 25) and Canevari (References 26, 27, 28),

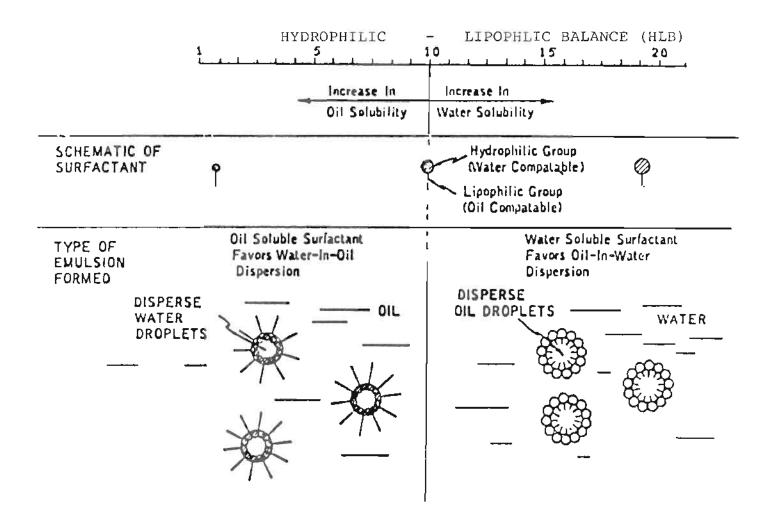


FIGURE 47 Influence of Surfactant Structure on Type of Dispersion.

among others. From the above discussion, one can see that the chemical dispersant (surfactant) will locate at the oil-water interface and reduce interfacial tension. This will then increase the spreading tendency of the oil film. More important, it promotes fine droplet formation which can be expressed as:

$$W_k = A_0/w \gamma_0/w$$

Where:

 W_k mixing energy, ergs A_0/w interfacial area, cm^2 Y_0/w interfacial tension, dynes/cm

Thus, for the same amount of mixing energy, a reduction of $\gamma_{O/W}$ will result in a corresponding increase in $A_{O/W}$.

It is important to emphasize that, the chemically dispersed oil does not sink. Rather, the surfactant merely enhances small droplet formation for a given amount of mixing energy. Smaller diameter oil droplets have a much lower rise velocity per the familiar Stokes Law. Hence, once the oil is chemically treated, and placed 3 to 5 feet below the surface of the water by the mixing process, it does not rise to the surface as readily, as illustrated by Figure 48. In the case of fuel neutralization, emulsified water and/or halon droplets will float on and in the JP-4. Due to Stokes Flow, they will settle very slowly, because of their greater density. But in the short time required to extinguish the fuel fire, they will not sink to the bottom of the fuel pool, if the droplets are small.

An example calculated to illustrate this effect of surfactants was presented by Canevari (Reference 29). If the above droplet equation is applied to a mixture of 100 gallons of sea water and 1 gallon of gasoline, the relationship between droplet size, D, mixing energy, $W_{\rm K}$, and interfacial tension, $\gamma_{\rm O/W}$ may be noted as follows:

 $\gamma_{\text{O/w}}$, Gasoline-Water Interfacial Tension = 48 dynes/cm; Wherein:

D, Dispersed Gasoline Droplet Diameter

= 150 microns

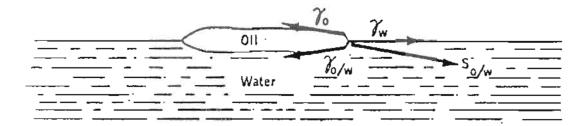
n, Number of droplets
Aw/o, Interfacial area
Wk, Work

= 2.14×10^9 = 151 square meters = 48 dynes/cm x 151 m²

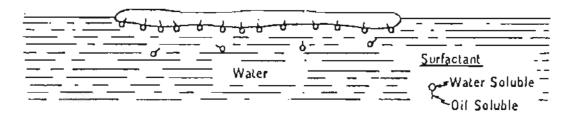
 $= 7.26 \times 107 \text{ ergs}$

= 5.35 ft lbs.

a) Oll Spill



b) Dispersant Reduces Interfacial Tension



c) Agitation Readily Forms Oil Droplets

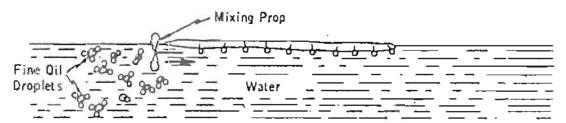


FIGURE 48 Dispersant Enhances Droplet Formation.

The above 150 micron oil droplet would have a rise rate of approximately 4 inches/minute in the water column. If a surfactant is added to the above system that would reduce the interfacial tension to a value of 7 dynes/cm, the resultant oil droplet diameter for the same mixing energy would be 22 microns. This "surfactant-stabilized" 22-micron oil droplet would now have a corresponding rise (or fall rate for water) of only 0.086 inches/min.

Many surfactants will aid in the formation of fine droplets in the above manner. It has already been noted that the surfactant structure (Hydrophilic - Lipophilic Balance) influences the efficiency of the emulsifier. However, a more subtle and less tractable requirement for an effective dispersant is the prevention of droplet coalescence after the fine oil droplets are formed. For fuel neutralization, the droplet emulsion need only be stable for relatively short times required to extinguish the fuel fire and inert the fuel until personnel and equipment are removed from the area. The above discussion regarding the dispersion mechanism for emulsions, cited the need for mixing energy, Wb. For oil spills, this is normally supplied by means of a work boat applying the chemical. However, consider the rate by which this work is accomplished by the boat's wake and propeller. A typical work boat may apply energy to a swath 50 feet wide at a speed of 5 knots, thereby only mixing 35 acres per hour of ocean. Therefore, in recent years, research has been directed at eliminating the need for the tedious, time consuming mixing process.

Canevari of Exxon has developed a "self-mix" dispersant formulation that requires essentially no energy to be applied to the oil-water interface to generate a dispersion of fine oil droplets. This has greatly enhanced the scope and potential of chemical dispersion particularly for large spills. For example, since mixing is no longer needed, aerial application alone would be feasible. If these self-mix surfactants are applied to the Fuel Neutralization Program, they could emulsify water and/or halon into the surface of the JP-4 fuel pool without mixing energy being required.

C. MECHANISM OF SELF-MIX DISPERSANTS

The mechanism of the self-mix chemical dispersants goes beyond the simple thesis represented by the droplet equation. In an ideal no-mixing system, true spontaneous emulsification (or "self-mixing") is postulated to occur in the following manner. The chemical surfactant formulation is made compatible with the oil. However, when the oil phase comes into contact with a water boundary rather than air, part of the surfactant has a strong driving force to diffuse into the water phase. In this transport process, a small amount of oil "associated" with the surfactant is carried into the water phase. A

continuation of this process produces a series of fine oil droplets migrating from the oil phase into the water phase as schematically shown by Figure 49.

In the graphical presentation of Figure 49, the surfactant formulation can be seen to be compatible with the oil phase as shown in (A). However, due to the nature of the specific compounds, there is a driving force for part of the formulation to diffuse into the water phase when it contacts an oil/water interface (B). During this diffusion, some oil associated with the surfactant as fine oil droplets, is carried along with the surfactant into the water column as shown in (C). In essence, a three-component system (oil, water and surfactant) is formed at the interface. As the surfactant diffuses into the water phase, the associated oil is thrown out of solution.

The migration of the surfactant from the oil into the water phase (in essence, the source of energy for spontaneous emulsification) comes from the redistribution of materials. For this system to work, the surfactant must be brought into contact with the internal phase.

As the surfactant diffuses through the interface, a reduction in interfacial tension occurs. Over the entire oil/water interface, there are dissimilar values of interfacial tension due to the somewhat random diffusion of the surfactant at varying sites along the interface. Any difference in interfacial tension produces a spreading pressure, which causes rapid movements of the interface. This interfacial turbulence also aids in the dispersion of the oil into the water phase.

Discussions with Canevari at Exxon indicated that finding the proper self-mixing emulsifier was a trial and error process. Therefore, find a self-mixing surfactant for fuel neutralization will require an experimental program in Phase II. If a self-mixing emulsifier can be found which will form a water/JP-4 emulsion, it will enable the surface of the fuel to be neutralized. The emulsifier can be mixed with the AFFF. It will also be possible to emulsify halon materials into the water of the AFFF as well. Considerable work was conducted on fuel gelling by the U.S. Army. Mr. Forest Schaekel was contacted in regards to the Army research. Recent work was related to gelling fuels with water emulsions. Two emulsifiers used by the Army are manufactured by the Clintwood Chemical Company and Scher Chemical Company. Various emulsifiers were obtained from the companies and experiments were performed to gel various fuel mixtures. It was found that mixtures of water and fuel become very viscous and

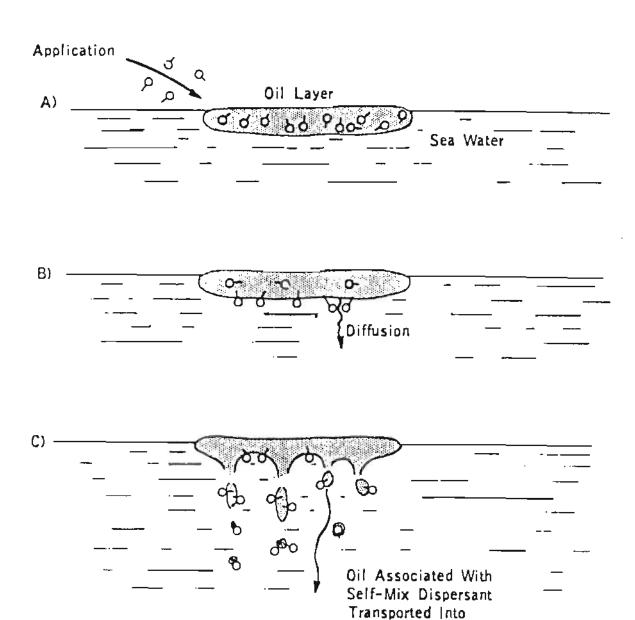


FIGURE 49 Mechanism of Self-Mix Dispersion

Water Phase As Fine Droplets thickened the mixture considerably. The emulsifiers tested, required mixing energy and the ideal emulsifiers would be self-mixing. Therefore, more experiments would be required to find the optimum emulsifier for the Fuel Neutralization Program. It was possible, however, to significantly thicken the fuel with small amounts of water and emulsifier.

SECTION V

GELS FROM SOLID MATERIALS

Considerable work has been conducted on sorbents for oil spill removal at sea. It was felt that this work could be related to the problem of JP-4 spills, therefore, a literature search was performed. Mr. Gerard Canevari of Exxon was contacted to discuss his work related to the absorption on oil spills.

Work by Schatzberg and Nagy (Reference 30) at the Naval Ship Research and Development Laboratory was reviewed. They studied the use of various inorganic, natural organic and synthetic organic products for their use as sorbents. Their results showed that synthetic organic sorbents were the most efficient. Since they are combustible they may contribute to the fire, therefore, inorganic products would be more suitable. However, inorganic sorbents can absorb three to five times their weight in oil. There were no test data on JP-4 and it would be necessary to conduct tests on these absorbents before any conclusions can be made about the use of these materials for fuel neutralization.

A. SOLID MATERIALS

Solid materials can be sprayed on the JP-4 spill to absorb the fuel and form a thickened mass. For example, it would be possible to spray sand into the fuel spill and thicken the fuel. The difficulty with this method would be the amount of sand which would have to be applied. from sinking oil spills at sea (Reference 31), indicate that an equal weight of sand would be required to sink fuel oil. At these ratios, the amount of material required makes this approach impractical. Further, even if a ratio of 1 to 5, or one part absorbent to 5 parts oil were possible, a tremendous amount of material would have to be applied in relation to fire extinguishants now being used. Since the greatest problem in extinguishing a postcrash fire is getting the fire trucks to the crash site quickly, the added weight would be overly restrictive. Consider it from another point of view, use of solid absorbents or any fuel neutralization additive for that matter, will require the reduction of the amount of AFFF the fire trucks can carry. Therefore, any additive must be more effective on a weight basis than AFFF. Most solid absorbents will only absorb the JP-4 fuel to thicken it. They will not retard the fire chemically, unless dry chemicals are used as the solid absorbent. From discussions, it appears that use of dry chemical is undesirable due to

compatibility with the jet engines. Therefore, it appears that inert solid absorbents would not be efficient enough to be effective fuel neutralizers. Naturally, it is possible that some solid absorbent, such as silica gel could be slurried with the AFFF and improvements could result as found in halofoams (Reference 7).

Another point, is that results by Fiala (Reference 6) showed that thicken fuel surfaces retarded the flow of AFFF so that the net result could be counterproductive to fire extinguishing. It is worthwhile to conduct some experiments in Phase II to verify some of the above conclusions.

Materials, such as silica, clays, or vermiculite can be slurried with the water used in the AFFF. These materials will drain into the fuel surface and gel the JP-4 fuel surface. While these materials are effective gelling materials, the question which has to be addressed is whether more effective results for fuel neutralization will result by some other method.

B. SOLID ABSORBENT MATERIALS

Results of (Reference 30) showed that polyurethane foams and polyethylene fibers were the most effective in absorbing oil spills. These materials are able to absorb 10 to 65 times their weight of Number 2 fuel oil. No tests were conducted for JP-4, except results showed that absorption decreased with more volatile oils. Even if it were assumed that a material could absorb 65 times its weight, it would take almost 4000 pounds of absorbent to gel a 250,000 pound JP-4 spill. These foams would be low density and therefore, bulky and difficult to disperse. Further, they would be highly combustible and, therefore, counterproductive as a fire extinguishant.

Another possibility would be to use these absorbents as a carrier for a material like halon 2402. The absorbents would absorb the halon, and the halon and absorbent would be slurried with the AFFF or sprayed separately. When the halon and absorbent reach the JP-4 surface, the halon would dissolve in the JP-4 and the absorbent would thicken the JP-4 spill.

Discussion with Dow Chemical related to their development of a material which swells on contact with JP-4. This material holds 10-20 times its weight of JP-4 and upon swelling, forms a fuel gel. Dow experimented with these absorbents saturated with fire-retardant materials such as halon 2402.

Materials like the Dow product, can be swelled with 2402 and mixed with the AFFF. The 2402 will dissolve in the JP-4 and absorb the JP-4 forming a fuel gel. Since the fire retardant is more volatile than the JP-4, it will evaporate and form a fire-suppressing vapor above the fuel. The solid absorbent materials can be slurried with the water used in the AFFF. Dow had little data on their material and therefore, quantitative data would have to be generated by experiments, during the Phase II effort.

It seems that the same process could occur more directly by simply emulsifying the halon into the water/AFFF. The halon/water will drain into the surface of the JP-4 spill and the halon will dissolve in the JP-4, while the water will emulsify and thicken the fuel surface.

SECTION VI

CHEMICAL KINETIC MODIFYING ADDITIVES

National Bureau of Standards has been doing considerable research on fire extinguishants over many years. A number of reports were reviewed concerning chemical kinetic modifying additives and dry chemicals. Some superkinetic modifiers, tested by NBS, are an order of magnitude better flame retardants than the halon materials. Unfortunately, little is known about the toxic effect of some of these materials. However, the performance of the superkinetic modifiers was so impressive that they should be evaluated further.

A. EFFECT OF ADDITIVES ON THE SPONTANEOUS IGNITION OF AIRCRAFT FUELS

Combustion processes may be altered radically by the addition of certain additives, but so far comparatively little work has been applied to the study of aircraft fuel problems.

Egerton and Gates (Reference 32) showed that 2.5 g/liter of lead tetraethyl raised the spontaneous ignition temperature of benzene by 18°, cyclohexane by 27°, heptane by 83°, and petrol by 82°. Using a concentration of 2 g/liter, Weerman (Reference 33) showed that it raised the spontaneous ignition temperature of petrol by about 100°, although Ormandy and Craven (Reference 34) had reported a decrease of 14° in the spontaneous ignition temperature of heptane when using the same additive in similar concentrations.

Weerman (Reference 33) also tested a large number of organic compounds of 22 elements, including lead, iron, mercury, bismuth, selenium, boron, chromium, tin, zinc, nickel, cobalt, and aluminum, as petrol additives. Increases of spontaneous ignition temperature of as much as 170°C (for iron pentacarbonyl) were reported.

Frank and Blackham (Reference 35) determined the effect of many amines, phenols, halogen compounds and other organic compounds on the spontaneous ignition temperature of dodecane. Lead tetraethyl was most effective in raising the spontaneous ignition temperature and several compounds; for example, p-nitroaniline and benzaldehyde, reduced it slightly.

Various workers have reported the ability of various organic nitrites and nitrates to reduce spontaneous ignition temperatures.

Thomas (Reference 36) measured the minimum pressure necessary to produce ignition of aviation fuel SR 312 containing various additives at 260°C. The undoped fuel ignited at a pressure of 4 psia. The addition of 1 percent of N-methylaniline only increased the pressure necessary to produce ignition to about 4.5 psia, while 10 percent of the same additive increased the limit to 9.7 psia. Dicyclopentadiene even at a concentration of 10 percent produced no effect. Lead tetraethyl was by far the most effective additive investigated and a concentration of 3 mg/Imp. gal increased the limit to 5.9 psia.

Work at the Boeing Company (Reference 37) on the spontaneous ignition of aviation fuels included an investigation of the effect of a number of additives. Of these, tetraisopropyl titanate was found to be the most promising. Tests using 0.25 percent of the total vapor of this material in a 0.23 cubic foot vessel showed an effectiveness equal to about 70 percent nitrogen dilution.

Sponsored work on fuels carried out by Shell Research Limited, was extended to include a study of the effect of various additives (Reference 38). It was shown that the blend of additives normally added to aviation fuels to reduce problems of icing, corrosion, etc., had no significant effect on the pressure needed to produce ignition in a 12 inch sphere at 250°C and 3:1 air-fuel ratio.

One percent of isopropyl nitrate produced a slight lowering of the pressure limit (4.1 to 3.75 psia). One percent by weight addition of iodoform, t-butyl acetate, p-cresol, bromoform and 4.4 methylene bis 2.6 ditertiary butyl phenol produced only insignificant raising of the limit, as did a blend of 1 percent t-butyl hydroperoxide with 1.5 percent of ethylene dibromide. One percent of tetraisopropyl titanate was also found to be effective, in contrast to the Boeing work. N-ethyl aniline raised the pressure limit from 4.1 to 9.3 psia, but only at a concentration of 10 percent by weight. One percent of methyl cyclopentadienyl manganese tricarbonyl. A concentration of 0.25 percent of the latter raised the limit to 8.7 psia.

One other important group of compounds inhibiting ignition is the amines. Amines inhibit the ignition of acetaldehyde/oxygen (Reference 39) and of diethyl ether/oxygen (Reference 40) in the low temperature region, the order of effectiveness being secondary > primary > tertiary. Both aromatic and aliphatic amines have been investigated for possible antiknock properties. They are considerably less effective than organometallic compounds in this, however, and lead tetramethyl is claimed to be 118 times as effective as aniline in suppressing knock (Reference 41). Salooja (Reference 42)

attributes the effectiveness of amines in inhibiting combustion to the conversion of active radicals to stable molecules by reaction with the hydrogen atom of the amino group. Differences between various amines are due to the case with which this reaction occurs and also to differences in stability of the amino radical so produced.

B. FLAME INHIBITION

From a mathematical model by Hastie (Reference 43), a figure of merit for an inhibitor, using burning velocity data, may be defined as:

$$\phi_{V} = \frac{[0]}{[1]} \frac{\delta V}{V_{O}},$$

where ϕ_V is the figure of merit for the inhibitor,

[0₂] is the initial oxygen concentration,

[I] is the initial inhibitor concentration,

Vo is the burning velocity in the absence of any inhibitor, and

δV is the change in burning velocity due to the presence of the inhibitor.

It is assumed that the flame is slightly fuel rich, i.e., the H atom is the dominant radical.

In practice, ϕ_V correlates with other measures of inhibitor effectiveness, such as blow-off limits and extinction limits for halogen inhibitors. It also follows from the definition of ϕ_V that the degree of inhibition should be proportional to the amount of inhibitor added to the flame. Experimental observations (e.g., see Lask and Wagner; Reference 44), show that this is approximately valid for a variety of homogeneous inhibitors.

Values of ϕ_V for a selected variety of inhibitor types have been calculated from the data of Lask and Wagner (Reference 44), and unpublished date of Wagner cited by Morrison and Scheller (Reference 45), for n-hexane fueled flames, and D. Miller et al. (Reference 46), for H₂ fueled flames. The values listed in Table 2 are given in approximate order of increasing effectiveness as flame inhibitors and we shall refer to this table later when discussing specific inhibitor types.

Only for CO₂ can the degree of inhibition be explained in terms of a physical effect such as cooling. The magnitude of ϕ_V greater than unity for the other inhibitors can only be explained in terms of chemical effects. Common commercial extinguishants such as Freons have ϕ_V values similar to the value of 8.4 given for Br₂. Of the two flame types considered

TABLE 2 RELATIVE EFFECTIVENESS, $\varphi_{\mathbf{V}},$ OF SELECTED FLAME INHIBITORS

Inhibitor *	Flam	e type
	n-hexane/air a φ.	H _z -air h φ _z
CO ₂	0.86	
CL	1.8	4-0.26
Si(CH ₂) ₄	3.9]
CCL	4.2	1
Br ₂	8.4]
SiCL	10.5	3.5
(CH ₄) ₂ PO ₄	23	1
SbCl _b	26	1
TiCL	30	10
SnCL	31	12.9
POCL	31	7.2
PCL	39	4.5
PB _{rs}	39	
CrO ₂ Cl ₂	≥ 244	
Fe(CO)	356	19
РЫ(СаНа)а	390	

^{*} From data given by Lask et al. . for a stoichiometric mixture.

From data given by D. Miller et al. for a mixture with 1.75 fuel equivalence ratio.

^{*} Amounts of inhibitor used varied from 0.015 percent to several volume percent.

⁴ Negative sign indicates flame speed increase rather than decrease.

in the table the n-hexane/air system more closely resembles the chemical conditions likely to occur in practical fire situations.

Halogen systems are among the most widely used commercial reagents for fire prevention and extinguishment. For example, one can cite (a) the early use of CCl₄ as a portable source of fire extinguishment; (b) the current use of Freons such as CF₃Br as an extinguishant particularly in connection with fuel fires associated with aircraft mishaps, and also for the protection of electronic equipment; and (c) the incorporation of phosphorushalogen or antimony halogen (among others) formulations in materials.

Halogen systems have also received the most attention by workers interested in the basic mechanism of flame inhibition. The present discussion is restricted to the retardancy aspects that involve vapor-phase chemistry in the inhibition process.

In practical fire systems the halogens can be mechanically introduced to the gas phase as with Freon protection systems, or by chemical means, as with the release of HCl from decomposing poly-vinylchloride, or as phosphorus chlorides or oxychlorides formed during decomposition of a polymer substrate, or as antimony halides from polymer substrates.

As is evident from the high ϕ_V values given in Table 2, halogen species rank as chemical inhibitors and must therefore interfere with the chemistry associated with flame propagation. Some clues as to the nature of this interference are provided from macroscopic observations such as: (a) the effectiveness of halogens increases in the order fluorides << chlorides < iodides (b) CF3Br is about four times more effective than CF4 in preventing combustion of n/hexane air mixtures; (c) CF3Br is a good inhibitor in hydrocarbon-air flames but is mediocre in H2-air flames; (d) Br2 has very little effect on CO-O2 flames but is effective when small amounts of H2 are introduced; and (e) in Br-substituted hydrocarbons and fluorocarbons the inhibitor effectiveness increases with the number of Br atom substitutions and, in certain instances, can be directly proportional to this number. For example, in a stoichiometric methane-air flame, the following ϕ_V values are found: Br [24], CHaBr [12], HBr [11], CF3Br [17]. The high value for CF3Br seems anomalous and this has been attributed to a possible role of the CF3 radical in flame inhibition.

It is apparent from the classification of inhibitor effectivensss given in Table 2 that nonhalogenated compounds such as $(CH_3)_3PO_4$, $Pb(C_2H_5)_4$ and $Fe(CO)_5$ are one to two orders of magnitude more effective than halogen inhibitors. However, systems of this type have not yet been utilized in practice,

except that lead tetraethyl has been used to modify the preignition knocking phenomena of internal combustion systems. It is not unreasonable to speculate that the modes of action in flame inhibition and knock prevention may be related. Unfortunately, despite considerable experimental effort, the mechanism of knock inhibition has not been definitively established.

The metal and phosphorus halides indicated in Table 2 also show a degree of inhibition which is in considerable excess of what can be accounted for in terms of their halogen content. This is particularly evident in the ${\rm H}_2$ -air flame where Cl₂ itself does not provide any flame inhibition. is clear that the metals and phosphorus can themselves lead to flame inhibition and, more importantly, to a much greater degree than the halogen inhibitors. The two order of magnitude difference in ϕ_V between Si(CH₃)₄ and Pb(C₂H₅)₄ suggests that the inhibition mechanism is particularly sensitive to the properties of the metal itself. In fact, some metals show no inhibition at all. For example, the addition of several percent of Al₂Cl₆ vapor to premixed fuel-rich CH₄/O₂ flames produced a reduction in burning velocity that could be accounted for entirely from the amount of halogen present (Reference 47).

Metals such as Fe, Cr, and Ti, and their oxides, have low vapor pressures under normal flame conditions and their introduction to flames can result in the formation of condensed particles. These particles are highly luminous and are readily observed in the region of the reaction zone and the post flame gases. It has been argued, therefore, that these metals perturb the flame chemistry via heterogeneous rather than homogeneous reactions. A clue to the possible effectiveness of heterogeneous, as opposed to homogeneous inhibition, is provided by the observation of Jost et al. (Reference 48), where the flame inhibiting effect of Fe(CO) a reached a limiting upper concentration level. At the higher concentration levels, condensed particles should form and the decreased rate of effectiveness with composition implies that heterogeneous inhibition is less effective than homogeneous reactions. The question of heterogeneous versus homogeneous inhibition has received considerable attention in connection with the function of the commercially used solid extinguishants such as the alkali metal bicarbonates.

It is found that about 10^{-3} mol fraction of powdered alkali metal salts such as K_2SO_4 , Na_2CO_3 , $KHCO_3$, and $NaIICO_3$ can reduce the flame speed of CH_4 -air flames by 50 percent. Thus ϕ_V factors of about 100 are indicated. Powders of alkali metal salts are also found to be more effective on a weight basis than CF_3Br in a counterflow diffusion flame (Reference 49).

Their effectiveness usually follows the order Li<Na<K<Rb. Carbonates are observed to be twice as effective as the alkali metal chlorides.

Flame temperature calculations (Dodding et al.; Reference 50) show that the effect of decomposing NaHCO3 on flame cooling is small and that the mode of inhibition must be chemical in nature. In general, the smaller the initial particle size of the powder introduced to the flame, the greater the degree of inhibition found (e.g., Dodding et al.; Reference 50; and Rosser et al.; Reference 51).

From these observations, arguments have been given in favor of both solid and vapor phase inhibition mechanisms. Rosser et al. (Reference 51) favored a gas phase mechanism, since they calculated that under flame conditions an appreciable vaporization and dissociation of the solid powders should occur. The more recent study of Birchall (Reference 52) using town gas-air flames also supports this view.

His observations of a relatively high efficiency for the alkali metal oxalates was accounted for by a model where the reactions resulted in the production of submicron size carbonate particles within the flame. These particles would then readily vaporize and decompose to yield the active inhibitor species. The following order for the effect of the anion on the alkali metal efficiency was indicated: oxide (i.e., oxalate) >cyanate>carbonate>iodide>bromide>chloride>sulfate>phosphate. This order represents the ease with which the alkali metal can be released to form the active species.

Fiala (Reference 6) also presents results of inhibition efficiencies of chemical compounds which is shown in Table 3. For comparison, the inhibiting efficiency of CCl4 (carbon tetrachloride) was chosen as 1 and the efficiencies of the other substances was expressed by the ratio of efficiency of the substance to that of CCl4. Unfortunately, little is known about the toxic effect of some of these materials. However, the performance of the superkinetic modifiers is so impressive, that it is felt that they should be evaluated further as possible additives for the Fuel Neutralization Program. Experimental testing would have to be conducted in the Phase II Program.

TABLE 3
EXTINGUISHING EFFICIENCIES OF CHEMICAL COMPOUNDS

Compound	Efficac	y c.	E.	C	Ε.
	0.1	киоз	1.4	(C ₂ H ₅) ₃ PO ₄	5.1
sio ₂	0.2	кЈ	1.6	(CH ₃) ₃ PO ₄	5.3
co ₂	0.2	CuCl ₂	1,9	K2C2O4 · H2O	5.8
so ₂	0.3	CH3Br	1.9	PBr 3	6.0
HC1	0.4	HBr	1.9	spc13	6.3
SIHCl	0.5	Na 2SIF6	2.1	K ₂ CrO ₄	6.3
NaCl	0.5	кнсо	2.3	NajAlF ₆	6.6
NH4C1	0.5	Na2C204	2.3	РРО	7.2
CHC13	0.7	K ₂ SO ₄	2.3	POC1 ₃	7.3
СОМФИ	0.7	CH2BrCl	2.4	TiCl4	7.3
socl ₂	0.8	sic14	2.5	BBr3	7.7
SF ₆	0.8	CP ₂ BrCl	2.7	к ₂ с ₂ о ₄	8.3
KC1	0.9	Alc13	2.8	K ₃ AlF ₆	8.8
Na 200 1	0.9	GeC14	2.8	PC1 ₃	9.7
ccl	1.0	SnCl ₄	2.8	PSBr ₃	9.3
so ₂ cl ₂	1.0	Ba (NO3) 2	3.0	PSCl3	10.6
с ₂ н ₅) 2. so ⁴	1.2	CP3Br	3.2	Ha2 [Fe (CH) 5NO] + 2H2O	15.5
KBr	1.2	x ₂ co ₃	3.2	K4Fe(CH)6.3H2O	16.4
NaHCO ₃	1.2	AsClg	3.6	K4Ee (CH) 6	46.1
s ₂ cl ₂	1.3	Na2SO3	3.9	cro ₂ cl ₂	57.5
I (CH ₃)	1.3	CF2Br2	4.5	Fe (CO) 5	81.2
				Pb(C2H5)4	98.6

SECTION VII

FUEL NEUTRALIZATION THROUGH USE OF CHEMICAL KINETIC MODIFIERS

Nowack (Reference 53) discusses the reduction of flammability of jet fuel vapors through the use of halogenated compounds in the fuel. This approach is centered around adding a halocarbon to the fuel vapor, not by means of direct injection into the atmosphere but by adding the halocarbon directly into the fuel. This approach can be applied to fuel neutralization by injecting the halocarbon into the fuel pool by emulsification with AFFF, absorption with solid absorbents or encapsulation. The halocarbon must be selected on the basis of certain physical parameters, which are its degree of volatility and flame-extinguishing characteristics.

To illustrate how the vapors of a fuel may be made inert by adding halocarbons into a fuel, reference must be made to the flammability envelope of certain fuels. Figure 50 depicts the flammability ranges of JP-4 and JP-5.

It can be seen that there are regions in which a fuel will provide sufficient vapors relative to the amount of air in order to provide a combustible condition. The ratio of fuel vapor-to-air depends upon the distillation characteristics and temperature of the fuel and the air pressure condition (altitude).

The region of flammability is bordered by the limiting extremes of these fuel vapor-to-air ratios, identified as the lean and the rich limits. Further observation shows that to provide a noncombustible vapor, these limits would have to coincide. The addition of a halocarbon to a fuel will narrow these limits depending upon the concentration of the halocarbon and its particular efficiency in flame extinguishment. To obtain some reference point, a preliminary evaluation of several halocarbons was conducted in an attempt to relate their combustion-abating capacity to some physical property. The investigation was carried out, using a JP-5 fuel with the halocarbon dissolved into it. The fuel and air were heated to 130°F at sea level pressure before exposure to a highenergy discharge spark. The combustion tube in which the vapors were ignited was 4 feet in length and 4 inches in diameter. The concentration of the halocarbon in the fuel was increased until combustion was completely eliminated.

Table 4 illustrates how various halocarbons inhibit combustion of JP-5 fuel vapors. The halocarbons which appear to provide more flame extinguishment per minimum concentration are also the more volatile, as in the case of the difluorodichloro and trifluorobromomethanes.

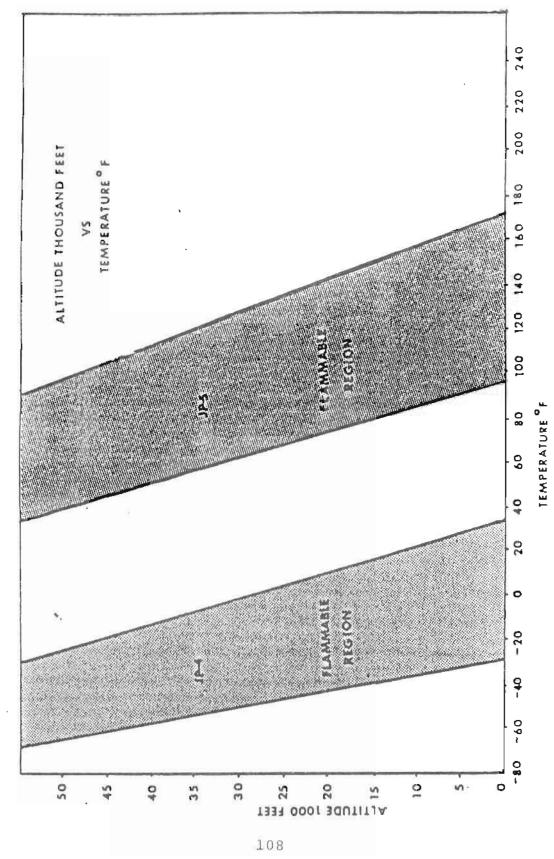


FIGURE 50 Flammability Limits of JP-4 and JP-5 Fuel.

TABLE 4

EFFECTIVE CONCENTRATION OF HALOCARBONS IN KEROSENE TYPE FUEL TO ELIMINATE COMBUSTIBILITY IN A CLOSED SYSTEM

FOUR-INCH DIAMETER COMBUSTION TUBE

PRESSURE: SEA LEVEL

TEMPERATURE OF FUEL: 130°F

HALOCARBON	(CF2Br)2	CH2C12	CF2Br2	CF2BrCI	CF2C12	CF3Br
Molecular Weight	259.9	6.48	8.602	165.4	120.0	6.841
Boiling Point OF	117.5	10H.0	76.1	25.0	-21.6	-72.0
Effective Concentration To Reduce Combustion						
% By Weight	>1.5	1.56	0.65	0.65	0.30	0.35
Concentration Mole %	0.58	0.18	0.31	0.39	0.25	0.235

The degree of volatility can be directly observed from the boiling points listed in Table 4.

A. NARROWING OF COMBUSTIBLE LIMITS

To further observe how the limits of a particular fuel are influenced by the addition of a halocarbon, a more complete study was conducted by obtaining experimental flammability loops at variable concentrations of a halocarbon. Tribromofluoromethane was used to demonstrate the narrowing of the limits rather than difluorodichloromethane since the latter compound was relatively ineffective in narrowing the limits of JP-4 type fuel. The lower temperature combustion limits were such that insufficient vapors of difluorodichloromethane could be obtained to produce a noticeable narrowing of limits at a reasonable concentration of this halocarbon in JP-4.

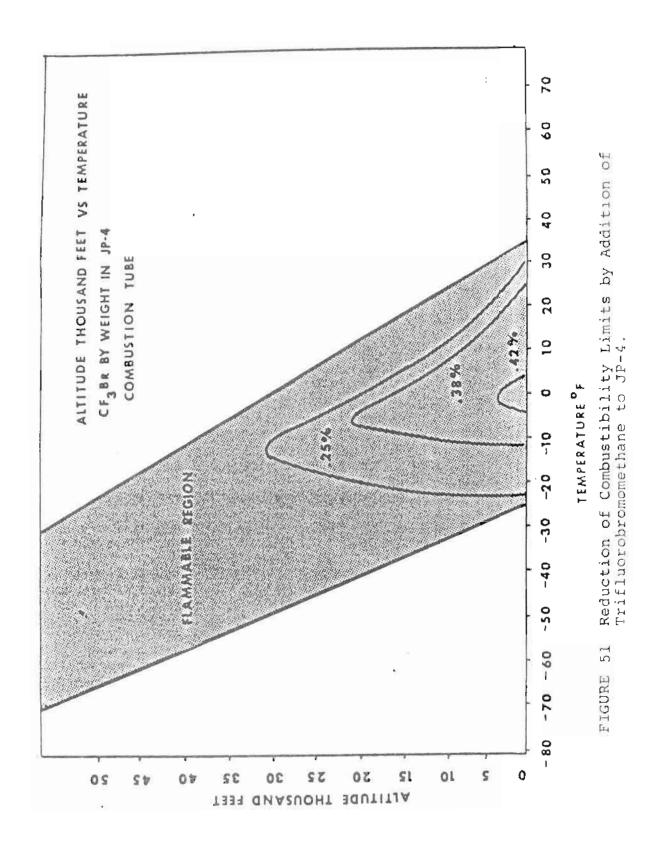
Figure 51 is a complete combustibility envelope with a JP-4 type fuel. Data again was obtained in the combustibility apparatus previously described. The reduction of the combustibility envelopes due to the presence of the halocarbon in the vapor can be seen. Complete elimination of the JP-4 flammability loop can be obtained from 0.45 percent by weight of trifluorobromomethane in the fuel.

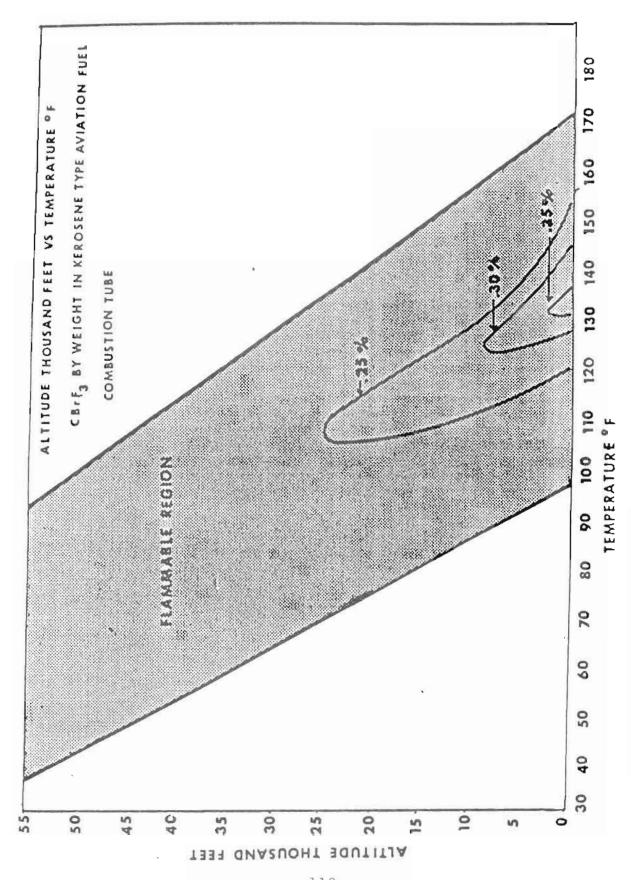
The same experiment again was repeated using JP-5 fuel and the data is shown in Figure 52. Only 0.38 percent by weight of trifluorobromomethane was required to completely eliminate the flammability loop of JP-5.

As a final analysis of these results, it is obvious that small amounts of trifluorobromomethane dissolved in JP-4 or JP-5 fuels can produce an inert atmosphere, in a closed system. However, if the fuel is allowed to sit in an open fuel pool, the volatile halocarbon will evaporate after a period of time. For fuel neutralization, this may not be a problem because the fuel only has to be made inert for a short period of time.

B. ELIMINATION OF FLASH POINT

To further illustrate some of the advantages provided by this method, simple closed-cup flash point studies were conducted. This test indicates the sea level pressure lean flammability limit of fuels in a partially enclosed system with temperature the variable. The degree to which the fuel vapors are inerted may be observed from the change in the flash point. The change increases from the fuel's normal flash point at the lean limit (2° for JP-4 and 135° for JP-5) to a point where no flash is observed. The increase in the flash point





Reduction of Combustibility Limits by Adding of Trifluorobromomethane to JP-5, Kerosene Type Aviation Fuel. FIGURE 52

depends upon the halocarbon and its concentration in the fuel, as shown in Figures 53 and 54.

In interpreting the curves it must be realized that as the lean limit or flash point is increased, similarly the rich limit must decrease. Decreasing rich limits were observed in Figures 51 and 52. Therefore, the line extended from the lean limit reaches a point where it is level, then it extends to the rich limit of the particular fuel (32°F for JP-4 and approximately 155° - 160°F for JP-5). The areas under these curves are regions of flammability. Hence in Figure 53 it can be seen that trifluorobromomethane (boiling point -72°F) is more effective in inerting JP-4 than difluorodichloro (boiling point -21°F) and difluorodibromomethane (boiling point 76°F).

The concentrations of the respective compounds in the fuel by weight to produce an inerted atmosphere were 0.13-0.15 percent, 2.5-2.8 percent and 7.5-8.0 percent. Trifluorobromomethane, which is more effective than the other two compounds, has a much lower boiling point and can therefore provide more inerting vapors than the less volatile compounds. However, if the same three compounds were dissolved in a higher boiling fuel, a different response occurs (see Figure 54). In JP-5 which has a lean limit or flash point at $135^{\circ}F$, the less volatile halocarbon, difluorodibromomethane, (boiling point $76^{\circ}F$), is almost as effective as the more volatile halocarbon. The effective concentrations (by weight) of the particular compounds to completely inhibit a flash of JP-5 were 0.6-0.7 percent difluorodibromo, 0.25-0.30 percent difluorodichloro and 0.2-0.25 percent trifluorobromomethane.

These data infer that the halocarbon used to inhibit a fuel should have a boiling point related to the front end distillation characteristic of the fuel. Ideally, the halocarbon used would not have to be too volatile, so that the time that the fuel would be inerted could be extended.

This same concept could be applied to the superkinetic modifiers discussed in Section VI. Due to their extremely high efficiency at flame inhibition, over an order of magnitude better than the halocarbons, they appear to have considerable promise for fuel neutralization. Since there are no experimental data on this concept, data would have to be developed in Phase II.

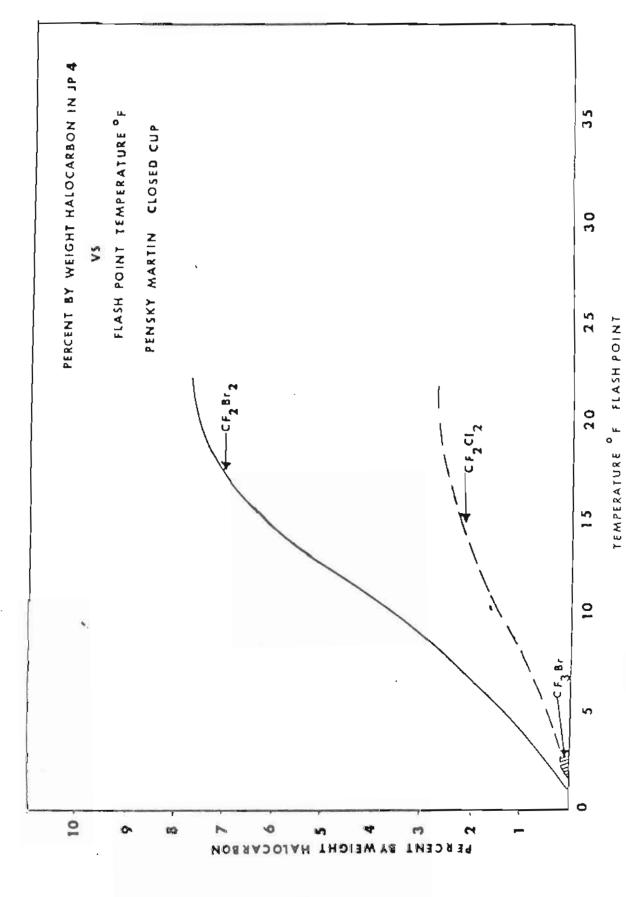
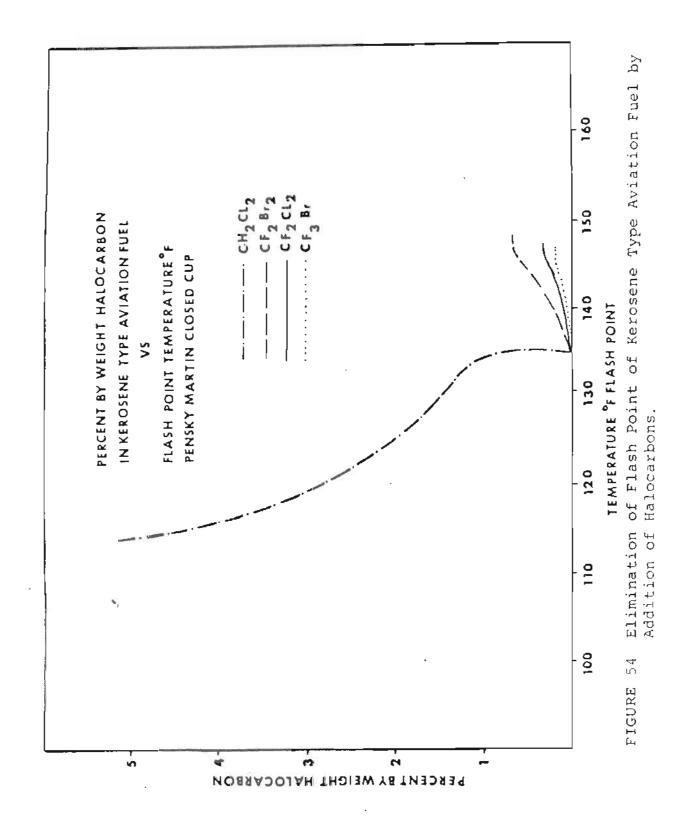


FIGURE 53 Elimination of Flash Point of JP-4 by Addition of Halocarbons.



SECTION VIII

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The objective of the Fuel Neutralization Program was to find a method or additive which will neutralize the unburned JP-4 fuel, during a fire, to prevent it from reigniting. Since AFFF is widely used by the Air Force, the most desirable method would be used in conjunction with the AFFF. The problem with extinguishing aircraft fires is primarily that of getting a limited quantity of extinguishant to the fire site in the minimum time. Since the amount of extinguishant that can be transported to the fire site is fixed by the number and capacity of the fire vehicles, any additive or method must be more efficient, on a weight basis than AFFF.

Water would be one of the most efficient materials for extinguishing fires in flammable fuels, except for its disparity in density which causes it to sink below the burning surface of JP-4. A water film formed by AFFF can reduce the vaporization of JP-4 from the fuel surface. JP-4 can be emulsified with water, several useful conditions can occur: 1) If a JP-4-in-water emulsion is formed, vaporization of the JP-4 fuel droplets would be reduced by the water film around the droplet; 2) The emulsion would result in the reduction of vaporization from the fuel pool and also stabilize the fuel spill so it could be covered The formation of fine droplets causes with the AFFF; and 3) the JP-4-in-water emulsion to float in the JP-4 fuel for longer periods of time before settling. Fine emulsions will be stable and JP-4-in-water droplets can float at the JP-4 surface, forming a fuel-neutralizing barrier.

The JP-4-in-water emulsifier can be added to the water either by premixing or on-line adding to the AFFF. The emulsifier will drain with the water from the foam, forming an emulsion on/in the JP-4 fuel surface. The advantage of such a system will be the small amount, perhaps a few percent by volume, of emulsifier required with the water. Emulsion formation usually requires mixing energy; however, using technology developed to disperse oil spills at sea, it was found that emulsifiers can be self-mixing. Finding a suitable self-mixing emulsifier to form a JP-4-in-water emulsion is an experimental process which will be conducted in a Phase II Program.

Halon materials are extremely efficient at extinguishing fires and flame inhibition. Fiala showed results that halon added to AFFF enhances the foam efficiency. It is also possible to form halon/water emulsions which can be dispersed with the AFFF. The halon/water emulsion will drain from the foam bubbles and form a halon/water emulsion with the JP-4 fuel surface. The halon/water/JP-4 emulsion will inert the fuel surface and form an inert thickened layer in the fuel. Other chemical kinetic modifiers are more than an order of magnitude more effective at flame inhibition than the halons. Most of these modifiers have not been used as practical fire extinguishants, but their outstanding performance merits further evaluation.

Evaporation rate is considerably reduced and flame spread rates are 60 to 150 times lower for thickened JP-4 compared to liquid JP-4. Thickening the JP-4 fuel would increase the time before the vapors would reach their lower explosive limit. Also, thickening the fuel would stabilize the spill and make it easier to cover with an AFFF blanket. Most of the work on fuel thickening was related to the FAA and Army programs for safety fuel. The Army concluded that fuel gelling was not compatible with aircraft fuel systems, because extremely high mixing energy was required to form the gel. Since it would not be possible to vigorously mix the gelling agent into an open JP-4 fuel pool, it was felt that self-mixing emulsifiers would be more applicable for fuel neutralization.

Another method of thickening JP-4 fuel utilizes solid absorbents and solid inorganic materials. Materials, such as silica, clays, or vermiculite can be slurried with water used in the AFFF. The material will drain into the fuel surface and gel the JP-4 fuel surface. Some of these materials absorb and swell upon contact with JP-4, forming a fuel gel. These absorbents can be saturated with fire retardant materials, such as halon 2402, which will dissolve in the JP-4 and absorb the JP-4 forming a fuel gel.

While these materials are effective gelling materials, the question to be addressed is whether more effective results for fuel neutralization will result by some of the other methods outlined. This will require experimental evaluation in Phase II.

The objective of this study was to determine which concepts are the most feasible for fuel neutralization. The most promising concepts include fuel thickening and neutralization by: emulsification with water and/or halon; gelling with

gelling agents, solid absorbents and solid inorganic compounds; and use of chemical kinetic modifying additives.

B. RECOMMENDATIONS

It is recommended that the above concepts be experimentally developed during the Phase II Program. Further, it is recommended that the most promising concepts be tested in a large-scale aircraft fire.

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APPENDIX A

SUMMARY OF METHODS OF FIRE NEUTRALIZATION

1. Emulsify Water and JP-4 With an Emulsifier Added into the AFFF.

The emulsifier would be added to the water either by premixing or on-line adding to the AFFF. The emulsified JP-4/water would have the advantage of gelling the surface of the JP-4 and reducing the evaporation rate of the JP-4. The water will have the effect of cooling and requiring more heat transfer for evaporation. Using self-mixing emulsifiers it is possible to form a JP-4-in-water emulsion which will inert and thicken the JP-4 fuel surface. When the emulsion forms a viscous mixture, a low volatile fraction layer will form a skin retarding evaporation.

2. Emulsions of Volatile Fire Retardants in JP-4

Halon materials, such as 2402, can be emulsified with water. Emulsions can be made with halon materials and water. This mixture can be used to form AFFF. The halon-water emulsion will drain from the AFFF, forming an emulsion on and in the surface layer of the JP-4. The emulsion will thicken the JP-4, reducing evaporation from the JP-4 surface. Further, due to the greater volatility of the halon materials, they will form a fire-retardant mixture above the layer of the fuel. Other fire retardants can also be added, which are more effective than the halons.

3. Fuel Gels Formed From Solid Absorbent Materials

Some of these materials absorb and swell upon contact with JP-4. The material holds 10-20 times its weight of JP-4 and, upon swelling, forms a fuel gel. The absorbents can be saturated with fire retardant materials, such as halon 2402. The 2402 will dissolve in the JP-4 and the solid absorbent will absorb the JP-4 forming a fuel gel. Since the fire retardant is more volatile than the JP-4, it will evaporate and form a fire-suppressing vapor above the fuel. The solid absorbent material can be slurried with the water used in the AFFF.

4. Fuel Gels Formed From Solid Materials

Noncombustible materials can be used to form JP-4 fuel gels. Materials, such as silica, clays, or vermiculite, can be slurried with the water used in the AFFF. The material will drain into the fuel surface and gel the JP-4 fuel surface.

APPENDIX A (Condinued)

While these materials are effective gelling materials, the question to be addressed is whether more effective results for fuel neutralization will result by some other method. Fine particulate of dry chemicals, such as purple K, could be used to gel the fuel and add fire retardancy at the same time.

5. Fuel Gels Formed From Gelling Chemicals

Various methods have been worked out to gel fuels in aircraft wing tanks and tankers at sea. These chemicals could gel the fuel and thereby reduce evaporation rates. They also could stabilize the fuel surface, which will enhance the suppression of the AFFF. Again, whether the amount of gelling chemical and mixing energy required makes this method the most satisfactory must be evaluated.

6. Chemical Kinetic Modifying Additives

JP-4 can be sprayed or foamed over with various additives such as the halon or superkinetic modifiers. These materials are extremely effective on a weight basis. Probably their most effective method of application would be in emulsion form, as discussed in Method 2.

APPENDIX B

DEFENSE TECHNICAL INFORMATION CENTER

LITERATURE SEARCH

FOR FUEL NEUTRALIZATION PROJECT

DEPARTMENT OF DEFENSE

RESEARCH AND TECHNOLOGY WORK UNIT INFORMATION SYSTEM

REPORT ON

FUEL NEUTRALIZAIDN FLASHBACK PREVENTION

DTIC REPORT NO. CY4844 FEB 18, 1985

REQUESTED BY

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DEFENSE TECHNICAL INFORMATION CENTER CAMERON STATION, ALEXANDRIA, VIRGINIA

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) AVIATION FUELS; (U) AIRCRAFT; (U) FUELS; (U) FLAMES (U) FIRES; (U) FIRE RESISTANCE; (U) EXPERIMENTAL DESIGN; (U) EQUIPMENT; (U) CRASHES; (U) THE LIGHT; (U) TOTAL TOTAL

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OBJECTIVE: (U) TO STUDY THE MECHANISMS OF MIST FLAMMABILITY PHENOMENA TO RESOLVE AMBIGUOUS INFORMATION ON IGNITION REQUIREMENTS, FLAME SPEEDS, AND FLAMMABILITY LIMITS OF MULTICOMPONENT FUELS DISPERSED IN SUCH HETEROGENEOUS SYSTEMS. RELEVANCE - THE ARMY HAS A NEED FOR METHODS FOR REDUCING FIRE VULNERABILITY OF AIRCRAFT TURBINE FUEL. THE PROPOSED STUDIES SHOULD PROVIDE DEFINITIVE RESULTS WHICH WOULD LEAD TO IMPROVED IN-FLIGHT FUEL FIRE RESISTANCE AND POST-CRASH FIRE RESISTANCE.

APPROACH: (U) APPROPRIATE EXPERIMENTAL DEVICES AND TECHNIQUES WILL BE DEVELOPED FOR QUANTITATIVE DETERMINATION OF THE AFOREMENTIONED FLAMMABILITY CHARACTERISTICS IN INITIALLY NON-TURBULENT SYSTEMS. BURNER STUDIES OF MIST FLAMMABILITY PHENOMENA AND ANTIMIST AGENT INFLUENCES WILL BE INITIATED.

PROGRESS: (U) 7606-7707 A RUGGED, MODULAR FLAME TUBE HAS BEEN DEVELOPED FOR USE IN STUDYING LAMINAR FLAME SPEEDS AND LEAN LIMITS OF BOTH PREMIXED VAPORS AND HETEROGENEOUS MIST SYSTEMS. THE FLAME TUBE DESIGN INCORPORATES A MIST INLET SLIT WHERE OPTICAL MEASUREMENTS CAN BE MADE. THE THIN SHEET OF MIST THEN EXPANDS IN THE FLOW AND FILLS THE CROSS-SECTION OF THE FLAME TUBE. AN AIR BLAST ATOMIZATION NOZZLE IS UTILIZED FOR MIST GENERATION. THIS NOZZLE BASICALLY ASPIRATES THE LIUID FUEL INTO THE AIR STREAM OF AN ULTRASONIC WHISTLE. A SPARK-GAP ASSEMBLY WITH A 25,000 VOLT POWER SUPPLY WAS SUPPORTED IN A NYLON PLUG AND INSERTED INTO THE IGNITOR MODULE. THE SAMPLE LINES FROM THE PROBES WERE ELECTRICALLY HEATED TO INSURE VAPORIZATION. THE WITHDRAWN SAMPLES OF FUEL/AIR MIXTURE WERE PASSED THROUGH A PLATINIZED ASBESTOS/COPPER OXIDE WIRE CATALYST BED MAINTAINED AT ABOUT 400C. THE EQUIVALENCE RATIO OF THE MIXTURE WAS THEN DETERMINED FROM THE MEASURED CO AND CO SUB 2 FORMED BY THE ESSENTIALLY COMPLETE OXIDATION OF THE HYDROCARBON. FORWARD LIGHT SCATTERING EQUIPMENT WAS ASSEMBLED, BUT THIS WAS NOT USED DURING THIS INITIAL YEAR OF THE STUDY PERIOD. DETAILS ARE IN ARO REPORT 14208.1-CX.

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PROCESSING DATE: 18 JAN 78

U S GOVY AND THEIR CONTRACTORS ONLY

DTIC FORMAT 850

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) AERODYNAMICS;(U) CHEMICAL AGENTS;(U) DECONTAMINATION:
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;(U) DYNAMICS ;(U) EXCIMERS ;(U) FIRE SAFETY ;(U) FLUDRESCENCE;(U) FUELS ;(U) INTERACTIONS (U) LASERS; (U) LIGHT SCATTERING ; (U) LIQUIDS ; (U) MATERIALS ; (U) MOLECULAR PROPERTIES ; (U) REPORT CONTROL NUMBER RESEARCH AND TECHNOLOGY WORK UNIT SUMMARY 09 JAN 85 CY4844 **DAOH0645** Summake SET TE WOAR SEELANTS DATE PAGE SUM- SI HAMMUR TO GHIA S ATZH HOLTLBISTZIG AS A. WOHK UNIT 24 DCT 84 CHANGE PROJECT NUMBER 10 NO./CODES PROGRAM ELEMENT WORK UNIT NUMBER TASK AREA NUMBER PR. 84 4 5 5 705 61102A 1L1611028H57 DB Conta dulling CONTAINING: Till C Present with bounties Consideration Const (U) CHARACTERIZATION AND DYNAMICAL STUDIES OF POLYMERS IN DIPOLAR (APROTIC) LIQUIDS 19251-C 0101 AERODYNAMICS 0704 PHYS CHEM 2004 FLUID ME HUCKHART METHOD IL PLANDING ORGANIZATION JUL 85 B. CONTRACT JUL 82 DA TT CCATACTICANT IN MESOURCES ESTIMATE C DATES EFFECTIVE ERPHATION PROFESSIONAL WORLYCARS JUL 84 JUL 85 FISCAL VLARS I MAMBER DAAG29-82-K-0143 4.7 \$ 118 1984 \$ 117,622P 1985 0.0 \$ 0 DALWA TO GHIS I CUM/TOT: 1 343,844 EXT TH AFFRONDIAL SOO DAGANIZATIO 26 PERSONHAL CACAMIZATION 040900 3704 256850 3623 DARCOM ARMY RESEARCH OFFICE NEW YORK, STATE UNIVERSITY-ALBANY ADDRESS ALBANY NY 12203 DURHAM NC 27709 PRINCIPAL INVESTIGATOR HAME CHU, B GHIRARDELLI, R G TELEPHONE A1P3 5184730365 1 L. I Pricing 9195490641 IT GINERA, UST ASSOCIATE INVESTIGATORS MAME MILITARY (U) POLYMERS ; (U) SOLUTIONS ; (U) APROTIC LIQUIDS ; (U) 2: Alemonos Biecese (Alemonia Security Description Come MOLECULAR PROPERTIES ; (U) LIGHT SCATTERING ; (U) FLUORESCENCE; (U) CHEMICAL AGENTS ; (U)

13 (Control Officer of AMORE & AMORE & Form more preparate invalue by number Properties and I provide Control OBJECTIVE: (U) INTERACTIONS OF POLYMERIC SPECIES IN THE SEMIDILUTE SOLUTION REGIME WILL BE STUDIED TO GAIN AN INSIGHT INTO THE AERODYNAMIC BREAKUP PROCESS OF SOLUTIONS, RELEVANCE. STRONG RELEVANCE OF THIS WORK TO CHEMICA THREAT ASSESSMENT, DECONTAMINATION, AND PROTECTIVE MATERIALS EXISTS. PERIPHERAL RELEVANCE TO THE FIRE SAFE FUELS EFFORT, PARTICULARLY ANTI-MIST AGENTS HAS ALSO BEEN CITED. APPROACH: (U) LASER LIGHT SCATTERING SIZE-EXCLUSION CHROMATOGRAPHY AND SAXS WILL BE USED TO CHARACTERIZE MOLECULAR PARAMETERS FOR A VARIETY OF POLYMERS. POLYMER DYNAMICS WILL BE STUDIED USING LASER LIGHT SCATTERING AND EXCIMER FLUORESCENCE. THIS INFORMATION WILL BE CORRELATED WITH RHEOLOGICAL STUDIES TO PROVIDE INSIGHTS INTO AERODYNAMIC PROCESSES. PROGRESS: (U) 8207-8306 LIGHT SCATTERING STUDIES ON PMMA AND ON THE TERPOLYMER, ACRYLDID K125 (3-6326) HAVE BEEN CARRIED OUT IN DILUTE SOLUTIONS. A PMMA SAMPLE WAS USED TO CALIBRATE THE INSTRUMENTATION. THE ANGULAR DISTRIBUTION OF ABSOLUTE SCATTERED INTENSITY OF ACRYLOID K125 WAS MEASURED IN METHYL ETHYL KETONE (MEK) AND IN DIOXANE (DIO) AT 30C. THE DIFFERENCE IN MOLECULAR WEIGHT FOR ACRYLOID K125 SUGGESTS THE PRESENCE OF 'AGGREGATION' FOR THE TERPOLYMER IN MEK. THEREFORE, ALL EARLIER INVESTIGATIONS ON THE CHARACTERIZATION OF ACRYLOID K125 IN MEK ARE OPEN FOR DISCUSSION. A SEARCH HAS BEEN MADE FOR ADDITIONAL GOOD SOLVENTS IN ORDER TO CHECK THE CHARACTERIZATION OF THE TERPOLYMER IN DIOXANE AND CCL4 IS BEING CONSIDERED AS A POSSIBLE CANDIDATE.

PROCESSING DATE: 31 JAN 85

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) ACCIDENTS ; (U) ASSESSMENT ; (U) AIRCRAFT FIRES ; (U) AIRCRAFT ; (U) AIR FLOW ; (U) FLUID DYNAMICS ; (U) FLOW SEPARATION ; (U) FLAMES; (U) FIRES ; (U) FIRE SAFETY ; (U) EXPERIMENTAL DATA ; (U) DAMAGE; (U) COMBUSTION ; (U) FUEL SPRAYS ; (U) GAS

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OBJECTIVE: (U) AF FUNCTION-ADVANCED AIRBREATHING COMBUSTION ENGINES FOR TERRESTERIAL AND AEROSPACE VEHICLES AND MISSILE PROPULSION ARE REQUIRED FOR WEAPONS DELIVERY AND DEFENSE, TRANSPORT AND RECONNAISSANCE. ALSO, RELIABLE FIRE AND EXPLOSION SAFE PROPULSION ENGINE COMPONENTS ARE REQUIRED CAPABLE OF RESISTING DESTRUCTION FROM ENEMY WEAPONRY AND ACCIDENT SITUATIONS. FUNCTIONAL DEFICIENCY-INSUFFICIENT FUNDAMENTAL UNDERSTANDING OF THE MECHANISMS AND PROCESSES ASSOCIATED WITH IGNITION, COMBUSTION AND ARRESTING OF FLAMES AND DETONATIONS IN REACTIVE FUEL-AIR MIXTURES ENCOUNTERED IN AIRBREATHING COMBUSTION ENGINES UNDER ACCIDENTAL AND COMBAT SITUATIONS IS HAMPERING THE DESIGN AND DEVELOPMENT OF EFFECTIVE MEANS FOR PREVENTION AND OR QUENCHING TO THESE FLAMES OR DETONATIONS. ALSO, INSUFFICIENT UNDERSTANDING AND DATA IS AVAILABLE TO THE COMBUSTION DESIGNER TO PERMIT HIM TO OVERCOME THE POSSIBLE PROBLEMS ASSOCIATED WITH COMBUSTOR STABILITY LIMITS IN ADVANCED COMBUSTOR CONCEPTS SUCH AS RAPID EXPANSION (DUMP), VORTEX AND CATALYTIC BURNERS (I.E., PREVENTION OR AVOIDANCE OF PREIGNITION, FLASHBACK AND BLOWOFF). OBJECTIVE-THE OBJECTIVES OF THIS RESEARCH ARE TO UNDERSTAND AND FORMULATE REALISTIC THEORETICAL AND ANALYTICAL REPRESENTATIONS OF THE MECHANISMS AND PROCESSES DESCRIBING (1) IGNITION AND FLAME STABILIZATION AND UNSTEADY COMBUSTION IN ADVANCED HIGH-TEMPERATURE, HIGH-PRESSURE AIRBREATHING COMBUSTORS AS WELL AS (2) FUEL-SPRAY PREIGNITION, IGNITION BY HOT SURFACES, FLASHBACK, BLOWOFF AND FLAME STABILIZATION BY SEPARATED FLOW-REGIONS, UNSYMMETRICAL FLAMEHOLDING SURFACES. ETC. ENCOUNTERED IN EXTERNAL FIRE AND VOID SPACE FIRE SITUATIONS. HOW WORK CONTRIBUTES-THIS EFFORT WILL PROVIDE ADDITIONAL UNDERSTANDING, EXPERIMENTAL DATA AND REALISTIC ANALYTICAL (MODELLING NOT NOW AVAILABLE) AND APPROACHES FOR PREVENTION OF PREIGNITION, FLASHBACK AND BLOWOFF IN GAS TURBINE COMBUSTORS, FOR IGNITION OF FUEL SPRAYS BY HOT SURFACES, FOR FLAMEHOLDING BY OBJECTS SUCH AS MANY OCCUR IN STRUCTURAL DAMAGE TO THE AIRFRAME, AND FOR FLOW AND FLAME STABILITY IN VOID SPACE FIRES. THE RESEARCH WILL ALSO AID IN PERFORMANCE AND FLAME STABILIZATION IMPROVEMENTS, WILL IMPROVE HAZARD ASSESSMENT FOR AIRCRAFT FIRES RESULTING FROM ACCIDENTAL OR COMBAT DAMAGE, AND CONTRIBUTE TO DESIGN AND DEVELOPMENT OF EFFECTIVE MEANS FOR PREVENTION AND QUENCHING OF FLAMES AND EXPLOSIONS AND THUS TO IMPROVE AIRCRAFT VULNERABILITY AND SURVIVABILITY.

APPROACH: (U) PHASE I - IGNITION OF FUEL SPRAYS WILL BE INVESTIGATED BY INJECTION OF A FUEL SPRAY INTO AN AIRFLOW OF KNOWN PROPERTIES PASSING THROUGH A HEATED PIPE SECTION. THE INFLUENCE OF SPRAY, AIR FLOW, AND SURFACE PROPERTIES WILL BE INVESTIGATED FOR EACH FUEL CONSIDERED. STABILIZATION OF FIRES BY LARGE SCALE FLAMEHOLDERS IS TO BE INVESTIGATED IN A COMBUSTION TUNNEL INITIALLY WITH V-TYPE AND L-TYPE GUTTERS USING THE WATER INJECTION METHOD DEVELOPED BY LEFEBVRE. EXPLORATORY INVESTIGATIONS OF THE FLOW IN PARTIALLY VENTILATED

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U S GOVT AND THEIR CONTRACTORS ONLY
DTIC FORMAT 850

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) *AIRCRAFT FIRES ; (U) ARMOR PIERCING AMMUNITION ; (U)

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OBJECTIVE: (U) DEVELOP FIRE EVENT FUEL FIRE NCTIONS, AND OT	-SAFETY DA	TA AND FUEL Y PROJECTILE	PROPERTY IN	FORMATION F			
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RETRIEVAL TERMS ASSIGNED BY DTIC (U) AIRCRAFT; (U) BEHAVIOR; (U) CHEMICALS; (U) CONTRÔL (U) CRASHES; (U) DRYING; (U) EXTINGUISHING; (U) FIRE PROTECTION; (U) FIRES; (U) FUEL ADDITIVES; (U) FUELS; (U) LINEAR SYSTEMS; (U) LOSSES; (U) MIST; (U) POLYMERS; (U) REMOVAL

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(U) SMOKE CONTROL; (U) ANTI-MISTING; (U) EXTINGUISHING; (U) FUELS;
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OBJECTIVE: (U) A) DEVELOP FIRE-SUPPRESSIVE HYDRAULIC FLUIDS FOR REDUCING HAZARDS IN SUBMARINE HYDRAULIC FLUID SYSTEMS, B) DEVELOP SMOKE CONTROL IN SHIPBOARD FIRES, C) DEVELOP A NEW DRY CHEMICAL FIRE EXTINGUISHING AGENT.

APPROACH: (U) A) STUDY EFFECT OF ASSOCIATION COLLOIDS AND EMULSIFIED WATER ON FIRE SUPPRESSIVE BEHAVIOR. B) STUDY DIELECTROPHORESIS AS A SMOKE REMOVING AGENT AND COMBINE THE CONCEPTS OF SMOKE KNOCK-DOWN BY WETTING WITH FIRE EXTINGUISHMENT BY FINE WATER MISTS. C) COMBINE THE CONCEPTS CONTROLLING FIRE EXTINGUISHMENT OF CLASS A AND CLASS B FIRES INTO A SINGLE ALL-PURPOSE DRY CHEMICAL OR MIX OF CHEMICALS.

PROGRESS: (U) A) TWO FIRE-SUPPRESSIVE HYDRAULIC FLUIDS ARE BEING EVALUATED. FIRE SUPPRESSIVE CHARACTERISTICS OF THESE TWO COMMERCIALLY AVAILABLE FLUIDS ARE EXCELLENT. MATERIALS COMPATABILITY AND FLOW CHARACTERISTICS TESTS ARE PLANNED. B) STUDY KNOCK-DOWN OF DENSE SMOKE IN CLOSED SPACES. EVALUATE EFFECTS OF CHARGE ON MISTS OF WATER AND AFFF SOLUTION. DEVELOP PORTABLE DEVICE TO DELIVER CHARGED MIST. C) AN EMPIRICAL RELATION HAS BEEN DEVELOPED (BASED ON THE HEAT-EXTRACTION PROCESSES WHICH OCCUR IN HYDROCARBON - AIR FLAMES) AND HAS BEEN USED TO CORRELATE AND PREDICT THE SUPPRESSION EFFECTIVENESS OF EXISTING AND PROPOSED AGENTS. A REPORT IS IN PUBLICATION. AN EXTENSIVE EXPERIMENTAL STUDY HAS BEEN MADE OF THE EXTINGUISHMENT OF THE HEPTANE DIFFUSION FLAME BY THE FIVE COMMON DRY CHEMICALS -KNCO(3) NAHCO(3), KC1, NH(4)H(2)PO(4) AND 'MOMMEX', A REPORT IS IN PREPARATION. THIS CONTRACT IS COMPLETE; HOWEVER, WORK CONTINUES UNDER CONTRACT NUMBER NOO014-83-C-0545.

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PROCESSING DATE: 30 MAR 84

IJ S GOVT AND THEIR CONTRACTORS ONLY DTIC FORMAT 850

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) AIRCRAFT FIRES ; (U) *AVIATION FUELS ; (U) AVIATION

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) AIRCRAFT FIRES ; (U) *AVIATION FUELS ; (U) CHEMICAL PROPERTIES ; (U) COMPATIBILITY ; (U) *FIRE SAFETY ; (U) *FLAMMABILITY; (U) FLUIDS; (U) PHYSICAL PROPERTIES ; (U) VAPORS; (U) VEHICLES ; (U) ANTIFOGGING DEVICES ;

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(U) AIRCRAFT FUEL; (U) FUEL MIST; (U) FLAMMABILITY; (U) ANTIMISTING AGENTS; (V) Granica, GRACINE is APPADACE IN PROCESS Guines described by except and all seals must become Code!

OBJECTIVE: (U) DEVELOP FLAMMABILITY DATA AND FLUID PROPERTY INFORMATION RELATING THE AMOUNT AND NATURE OF FLUID CONSTITUENTS TO FIRE AND EXPLOSION HAZARDS AND SYSTEMS COMPATIBILITY TO PERMIT DEVELOPMENT OF FLUIDS WITH REDUCED FIRE VULNERABILITY.

APPROACH: (U) THIS FLUID FIRE SAFETY PROJECT ADDRESSES ALL FLAMMABLE FLUIDS EMPLOYED IN ARMY MOBILITY EQUIPMENT. THE APPROACH INCORPORATES - EXPERIMENTAL FLAMMABILITY - HAZARDS EVALUATIONS - MIST FLAMMABILITY STUDIES - BULK LIQUID IGNITION AND FLAME PROPAGATION INVESTIGATIONS - AND FLUID COMPOSITION TAILORING, INCLUDING ADDITION OF CHEMICAL FLAME INHIBITORS AND/OR ANTIMIST ADDITIVES. PHYSICAL, CHEMICAL, AND RHEOLOGICAL PROPERTIES ARE MEASURED AS NECESSARY TO ADEQUATELY CHARACTERIZE THE FLUID BLENDS AND TO DEVELOP IMPROVED UNDERSTANDING OF FLUID FLAMMABILITY MECHANISMS.

PROGRESS: (U) 75 06-75 08 - WORK ON FLUID FIRE SAFETY RESEARCH WILL BE REPORTED ON AGENCY ACCESSION NO. DA DM 3801 UNDER THE NEW CONTRACT WITH SOUTHWEST RESEARCH INSTITUTE.

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PROCESSING DATE: 16 OCT 75

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RETRIEVAL TERMS ASSIGNED BY DTIC (U) ADDITIVES ; (U) MIST ; (U) MOBILITY ; (U) REDUCTION ; (U) RHEOLOGY ; (U) SYSTEMS ANALYSIS ; (U) VULNERABILITY ; (U) ANTIFOGGING AGENTS; (U) ARMY ; (U)

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(U) FLUID FI	RE SAFETY RESE	ARCH FOR AR	M Y AIR AND	GROUND VEHI	CLES				
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(U) FIRE-SAFE : (U) DIESEL: (U) TURBINE : (U) FUEL :

OBJECTIVE: (U) DEVELOPMENT OF FUELS FOR ARMY COMBAT/MOBILITY EQUIPMENT WHICH ARE CAPABLE OF YIELDING REDUCED FUEL FIRE BULNERABILITY HAZARDS.

APPROACH: (U) SURFACTANT-STABILIZED DIESEL FUELS CONTAINING SUFFICIENT AMOUNTS OF DISPERSED WATER TO RENDER THEN SELF-EXTINGUISHING WILL BE EVALUATED AND OPTIMIZED. THIS RESEARCH WILL INCLUDE ESTABLISHING REALISTIC SURFACTANT-COMPOSITION AND WATER-CONTENT REQUIREMENTS. SYNERGISTIC EFFECTS AND POTENTIAL TRADE-OFFS STEMMING FROM THE POSSIBLE INCLUSION OF OTHER ADDITIVES IN THE FIRE-RESISTANT FUEL (FRF) FORMULATION WILL BE SCRUTINIZED. ENGINE PERFORMANCE AND ENDURANCE WILL BE INVESTIGATED WITH FRF.

PROGRESS: (U) (8102-8112) FRF FORMULATION INVESTIGATIONS ESTABLISHED WINDOWS FOR NO-FAILURE MICROEMULSIONS. THESE WINDOWS IDENTIFY THE MAXIMUM AND MINIMUM TOTAL AROMATIC RING CARBON CONTENT (TARC) OF THE BASE FUEL, VERSUS THE TOTAL DISSOLVED SOLIDS (TDS) OF THE WATER AND THE TOTAL ACID NUMBER (TAN) OF THE SURFACTANT. FRF INVESTIGATIONS HAVE ALSO INCLUDED EVALUATION OF DIESEL FUEL ADDITIVE EFFECTS ON STABILITY AND PERFORMANCE. THE FOLLOWING REPORTS WERE ISSUED: A) INVESTIGATION OF FIRE-VULNERABLITY-REDUCTION EFFECTIVENESS OF FIRE RESISTANT DIESEL FUEL IN ARMORED VEHICULAR FUEL TANKS., AFLEL REPORT NO. 30, AD A080129. B) RESEARCH ON FIRE-RESISTANT DIESEL FUEL, AFLEL REPORT NO. 145, AD NO. IS BEING OBTAINED.

PROCESSING DATE: 10 FEB 82

U S GOVT AND THEIR CONTRACTORS ONLY

DTIC FORMAT 850

RETRIEVAL TERMS ASSIGNED BY DTIC (U) AIR ;(U) ADDITIVES ;(U) FUELS ;(U) ENVIRONMENTS;(U) CONCENTRATION(CHEMISTRY);(U) BOUNDARIES ;(U) AIRCRAFT ;(U) AIR FLOW ;(U) WINGS ;(U) LEADING EDGES ;(U) IGNITION ;(U) VELOCITY ;(U) TORCHES ;(U) PROPANE ;(U) TEMPERATURE ;(U)

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ANTI-MIST FU	ELS ; (U) FUEL F	TRE SUPPRE	SSION	(U) AIRCRA	V. 11.5		/IVABILIT	Y ; (U)	

OBJECTIVE: (U) ESTABLISH FLAME PROPAGATION CHARACTERISTICS OF ANTI-MIST FUELS WHEN THE FUELS ARE RELEASED IN AIRFLOW CONDITIONS REPRESENTATIVE OF IMPACT SURVIVABLE AIRCRAFT CRASHES. FIRE SUPPRESSION OF FUEL WILL SIGNIFICANTLY INCREASE THE SURVIVABILITY OF MOTORIZED VEHICLES.

APPROACH: (U) FUEL SPILLAGE/AIR SHEAR TESTS WILL BE CONDUCTED WITH ANTI-MIST FUELS TO ESTABLISH THE INTERRELATIONSHIPS BETWEEN FIRE REDUCTION EFFECTIVENESS AND ADDITIVE CONCENTRATION, FUEL TEMPERATURE, FUEL CONDITION, AND AIRFLOW TEMPERATURE VELOCITY. ANTI-MIST FUEL WILL BE EJECTED FROM THE LEADING EDGE OF A SIMULATED WING SECTION INTO AN AIRSTREAM OF 100-120 KNOTS AND A PROPANE TORCH IGNITION ENVIRONMENT.

PROGRESS: (U) (DEC 1976 THROUGH MAY 1977). FINAL REPORT FORWARDED TO SPONSOR. TASK COMPLETED.

PROCESSING DATE: 17 AUG 77

U S GOVT AND THEIR CONTRACTORS ONLY

UNCLASSIFIED

RETRIEVAL TERMS ASSIGNED BY DTIC (U) FIRE SUPPRESSION ;(U) ENVIRONMENTS;(U) AIR FLOW ;(U)

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FIRE SUPPRESS VEHICLES. APPROACH: (LESTABLISH THE CONCENTRATION FUEL WILL BE 100-160 KNOTS	IN AIRFLOW CONSION OF FUEL WI J) FUEL SPILLAGE INTERRELATION N, FUEL TEMPERA EJECTED FROM 1 S AND A PROPANS J) (JULY 1977 -	GE/AIR SHEAR SE/AIR SHEAR SSHIPS BETWE STURE, FUEL THE LEADING TORCH IGNI	CANTLY INCR R TESTS WILL EEN FIRE REI CONDITION, EOGE OF A: TION ENVIRO	BE CONDUCTION I AND AIRI SIMULATED DNMENT.	SURVIVA DUCTED W EFFECTIV FLOW TEN D WING S	BILITY OF WITH ANTI- MENESS AND MERATURE ECTION IN	MOTORI MIST FU ADDITI VELOCIT YO AN A	ZEO ELS TO VE Y. ANTI-N IRSTREAM	
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UNCLASSIFIED RETRIEVAL TERMS ASSIGNED BY DTIC (U) JET ENGINE FUELS ;(U) FIRE SUPPRESSION ;

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(U) FIRE SUPPRESSION; (U) ANTI-MISTING;
1) Titherica, Obditive 11 AMBOACH M MODELS Business understance purprises adjusted by manhabit Process again of back with bosoning Capabilitation County

OBJECTIVE: (U) TO DEVELOP SUPERIOR ANTI-MISTING ADDITIVES FOR JET FUEL THROUGH AN IMPROVED UNDERSTANDING OF THEIR FUNCTIONS AND RELATED PHYSICO-CHEMICAL CHARACTERISTICS.

APPROACH: (U) TEXT NOT AVAILABLE

PROGRESS: (U) NO PROGRESS MADE IN FY 81. PROJECT TERMINATED BY NAVAIR.

PROCESSING DATE: 31 AUG 81

U S GOVT AND THEIR CONTRACTORS ONLY DTIC FORMAT 850

RETRIEVAL TERMS ASSIGNED BY DTIC (U) ATOMIZATION ; (U) AIRCRAFT ENGINES ; (U) CAPILLARY TUBES (U) INTENSITY : (U) CHEMICAL COMPOSITION : (U) GAS TURBINES: (U) FUEL SYSTEMS: (U) FUELS : (U) MOLECULAR WEIGHT : (U) TURBINES : (U) FIRE SAFETY : (U) JET ENGINE FUELS : (U) POLYMERS : (U)

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(U) FIRE-SAFE FUEL; (U) TURBINE FUELS; (U) JET FUELS serie Locarity Constituent Code

OBJECTIVE: (U) TO DEVELOP, AS PART OF A DOT/DOD EFFORT, A SUITABLE METHOD OF RESTORING FILTRATION, ATOMIZATION AND OTHER ESSENTIAL PROPERTIES TO FM-9 (IMPERIAL CHEMICAL INDUSTRIES, LTD. PRODUCT DESIGNATION) ANTIMISTING FUEL FOR USE IN AIRCRAFT TURBINE ENGINES AND FUEL SYSTEMS.

APPROACH: (U) INVESTIGATE VARIOUS POLYMER DEGRADING CONCEPTS (MECHANICAL, CHEMICAL, THERMAL, ULTRASONIC, ETC.) CONSIDERED FEASIBLE FOR RESTORING ANTIMISTING FUELS TO AIRCRAFT OPERATING CONDITION IN TERMS OF FLOW, ENERGY REQUIREMENTS, AND ANY OTHER SIGNIFICANT PARAMETERS.

PROGRESS: (U) 7903-7909 - DATA HAVE BEEN OBTAINED TO CORRELATE DEGREE OF DEGRADATION WITH FLOW IN POROUS MEDIA, AND IGNITION RESISTANCE WITH THE SPINNING DISC ATOMIZER. THE LATTER SHOW CLOSE CORRESPONDENCE WITH THE PASS/FAIL WIND VELOCITY IN FAA'S WIND SHEAR TEST. A FINAL REPORT ENTITLED "RESTORING ESSENTIAL FLOW AND IGNITION PROPERTIES TO ANTIMISTING KEROSINE (AMK) FOR TURBINE AIRCRAFT OPERATIONS" WAS APPROVED AND IS UNDERGOING FINAL REVISION.

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PROCESSING DATE: 31 DEC 79

RETRIEVAL TERMS ASSIGNED BY DTIC (U) AVIATION ACCIDENTS; (U) *AVIATION FUELS; (U) AVIATION SAFETY; (U) *FIRES; (U) FUEL TANKS; (U) HAZARDS; (U) *HELICOPTERS; (U) IGNITION; (U) IMPACT TESTS; (U) SIMULATION; (U) SURVIVAL (PERSONNEL);

RESEARCH	AND TECHNOLOGY	WORK UNIT	SUMMARY	DAOC4629		30 JUN		REPORT CONTROL NUMBER CY4844
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(U) SIMULATE	D CRASH TESTS	OF ARMY HEL	ICOPTER TUR	BINE FUELS				
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(U) AIRCRAFT FUEL; (U) FUEL MIST; (U) ANTI-MISTING AGENTS;
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OBJECTIVE: (U) TO DEFINE THE POST-CRASH FIRE HAZARD POTENTIAL FOR MODIFIED ARMY HELICOPTER TURBINE FUELS.

APPROACH: (U) SIMULATED FULL-SCALE FUEL TANK IMPACT TESTS WILL BE CONDUCTED USING CANDIDATE FUELS. TEST PARAMETERS WILL BE SELECTED TO ENCOMPASS SURVIVAL CRASH IMPACTS AS WELL AS VARIOUS POTENTIAL IGNITION SOURCES.

PROGRESS: (U) 73 04-74 06 - THE CONTRACT IS COMPLETED AND A FINAL REPORT HAS BEEN ACCEPTED. THE FINAL REPORT, DATED NOVEMBER 1973, IS TITLED 'SAFETY EVALUATION OF ANTI-MIST FUELS' AND HAS BEEN ASSIGNED AD 773035 BY DEFENSE DOCUMENTATION CENTER.

PROCESSING DATE: 17 SEP 74

U S GOVT AND THEIR CONTRACTORS DNLY

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UNCLASSIFIED

RETRIEVAL TERMS ASSIGNED BY DTIC (U) CHEMICAL PROPERTIES ; (U) ANOMALIES ; (U) RESISTANCE (U) POLYMERS ; (U) FUELS ; (U) FLUID FLOW ; (U) RHEOLOGY ;

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