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**DEVELOPMENT OF FUEL NEUTRALIZING
AGENTS TO PREVENT FLASHBACK ON
AIRCRAFT FIRES**

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The object of this study was to explore chemical modification of extinguishants currently used against postcrash fuel-fed fires to inhibit reignition, i.e., improve "burnback" control, without compromising the efficacy of flame knockdown. A formulation was developed as an additive to AFFF, for delivery during fire extinguishment which succeeded in 16-inch laboratory trials, but not to the same extent in 6-foot field tests. Several causes were considered and reformulation recommended. Three other approaches, each with formulations, also showed potential for significant reduction of fuel reignition if administered subsequent to flame knockdown by AFFF. One permits resealing by AFFF, another, instant emulsification of water and JP-4, and a third, gelling of the fuel. (25) *Fire safety, *Aviation fuels,				
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EXECUTIVE SUMMARY

This research was undertaken to study modifications of the chemistry of extinguishment of postcrash fuel-fed fires which could both improve burnback prevention and be compatible with field practices and equipment. ³⁶ Currently, aqueous film-forming fluorosurfactant, AFFF foams, are highly effective in "flame knockdown" and extinguishment, but they also permit fuel to reignite.

Past efforts were surveyed and two approaches decided upon. In one, improved separation of the fuel and oxidizer was attempted in two ways: toughening the foam water draining film to act as a vapor cap or gelling the fuel to reduce hydrocarbon vapors. In the other approach, cooling of the reaction zone which could instantly emulsify water into the fuel formulae were developed and studied in small and larger-scaled benchtests and six-foot field tests. All procedures and equipment, related to foam delivery, density and burnback extinction, were carried out or used in accordance with military specifications MIL-F-24385.

In the laboratory, the sealing characteristics of control and experimental films of AF³ on top of JP-4 were determined spectrophotometrically in an apparatus adapted from one described in the literature (Figure 1, Reference 29). These scaling curve profiles of AF³ admixed with various chemicals, permitted observations of the effect of these chemicals on both the speed of film spread and the durability of the film's efficacy against permeation by hydrocarbon fuel vapors.

Several formulations were effective in large-scale bench tests. In one, the speed of extinguishment of a fuel-fed fire by AF³ was increased by a factor of 2-3 times. This was reproduced in 6-foot diameter burn tests carried out according to MIL SPEC F-24385D. In other formulations, emulsification of JP-4 with nozzle water was achieved using conventional water-spray-application techniques. A milky emulsion formed that suppressed ignition for more than 1 hour in large-scale benchtests. The emulsion proved to be less stable in 6-foot tests than in the large-scale benchtests and improved burnback was not demonstrated in 6-foot tests. A number of possible causes for the differences between the field and the laboratory tests are identified and discussed. As in any extensive screening effort, a number of promising formulations are worthy of further study.

Specific results and conclusions are therefore summarized below in each category of effort.

Rapid Flowing Tough Film/Foam

Addition of a starch grafted copolymer to a mixture of aqueous film-forming and protein-containing fluorosurfactant foams produced a film with both enhanced spread speed and durability. Small field tests of these blends are recommended (See Figure 8 and Table 4).

Fuel Gelling

A commercially available polymer with outstanding fuel gelling capability at concentration levels of 0.2 percent, weight/volume, was identified and tested. The speed of solubility of the polymer must be increased, however, to make it eligible for field applications. This may be accomplished by chemically modifying the polymer either intrinsically or in a coating. It is recommended that this be proposed as an Air Force contract research task in an SBIR solicitation as a "Request For Proposal" to industry.

Cooling of Reaction Zone

Studies were made of the effect of emulsifiers on the sealing characteristics of AF³ films. Forty-nine commercially available chemicals, representing nine substantively different emulsifier chemical families (see Table 5) were selected for testing from the food, cosmetic, paint and drug industries. If successful, any one of these already had acceptable handling and environmental toxicity characteristics required to position the experimental formula for application in the field. The results are summarized in Figures 19-33.

Levels of emulsifier concentration which were not damaging to the AF³ initial percent sealing were generally .05 to .5 percent (w/v). At a 1 percent level, the initial sealing by AF³ was reduced to 10-20 percent from 80-95 percent. Several emulsifiers permitted AF³ to reseal, forming a vapor cap after 5-10 minutes, during which the low-boiling-point (highly volatile) components of the JP-4 had been vaporized. Clindrol 101 CG, Corexit 9550 and Neodol 25 (Figures 24, 25 and 26) were three such species. These deserve further study as additives to AF³, in small-scale burn tests designed to detect improved burnback resistance after 5-10 minutes.

We then focused on a search for chemicals which could emulsify a maximum amount of water into the JP-4 in a minimum time and with minimum mixing energy. Water, with its great heat capacity, could cool the reaction zone if intermixed with fuel. The minimum water:fuel ratio was 1:2 to permit maximum water incorporation independent of emulsifier concentration within a range of 0.5-5.0 percent w/v. From the studies of efficacy of AF³ on emulsified fuel (Table 6), it will be remembered that AF³ efficacy is profoundly affected above 1 percent emulsifier concentration, even for those emulsifiers which permit resealing and vapor cap on the higher boiling point volatiles, i.e., after 5-10 minutes.

A benchtop burn test was designed in which a torch flame was directly applied to emulsified "pea soup" mixtures of JP-4 and water. Hundreds of combinations were screened and found to vary in ease and stability of emulsification and ignitability. Many formulations easily formed good JP-4/water emulsions but burned easily. These are summarized in Tables 16 and 17. Others did not form emulsions easily, but once shaken hard, did resist ignition by flame contact for over 10 minutes. Dioctylsulfo-succinates performed best in both emulsification and burn trials and were blended with fluorosurfactants and water structuring polymers in subsequent screens to search for a self-mixing, nonburning formulation. Two formulae were chosen as best (Table 24), and developed for larger-scale benchtests.

scaled down to 16 inches from full-scale MIL-F-24385 test specifications. These revealed to us the suitability of these emulsion-forming formulae for nonburning as opposed to burning spills (Table 27). Any additive to an agent being used to extinguish flame must permit effective separation of fuel and oxidizer.

In the field tests, Fuel Neutralizing Formula 1 (FN-1) dramatically reduced the time to extinguish a burning fire, compared with AFFF alone and also prevented ignition of a nonburning spill, by periodically applied spark, for over one hour, as also observed in the 16-inch laboratory tests. FN-2, which formed a cloudy "pea soup" emulsion immediately upon mixing with JP-4, did not delay or prevent burnback as effectively in the 6-foot field tests as in the 16-inch laboratory tests (Table 30). Factors which could have caused this disparity included pan geometry, water properties, ignition source, and chemical sources were reviewed.

In exploring chemical inhibition of fire by additives to AF³, the only experiments we carried out were simple tests using the liquid Halon 2402. All other additives would have required, if successful, modification of existing delivery equipment and practices in the field. A minimum of 16 percent by volume was required to extinguish the flame of burning JP-4 in laboratory tests. This was impractical and abandoned for further development.

Recommendations

On flaming fuel extinguished by AFFF, four types of chemicals, to be used with or subsequent to AFFF, were observed to significantly improve extinguishment time or burnback prevention. FN-1, which succeeded in both aspects, in large-scale laboratory tests, should be modifiable to succeed in 6-foot and then 100-foot tests. The key discovery is that a water-structuring polymer in conjunction with a biological, polar polymer and fluorosurfactant as found in AFFF, all at correct concentration levels, can both enhance knockdown speed and seal vapors to inhibit fuel reignition.

We recommend this be used as the basis for developing an improved performance AFFF formulation. Three other approaches showed significant potential to improve AFFF performance if delivered after the flame knockdown.

In one, a category of emulsifiers, at the correct concentration levels, was observed to permit AFFF to reestablish a vapor cap on the spilled fuel. In another, a different category of emulsifiers, if delivered subsequent to extinguishment by AFFF, could instantly intermix the water into the fuel, forming a cloudy "pea soup" emulsion, which offered the most promising tactic against burnback, with minimum alteration of current field equipment and practice.

Finally, one fuel gelling additive, which also could be delivered subsequent to flame knockdown by AFFF, showed sufficient efficacy at low enough concentrations to warrant recommending a study which modifies it to increase the speed of its solubility to permit meaningful practical trials with it.

PREFACE

This report was prepared by Beltran, Inc., 1133 East 35th Street, Brooklyn, N.Y. under Air Force Contract F08635-87-C-0302 for the Air Force Engineering and Services Center, Engineering and Services Laboratory, (AFESC/RDCF), Tyndall AFB, Florida 32403-6001.

The performance period for this effort was between August 15, 1987 and September 30, 1989. Mr. Richard N. Vickers and Mr. Joseph L. Walker were the HQ AFESC/RDCF Project Officers.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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


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LIST OF ABBREVIATIONS

AF ³	Aqueous Film Forming Foam
AFFF	Aqueous Film Forming Foam
cm	Centimeter
DOSS	Dioctyl Sulfosuccinate
FM	Fluorosurfactant Mixture, Based on 3M Proprietary Fluorosurfactants, "Fluorads"
FN	Fuel Neutralizing
FP ³	Film Forming Fluoroprotein
FFFP	Film Forming Fluoroprotein
JP-4	Jet Plane Fuel Number 4
ml	Milliliter
PAM	Polyacrylamide
PG	Propylene Glycol
PVP	Polyvinyl Pyrrolidone
SW	Sticky Water

SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of this effort was to evaluate a variety of new approaches and methods of "neutralizing" fuel that could be spreading from a downed aircraft or spilling from another source. Approaches were explored that would be applicable to both burning or post extinguishment/fuel spilling situations. Approaches were also explored that would be used to suppress ignition for the case of a nonburning fuel spill.

B. BACKGROUND

Problems observed by Air Force fire fighting personnel with the current extinguishants and application procedures led to this study to evaluate several new concepts to improve "fuel neutralization." The problems focused primarily on a need for permanently securing (preventing ignition or reignition) of a fuel accident into which additional fuel could be entering. Permanent securing was defined as providing a safe environment for a time sufficient to remove personnel and remove involved equipment. Additionally, securing was defined to include modifying the fuel to a form in which it could be easily removed or cleaned up, thereby making the area of the airfield around the accident rapidly available for continued aircraft operations. Current securing procedures (foam blanket) provide a limited ignition suppression time and do not suppress the potential for reignition when the blanket is broken during cleanup. The history and technology of fire extinguishment and extinguishing agents and, specifically, with respect to postcrash fires, has been presented in Section II, Technical Discussion, as it was so extensive. Our approach to this research throughout was rationalized and based upon specifics of this background information.

C. SCOPE/APPROACH

A careful consideration of the variety of mechanisms of halting or interfering with an ongoing oxidation reaction or reducing the potential for initiation of an oxidation reaction (ignition) in a fuel spill or in postcrash fuel-fed fires provided the basis for the techniques studied in this program.

"Fuel Neutralization" is defined to mean the rendering of spilling or spilled fuel to become non-burning, and/or extending the time to reignition (typically measured by the "burnback" time in standardized tests). The concepts considered included chemically modifying the current extinguishant so as to:

1. create a strong sealing "cap" on the hydrocarbon fuel that would reduce vaporization, either by adding a water structuring

compound to make the foam "tougher" and less permeable to vapor, or by adding a fuel gelling compound to the fuel to reduce the rate of hydrocarbon vapor generation.

2. intermix extinguishant water into the non-burning fuel through the use of low-energy or "self-mixing" emulsifiers. These emulsifiers would be added along with the current extinguishant (AFFF) or after (as a separate application).
3. add halons or other volatile oxidation chain breaking agents into the water-AFFF stream.

Each of these approaches was developed upon consideration of each of three extinguishing mechanisms of fires in general, and in particular, as applied to fuel spill or postcrash fuel-fed AFFF extinguished fires.

SECTION II

TECHNICAL DISCUSSION

A. THEORY OF FIRE EXTINGUISHMENT

Fire can be defined as the high-temperature oxidation of materials, accompanied by a luminous flame. It occurs when a fuel contacts an oxidizer and the temperature is raised to the point that a chemical reaction takes place. If this reaction generates more heat than is lost to the surroundings, the reaction will self-propagate without the aid of an outside heat source as long as there is an adequate supply of fuel and oxidizer. The flame and hot gases generated in a fire are important in fires that involve solid and liquid organic fuels because most of the oxidation reactions take place in the gaseous phase. The flame then serves as the source of heat needed to pyrolyze and/or evaporate the solid or liquid fuel into the reaction zone.

A fire can be extinguished if the oxidation reaction is inhibited by one or more of the following mechanisms:

The physical separation and/or dilution of fuel and oxidizer.

Cooling of the reaction zone at such a rate that the reaction cannot self-propagate.

Chemical inhibition of the oxidation reaction by chemical scavengers that sever the chain-breaking reaction chain.

1. Separation of Fuel and Oxidizer

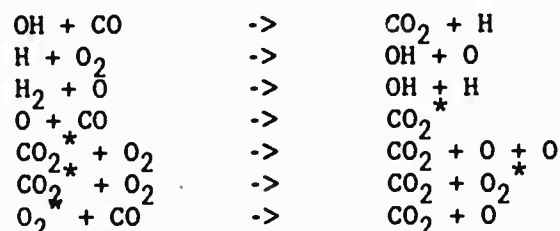
If the fuel and the oxidizer are physically separated by a layer of an inert material, obviously no chemical reaction can take place. The extinguishing (inert) material can be either gaseous, liquid or solid and its choice depends on the reacting fuel and oxidizer. Similarly, the fuel or oxidizer can be diluted by an inert material to such an extent that the rate of chemical reaction (which is a function of concentration) is reduced to a point where the rate of heat generation cannot keep up with heat losses. The temperature of the reaction zone will drop below the ignition temperature and the fire will be extinguished.

2. Cooling of the Reaction Zone

The chemical reaction between fuel and oxidizer can be slowed or stopped by adding inert coolants which absorb a large fraction of the generated heat and thus increase heat losses from the reaction zone. Depending on the method of application, these extinguishants may operate by cooling the liquid- or solid-fuel surface directly, by attenuating radiation from the flame to the fuel surface (thus reducing the rate of fuel generation), by cooling the flame itself to below the ignition temperature, or by a combination of these mechanisms.

3. Chemical Inhibition

Oxidation reactions of organic compounds generally involve a sequence of intermediate reactions which produce short-lived radicals such as OH, O and H and activated molecules such as O_2^* and CO_2^* . Examples of these reactions are (Reference 1):



If one or more of these radicals is removed by a competing reaction with an external additive, the overall oxidation reaction is slowed and the rate of heat generation is reduced to such a level that the fire may be extinguished. Halogenated hydrocarbons (halons) are known to be good chemical inhibitors. It is believed that they generate free halogens and hydrogen halides which react readily with and remove H and OH radicals in the flame. On the other hand, alkali metal carbonates (e.g., Na_2CO_3) and other metal compounds (e.g., iron pentacarbonyl) are believed to dissociate into metal radicals which deexcite the activated carbon dioxide (CO_2^*) and oxygen (O_2^*) molecules before they can react any further (Reference 2).

B. FIRE EXTINGUISHING AGENTS

1. General

Existing fire extinguishing agents generally combine one or more of these extinguishing mechanisms. Historically, water has been the most commonly used extinguishing agent. Its high latent heat of vaporization, relative abundance, low cost, and ease of handling have contributed to its wide use even though the usual methods for its application to a fire are highly inefficient. Only a fraction of the water applied to a fire goes into extinguishment. Most of it runs off to unaffected areas. The efficiency of water can be increased dramatically by adding gelling agents which reduce runoff and help separate the fuel from the oxygen source. (Reference 3) Carbon dioxide extinguishes fires mainly by oxygen dilution and separation of the fuel from the oxygen in the air and, to a lesser extent, by cooling.

Dry chemicals (sodium and potassium carbonates) combine flame radiation attenuation with chemical inhibition. Ammonium phosphate powder does both, and melts onto and seals the burning surface from oxygen. Aqueous foams provide a means for conserving water while separating the fuel from air. As discussed earlier, gaseous and liquid halogenated hydrocarbon extinguishants inhibit the flames by dissociating into halogens and hydrogen halides which break the reaction chains.

Different test procedures and apparatus have been used to estimate or quantify extinguishing efficacy of many chemicals (References

4, 5, 6, 7, 8, and 9). A very approximate comparison of hydrocarbon-air combustion inhibition efficiencies for a great variety of compounds is shown in Table 1 (Reference 10). The inhibition efficiency of CCl_4 (carbon tetrachloride) was chosen as 1 and the efficiencies of the other substances was expressed by the ratio of its efficiency to that of CCH_4 . Fire extinguishment test methods vary greatly, and not one substance has yet been tested by all methods and proved to be an accurate barometer by which to compare the methods.

2. Aqueous Film Forming Foams (AFFF)s

Firefighting foams were first used to extinguish flammable liquid fires in the early 1900s when foam was generated by mixing solutions of sodium bicarbonate and aluminum sulphate containing a foam stabilizing agent. This was known as "chemical foam" and was still frequently used in extinguishers until quite recently. Problems of size and maintenance of equipment made the "chemical foams" unsatisfactory.

The use of foam began to grow rapidly in the 1930s with the development of foaming agents and foam generating equipment which could produce foam in relatively simple equipment by entraining air. This foam was denoted as "mechanical foam." Some of the earliest foam stabilizing agents used in "chemical foam" were based on proteins. Saponin-type foam compounds were widely used in the 1930s, and the first aircraft crash trucks used saponin-based foams. The saponin protein foams exhibited poor heat resistance and the foam would separate and fuel would reignite. By the late 1930s, hydrolyzed protein foams had been developed that improved heat resistance.

As a result of a burst of government-sponsored research in the 1950s and 1960s, new foam agents were developed. Tuve and others at the U.S. Naval Research Laboratories were exploring vapor suppression compounds. The investigators found that certain fluorocarbon surfactants gave a film on hydrocarbon fuels which greatly reduced the rate of vaporization of the fuel. The combination of the fluorocarbon surfactants with detergents and stabilizers resulted in a new generation of easily handled and applied foams, known as AFFF. AFFFs have been developed since 1972 for extinguishing fire of flammable liquids, especially in postcrash fuel-fed fires (Reference 11). These foams contain perfluorocarbon surfactants, with nonpolar and polar functional end structures to render them partially soluble in both hydrocarbons and water, and capable of the Langmuir orientation at the interface. They are, therefore, highly surface-active in both water and organic liquids and lower the surface tension of water approximately 80 percent and JP-4 36 percent.

These AFFF compounds can be used 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 perhaps enabling resealing of breaks; second, with the foam floating on the surface of the JP-4, the water film can drain from the bubble, to yield a film of water floating on the JP-4. The water film floats on the surface of the JP-4 because of surface forces of the oriented surfactant on the "skin" of JP-4.

The floating film of surfactant solution can "vapor proof" a JP-4 surface, even after the foam is gone. Vaporization is necessary for a liquid fuel to burn since combustion only occurs in the vapor phase. Further, the fuel/air ratio must 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. 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 and reignition can occur. Furthermore, when the fuel pours from under the edges of the AFFF blanket or splits the AFFF film/foam blanket, reignition can also occur.

There are indications that AFFF may absorb fuel components into the foam mixture; eventually the foam is destroyed or sufficient fuel components are added to the foam for reignition to occur.

C. POST-CRASH FIRES

In a postcrash fire of an airplane all categories of fire may occur. The accident statistics show, that one has to deal with Class A, B, under some circumstances Class C and also Class D and Class E fires.

Class A fires mostly consist of fires of plastic materials, widely used for the interior of an airplane and for cable insulation. Plastics are also finding use in parts of the wings and the fuselage structure. The fire of the cargo of an airplane is also often a Class A fire. Fires of metals (Class D fires) have been observed too, as well as fires in the electrical insulation. (Class E fires).

The most frequent and severe fires following a crash of an airplane are class B fires, the fuel fires. This study addressed itself only to fuel fires. Aircraft ground fires can occur from many causes but are frequently the result of the ignition of fuel liberated from ruptured tanks in a postcrash situation or the result of a refueling spillage.

In postcrash situations the rapid deceleration of the aircraft invariably leads to the rupturing of components containing fuel. Friction heating of the metal components, as well as "hot spots" in aircraft propulsion systems provide a multitude of ignition sources. Fuels are usually atomized to form easily ignitable mists in the crash environment, the "mist fireball" then acts as an ignition source for a pool fire. In spite of the vast amounts of research into postcrash fire suppression, Horeff (Reference 12) has estimated that fire is the cause of 40 percent of the fatalities in aircraft accidents and reduces survivability from 65 to 42 percent.

Aircraft refueling (ramp) fires have been identified as the seventh most significant incident (Reference 13) in the aircraft statistical data

TABLE 1. EXTINGUISHING EFFICIENCY OF CHEMICAL COMPOUNDS (Reference 10).

Compound	Efficacy	C.	E.	C.	E.
N ₂	0.1	KNO ₃	1.4	(C ₂ H ₅) ₃ PO ₄	5.1
SiO ₂	0.2	KJ	1.6	(CH ₃) ₃ PO ₄	5.3
CO ₂	0.2	CuCl ₂	1.9	K ₂ C ₂ O ₄ ·H ₂ O	5.8
SO ₂	0.3	CH ₃ Br	1.9	PBr ₃	6.0
HCl	0.4	HBr	1.9	SbCl ₃	6.3
SiHCl ₃	0.5	Na ₂ SiF ₆	2.1	K ₂ CrO ₄	6.3
NaCl	0.5	KHCO ₃	2.3	Na ₃ AlF ₆	6.6
NH ₄ Cl	0.5	Na ₂ C ₂ O ₄	2.3	PbO	7.2
ChCl ₃	0.7	K ₂ SO ₄	2.3	POCl ₃	7.3
NaNO ₃	0.7	CH ₂ BrCl	2.4	TiCl ₃	7.3
SOCl ₂	0.8	SiCl ₄	2.5	BBr ₃	7.7
SF ₆	0.8	CF ₂ BrCl	2.7	K ₂ C ₂ O ₄	8.3
KCl	0.9	AlCl ₃	2.8	K ₃ AlF ₆	8.8
Na ₂ CO ₃	0.9	GeCl ₄	2.8	PCl ₃	9.2
CCl ₄	1.0	SnCl ₄	2.8	PSBr ₃	9.2
SO ₂ Cl ₂	1.0	Ba(NO ₃) ₂	3.0	PSCl ₃	10.6
(C ₂ H ₅) ₂ SO ₄	1.2	CF ₃ Br	3.2	Na ₂ [Fe(CN) ₅ NO]·2H ₂ O	15.5
KBr	1.2	K ₂ CO ₃	3.2	K ₄ Fe(CN) ₆ ·3H ₂ O	16.4
NaHCO ₃	1.2	AsCl ₃	3.6	K ₄ Fe(CN) ₆	46.3
S ₂ Cl ₂	1.3	Na ₂ SO ₃	3.9	CrO ₂ Cl ₂	57.5
Si(CH ₃) ₄	1.3	CF ₂ Br ₂	4.5	Fe(CO) ₅	81.2
				Pb(C ₂ H ₅) ₄	98.6

kept by North Atlantic Treaty Organization (NATO). In fact, these incidents represent a significant fraction of all reported aircraft incidents. During refueling, despite the use of equipment such as dry-break, quick-disconnect couplings, dead-man-control, and automatic fuel shutoff (Reference 14), fuel spills are inevitable. With fuel loading rates as high as 600 gal/min., a large spill can occur in a relatively short time.

Ignition sources can exist due to faulty grounding equipment or "hot spot" ignition caused by "hot" fueling with engines idling on combat aircraft and patrol aircraft. Others may be fueled with APU's running. Electrostatic ignition of fuel vapors (Reference 15 and 16) can occur in tanks filled with reticulated foam. In any case, the possibility exists for a fuel spill to occur and ignite with fuel continuing to enter the fire due to leakage or tank rupture.

It is apparent that a high probability exists for a pool fire of jet turbine fuel to occur with additional fuel being added to the fire. Much research has been performed on the extinguishment of the fire using Aqueous Film-Forming Foam and dry extinguishing agents (Reference 17). In this report Aqueous Film-Forming Foam has been abbreviated both as AFFF and AF³. Film Forming Fluoroprotein has similarly been abbreviated both as FFFP and F³P. The problem of continuing fuel input is important enough that equipment simulating cascade, spray and rod-type fuel inputs has been tested with various extinguishing agents and techniques (Reference 18).

In summary, these fuel fires can be divided roughly into two groups, the quasi two-dimensional pool fires and three-dimensional fires from jets or sprays or flowing fuel. Pool fires are called "quasi two-dimensional" as they flow over uneven surfaces and out from under foam blankets. Dry powders and halons are the best extinguishing agents known for the extinguishment of three-dimensional fires because they can be distributed into the space occupied by the flames. But these agents do not prevent reignition of the already extinguished fuel by hot surfaces or residual flames.

Extinguishing foams are best suited for the extinguishment of pool fires in the presence of reignition sources. Reignition is not prevented, however, with these foams as they are currently composed. These foams are also currently used on unignited flammable liquid spills and to prevent reignition of fires after extinguishment (References 19, 20, 21, and 22).

Conventional firefighting foams are limited in the length of time they can keep a flammable liquid from reigniting. The water drains from the foam, the foam bubbles coalesce, and the foam becomes saturated with the flammable liquid. The "securement" time depends on the type of foam used, the method of foam application, the flammable liquid involved, and the depth of the foam layer applied. Securement time includes the time both to extinguish the fire and to eliminate reignition or burnback. Generally, the securement time in postcrash fires is less than 1 hour, and in some situations may be only minutes (Reference 23).

Cleanup of a flammable liquid spill, or draining of a storage tank, generally takes longer than 1 hour and may take several days. This would

require reapplication of the foam to continue to prevent reignition or burnback. Reapplication of the foam is expensive and may result in a greater clean up effort, but in current practice is essential for site safety.

SECTION III

EXPERIMENTAL PROGRAM

This section details general considerations, apparatus, experimental and test procedures and results associated with each of the approaches outlined above.

A. SEPARATION OF FUEL AND OXIDIZER

Two approaches to achieve the separation of fuel and oxidizer were studied. In one, water-gelling polymer agents were mixed into aqueous AFFF solutions, in the other, fuel-gelling polymers were mixed with JP-4. In the first case, an attempt was made to seal off hydrocarbon vapors from air by toughening the permeability of the aqueous foam/film. In the second case, emphasis was placed on the reduction of volatiles by reducing the vapor pressure of the gelled fuel.

Any polymer which can gel a solvent, aqueous or organic, must be;

1. high molecular weight ($>10^6$)
2. very soluble in the solvent (H_2O or hydrocarbon)
3. very highly crosslinked ($\sim 1/2$ percent)
4. very rapidly dried from the solvent in which it was "infinitely" soluble.

Polymers which possess these characteristics were identified, for both the aqueous and organic solvents, for our study.

1. Rapid Flowing Tough Film/Foam

Increased vapor pressure and decreased surface tension of hydrocarbons with heat causes hot fuel to actively percolate up into the hot AFFF foam. The effect of temperature on fuel is greater than that of the water. The balance is further decreased because the foam has drained a lot of its water content to the rapid-knockdown film. The increasing evidence that the foams themselves can ignite (References 24, 25, 26, 27, and 28) is understandable, even though the fluorosurfactants themselves are not easily ignitable. A water-gelling agent delivered in parallel (simultaneously but separately) with AFFF may improve the foam's efficacy in two ways. The foam may retain more water after early draining of a knockdown film, making it more impermeable to hot hydrocarbon vapor. Also, the liquid aqueous film, advancing over the fuel, may gain some structure from the gelling polymer and may itself become more impermeable to the hot fuel below it.

We assembled an apparatus to quantitatively measure the sealing efficacy of the AFFF film in conjunction with aqueous gelling actives. The design is based on one found in the literature which we adapted to permit measurements of sealing characteristics with increasing temperature.

a. Apparatus and Experimental Procedure

Our laboratory-scale screening tests were made on apparatus adapted from one devised by Nicolson and Artman at CIEA-GEIGY (Reference 29), Figure 1.

The Perkin Elmer IR recording spectrophotometer model 1320 was set at 2973 cm^{-1} , a prime absorption wavelength for the C-H bond. Fresh JP-4 was placed in the petri dish and the space above it was flushed with N_2 , at a flow rate of about $770 \pm 200\text{ ml/min}$. It was important to use fresh JP-4 as standing samples easily lost the lower boiling point volatiles and made reproducibility difficult. Another factor affecting reproducibility was the method of sampling the atmosphere above the JP-4 or the "sweeping method."

Sweeping could be accomplished either by pulling air through the system, (vacuum-connected to the IR purge exit) or by pushing a gas, e.g., N_2 , through the system. The advantage of using the positive pressure was greater control of reproducibility of the flow rate. The drops formed at the tip of the syringe became much larger, however, than they did under the negative pressure. The heavier drops dropped through the fuel instead of staying on top and spreading. Comparisons were made only on samples observed by the same sweeping method. The film-forming sample delivery system was composed of a Sage model 255 variable-speed syringe pump on which was mounted a 1 - cc glass hypodermic syringe fitted with a 3 inch 22 - gauge needle. An Omega temperature control unit and Brooks flow control valve were fitted under and above the sample chamber.

Curves are automatically plotted of the percent seal versus time. The shape of these curves can be related to three key characteristics of any novel film formulation: the speed, quality and durability of the seal against the hydrocarbon vapor. Formulations which appear equivalent at room temperature can then be further evaluated by performance with increasing fuel temperature. Several blank runs were made on the JP-4, at 10°C increments, to test the apparatus and determine the time of vaporization of the higher chain length hydrocarbons between 30 and 60°C . The results are shown in Figure 2 and Table 2. Increased transmittance indicates less absorption by the hydrocarbon, i.e., less concentration in the vapor as time progress.

TABLE 2. VAPORIZATION OF JP-4 AT VARIOUS TEMPERATURES.

Temp ($^\circ\text{C}$)	30	40	50	60
"Take-off time" (a) (sec)	145	250	330	370

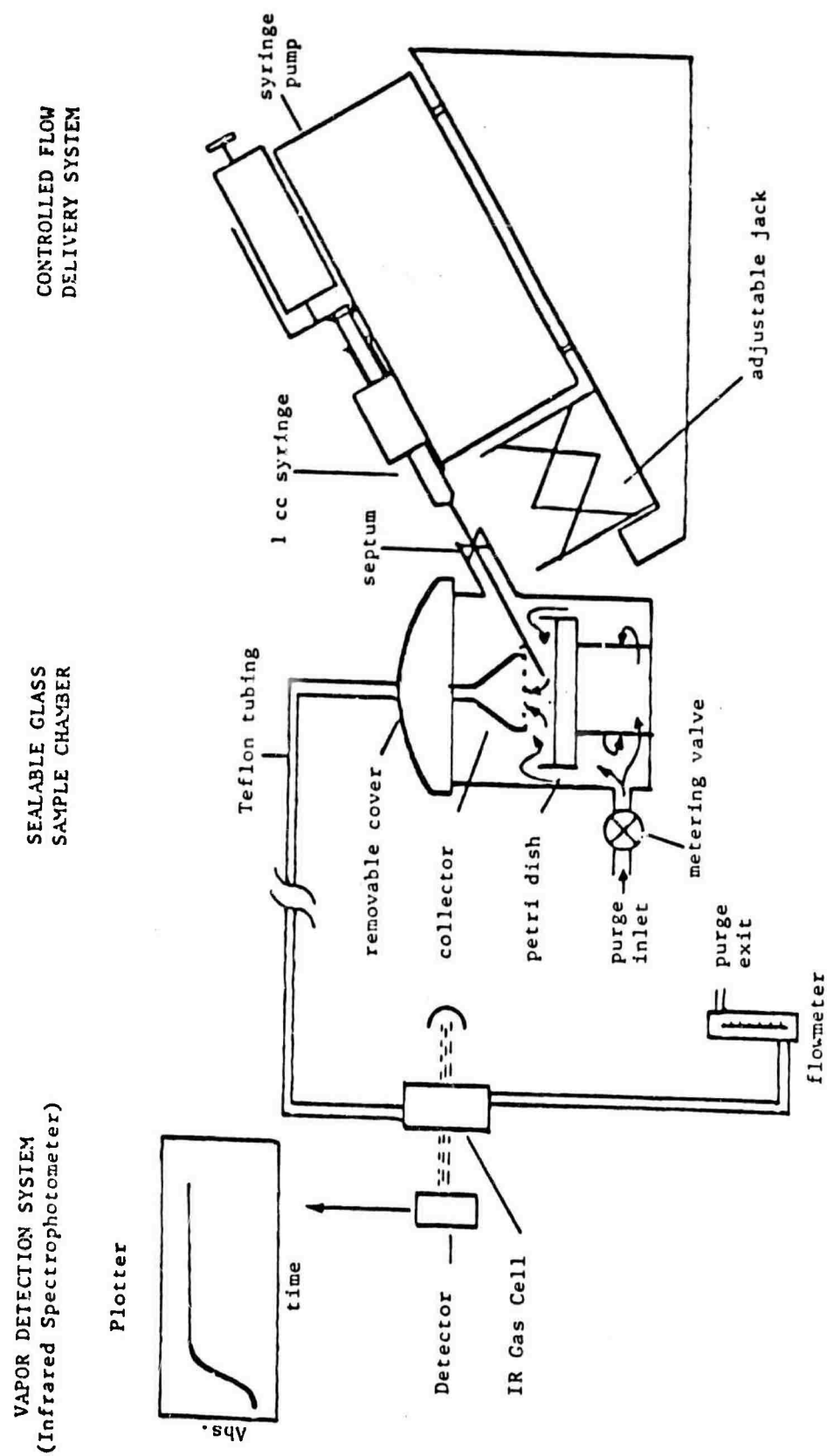


Figure 1. Apparatus for Evaluatin AFFF Sealing Characteristics (Reference 29)

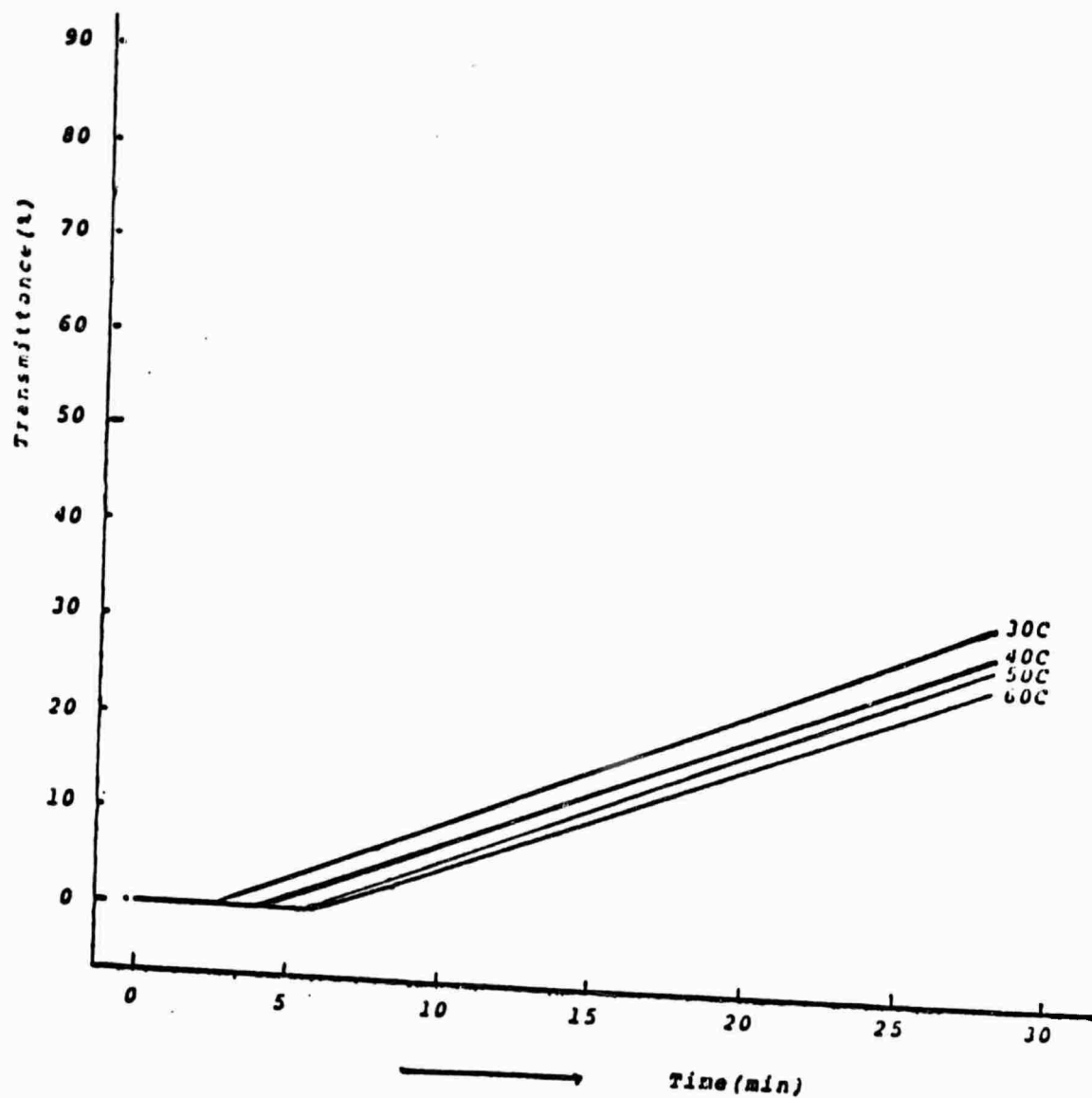


Figure 2. Vaporization Rates of JP-4 at Various Temperatures

Since higher boiling fractions vaporize at higher temperatures, optimized emulsifying systems can thus be further tested for performance in sealing characteristics, even though these temperatures are far below that of flaming fuel. The sealing characteristics of AFFF also change with temperature. The percent seal, as measured by percent transmittance $-(\text{Abs}_{\text{max}} - \text{Abs}_{\text{obs}})/(\text{Abs}_{\text{max}} - \text{Abs}_{\text{min}}) \times 100$ is shown in Figure 3.

This test defined the 50°C maximum as adequate to stress-test our compositions. The test further served to define the effect of experimental procedure on the results in the following manner.

As described above, two sweeping methods were used to move the hydrocarbon vapor from above the petri dish into the IR sample cell. In one, the vapor was carried by nitrogen gas swept into the sample chamber, in the other a vacuum was pulled from the outlet of the IR gas cell, sweeping with air. In both cases, the flow rate is controlled exactly by the Brooks flow control valve, on which a setting of 770 cm³/min was equivalent to 0.2 ml sample per minute. The droplet size, however, is smaller under a pulled vacuum and tends to stay on the surface. A larger, heavier droplet is formed under positive nitrogen pressure and can drop through the fuel, preventing an aqueous layer from forming. We therefore generally pulled air through the chamber over a 10 ml aliquot of JP-4 in a petri dish, with surface area of approximately 80 cm². The sealing characteristics of various water-gelling additives and emulsifiers and their effect on 3 percent AF³ were then studied. Examples of specific experiments related to water gelling are listed in Table 3. These tests were used to screen for materials which did not interfere with the speed and efficacy of sealing by AF³. The time required to cover fuel surface was measured in seconds. The same apparatus was used to study the effect of varied emulsifiers on the sealing characteristics of AFFF. See Section III B.

b. Water Gelling Compounds

A wider appreciation of the role of "structured liquids" has been gained over the past 10 years from both polymer and biochemical studies. In both of these fields, very long-chain molecules "structure" the liquid they are in, so that the order of a solid physical state is combined with the mobility of a liquid physical state. This is true in each of the two classes of liquids on earth, hydrocarbons and aqueous solvents, with the polar polymers dissolving and tending to gel the aqueous media and the non-polar ordering, or tending to "gel" hydrocarbon media. These polymers travel in solution with a great many solute molecules "attached" by electrostatic and configurational forces. These polymers are called "thickeners" or gelling agents and are said to be solvent "swellable," and if they can be cycled between dry and wet states, they are said to be able to "reversibly absorb" the solvent. We decided to study the possibility that a solution of these in the aqueous phase could lead to a "tougher" or more highly structure film of water capping the hydrocarbon fuel.

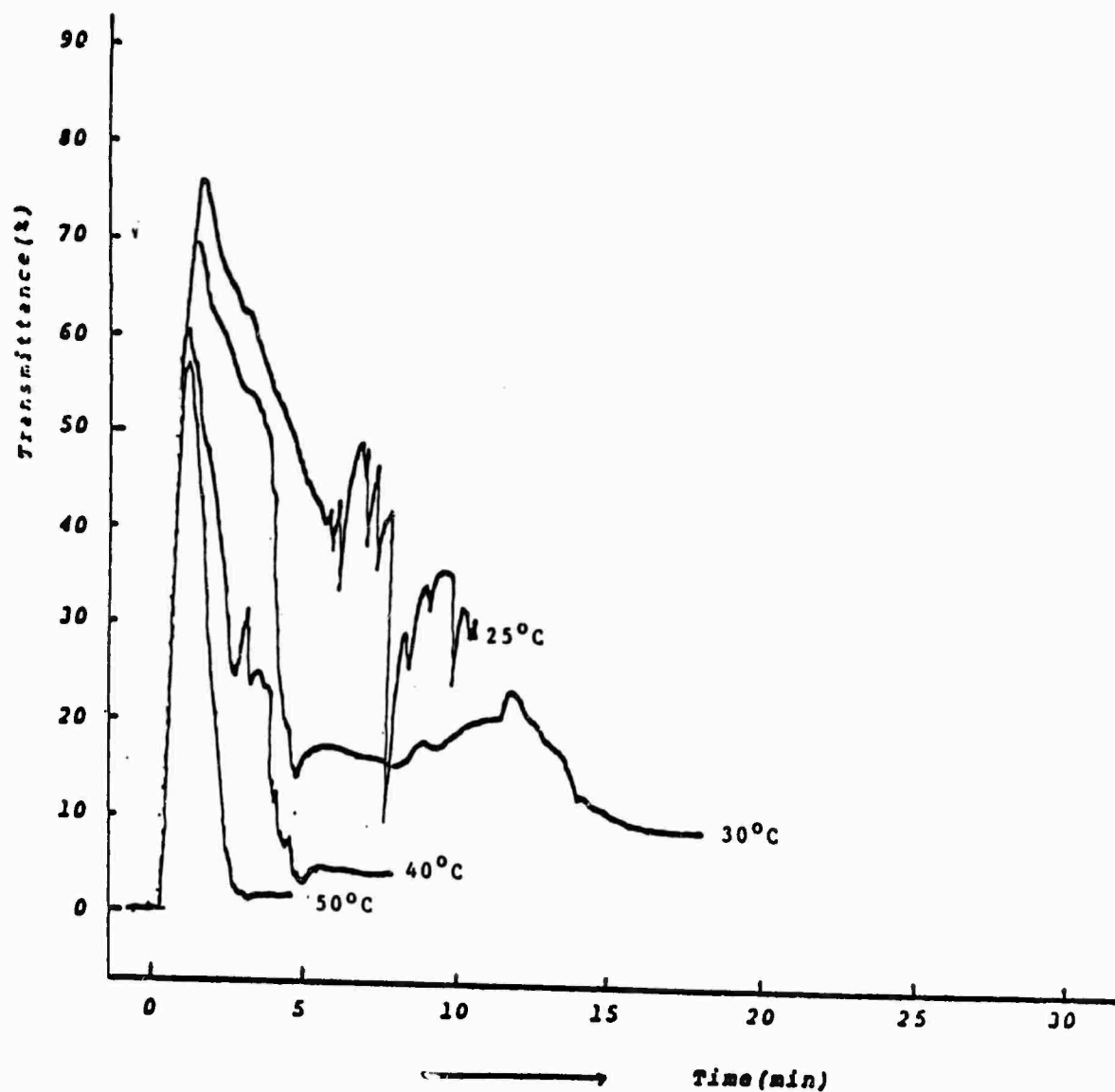


Figure 3. Sealing Curves of Neat AFFF Tested at Various Temperatures (30-50)

TABLE 3. WATER STRUCTURING COMPOUNDS.

<u>Compound Name</u>	<u>Source</u>
Carboxymethylcellulose	Aldrich Chemical Co.
Poly (vinyl alcohol) Av.MW. 86,000	Aldrich Chemical Co.
Poly (acrylamide) carboxyl modified AV.MW. 200,000	Aldrich Chemical Co.
Albumin (denatured protein)	Aldrich Chemical Co.
Poly(acrylic acid) Av.MW. 1,000,000	Polysciences Inc.
Poly(methylvinylether/maleic acid) low MW.	Polysciences Inc.
Viscarin GP109	FMC Corp.
Acrysol ICS Thickener	Rohm & Haas
Polyvinyl pyrrolidone PVP-K-90	GAF Chemicals Corp.
Poly Clar AT	GAF Chemicals Corp.
Sticky Water Starch copolymer (acrylamide)	Geo. Acaley Assoc. Inc.
Super Slurper Starch copolymer (acrylamid)	Ed. Kirkland Super Absorbant Co.

A number of "water thickeners" and gelling agents were tested as additives to AFFF solutions, delivered as a film onto JP-4 in the film characterizing apparatus (Section III A.1.a.). They were screened for efficacy in reducing the hydrocarbon vapor concentration above the JP-4. The compounds that were obtained and tested are shown in Table 3.

The last two compounds are extremely water swellable, being able to reversibly absorb 300-600 times their weight in water, depending upon the ion content and pH of the water. These polymers are variations of starch-polyacrylonitrile [S-PAN] graft copolymers [PAN MW. $\sim 8 \times 10^5$] first developed by the U.S. Department of Agriculture in Peoria, Illinois in 1969 (Reference 30). Our contact at USDA is George Yelenosky. We were unable to obtain a sample of "Water Lock"^(TM) from Cal Blystra at International Environmental Technologies, Ltd., but believe it is probably of a similar chemical family. Most of the other compounds are consumer-

safe products used as texture modifiers, thickeners, emollients or stabilizers in a wide variety of applications including foods, cosmetics and household products. The commercial products requiring trademarks have been listed in the notice on the inside front cover of this report.

c. Observations and Results

All the thickeners were used as additives to AFFF within a 0.1 - 1 g/ml final concentration range. The starch copolymers were used in the range of 0.01 - 0.05 g/ml in final solution. The concentrations of stock solutions were determined by maximum solubility of each compound in tap water, pH ~ 7, at R.T.

In the apparatus as we used it, the water structuring compounds did not extend the life of the AFFF film and the impermeability of the film to hydrocarbon vapors. In Figure 4, typical consecutive recordings are shown of the sealing characteristics of AFFF and one of these additives, albumin (0.05 percent). Compared to the curve of neat AF³ (3 percent, 25°C, Figure 3), these additives reduced the quality and speed of the film formation. Only 20-30 percent of the HC vapors were sealed off as compared with 70-75 percent in Figure 3. The percent transmittance is equivalent to percent sealing of vapors, remembering that 100 percent transmittance at 2973 cm⁻¹ indicates no C-H bond absorbance, or no hydrocarbon vapor present. Figure 4 also gives a good idea of the range of reproducibility of the film-sealing profile for one composition. In Figure 5, the sealing curve of AF³ (3 percent) and a starch copolymer, "Sticky Water" is shown. Again, the percent sealing is reduced, but the stability of the film is somewhat extended, compared to neat AFFF. In Figure 6, the curves of "neat" F³P (Ansul) can be seen to promote extended film stability, probably arising from the protein content which it has in addition to the fluorosurfactants in common with AF³. The spikes in the curves were formed when bubbles broke. The seal ranged from 75-87 percent and lasted 12 minutes in the first sample and ranged from 70-77 percent and lasted 18 minutes in the second sample. When the house vacuum was used to pull air through the system at 190 millimeters per minute, the same material gave a sealing curve that lasted 50 minutes at about 83 percent seal, and another 20 minutes at 42 percent seal (see Figure 7). Although the variability under N₂ was great (Figure 6), some useful comparisons were able to be made. The compositions containing the starch copolymers and blends of AF³ and F³P performed as outstanding films in all three aspects; improved spreading time, equal to AF³ or superior percent sealing, and dramatically improved film seal durability (Figure 8).

As long as the experimental conditions and settings were comparable for a series, the curves were fairly reproducible and sufficiently sensitive to discriminate between the performance of AF³ and F³P, Table 4, showing a slightly greater percent and more lasting seal from F³P after more than doubling the sealing times recorded for AF³, somewhat as expected from field observations. In slightly different combinations, the mixture of AF³, F³P and Sticky Water was used in the 6-foot pan test, in the ARA supervised field tests at Tyndall Air Force Base to give dramatically reduced sealing times (See III B.1.d.), a possibility indicated in these early tests.

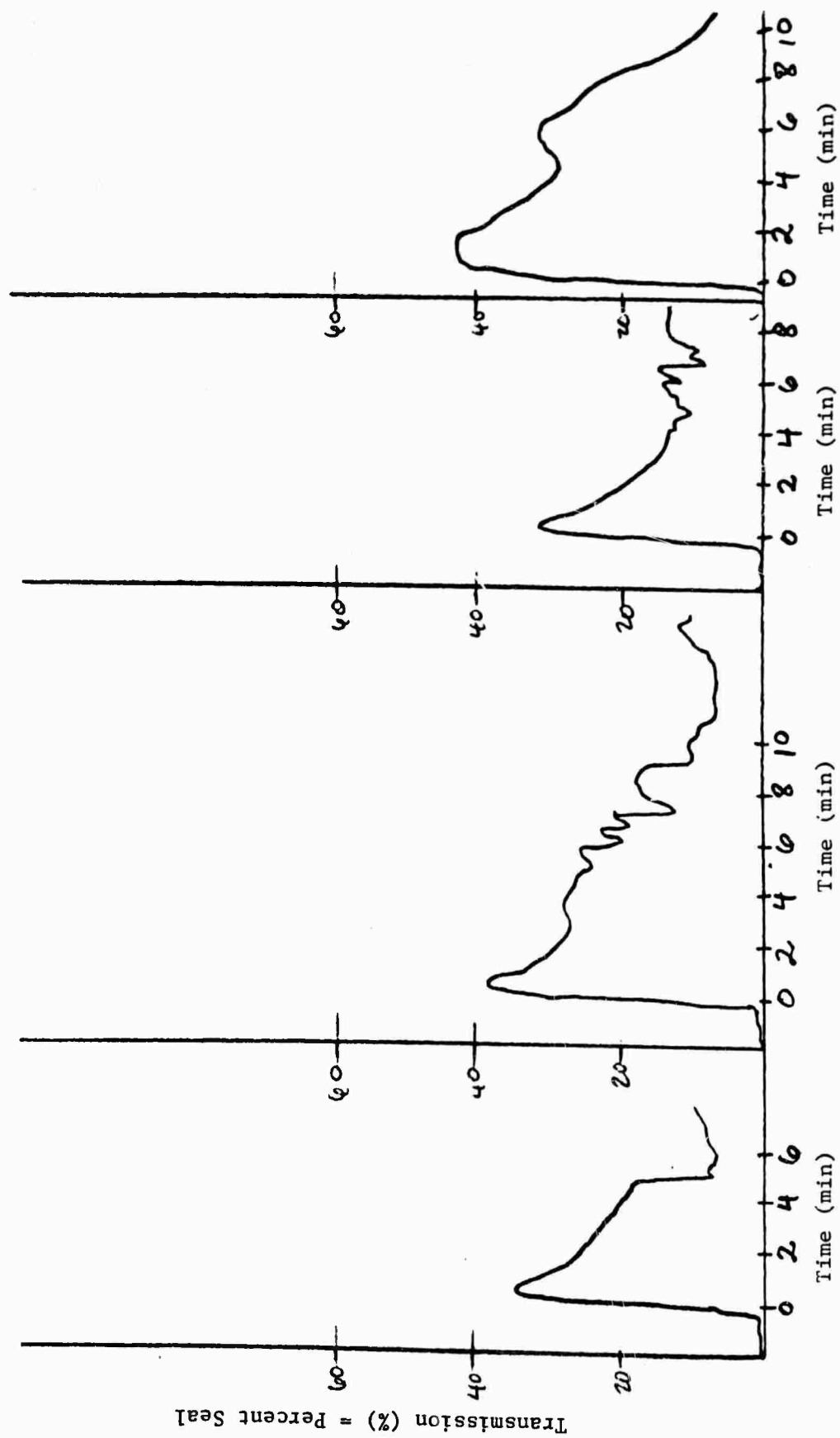


Figure 4. Sealing Curves of AFFF (3%) with Albumin (.05%)

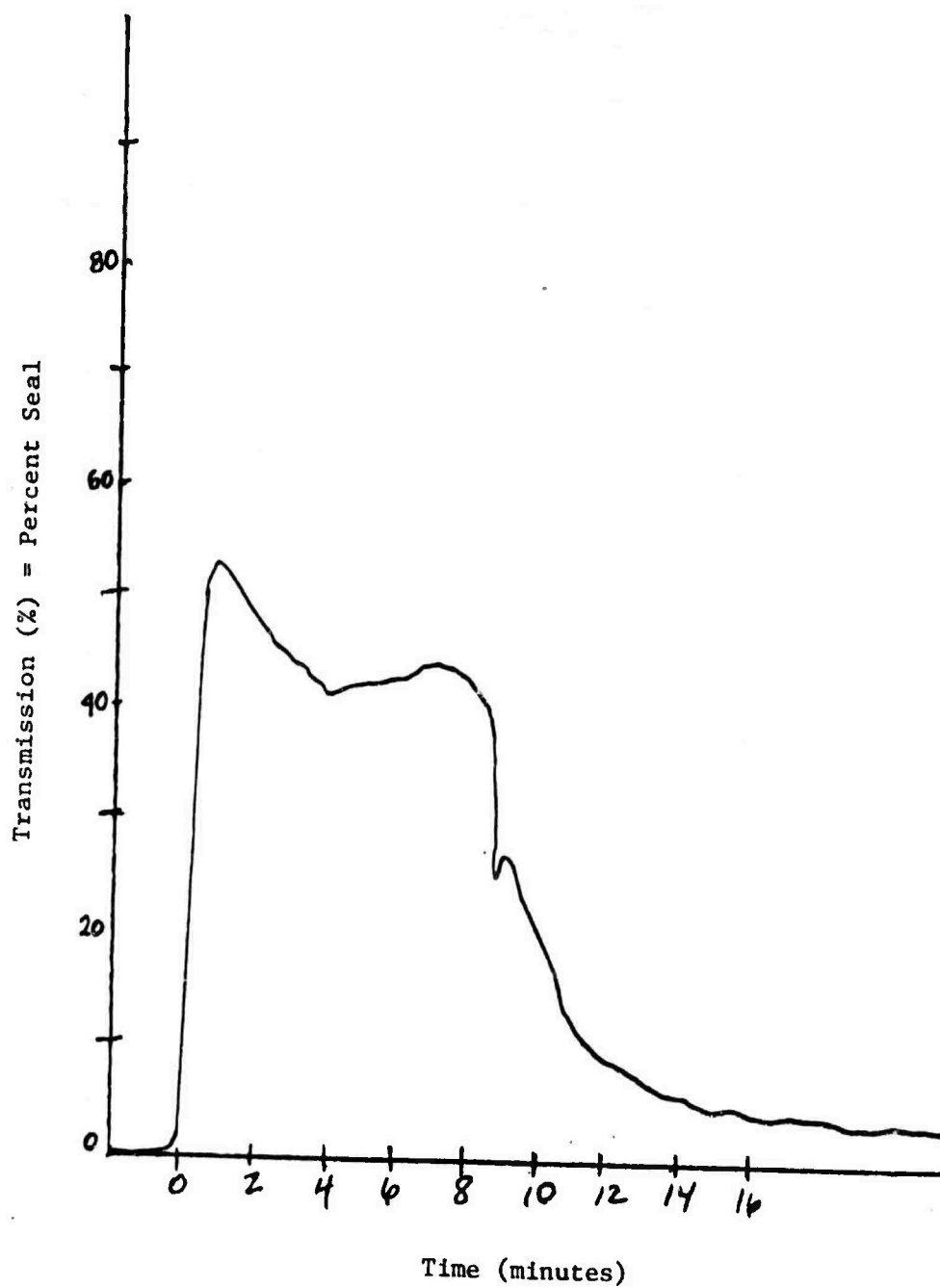


Figure 5. Sealing Curve AFFF (3%) with Sticky Water (.05%)

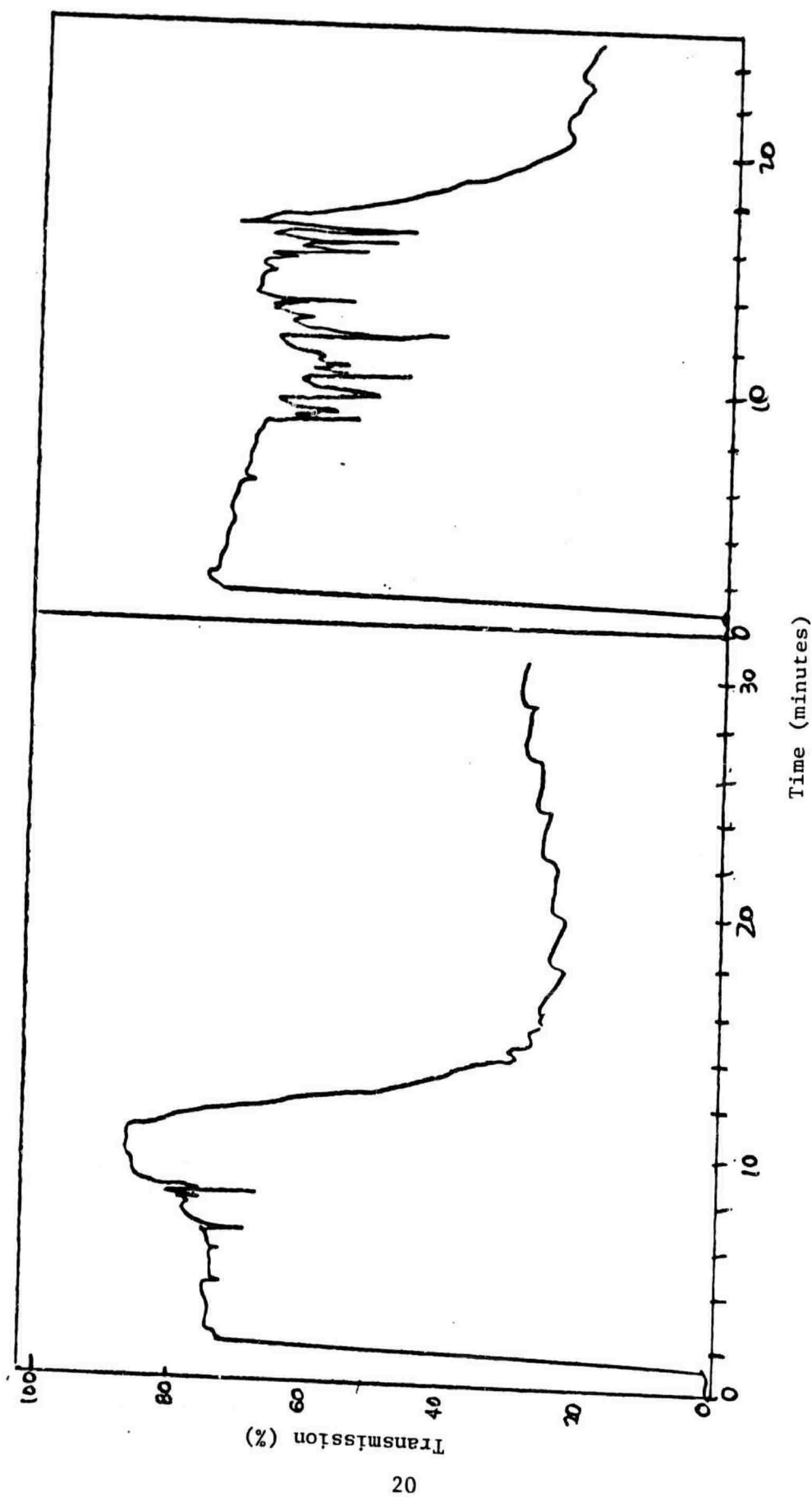


Figure 6. Sealing Curves of FFFP (3%) in N₂, 770 cc/min.

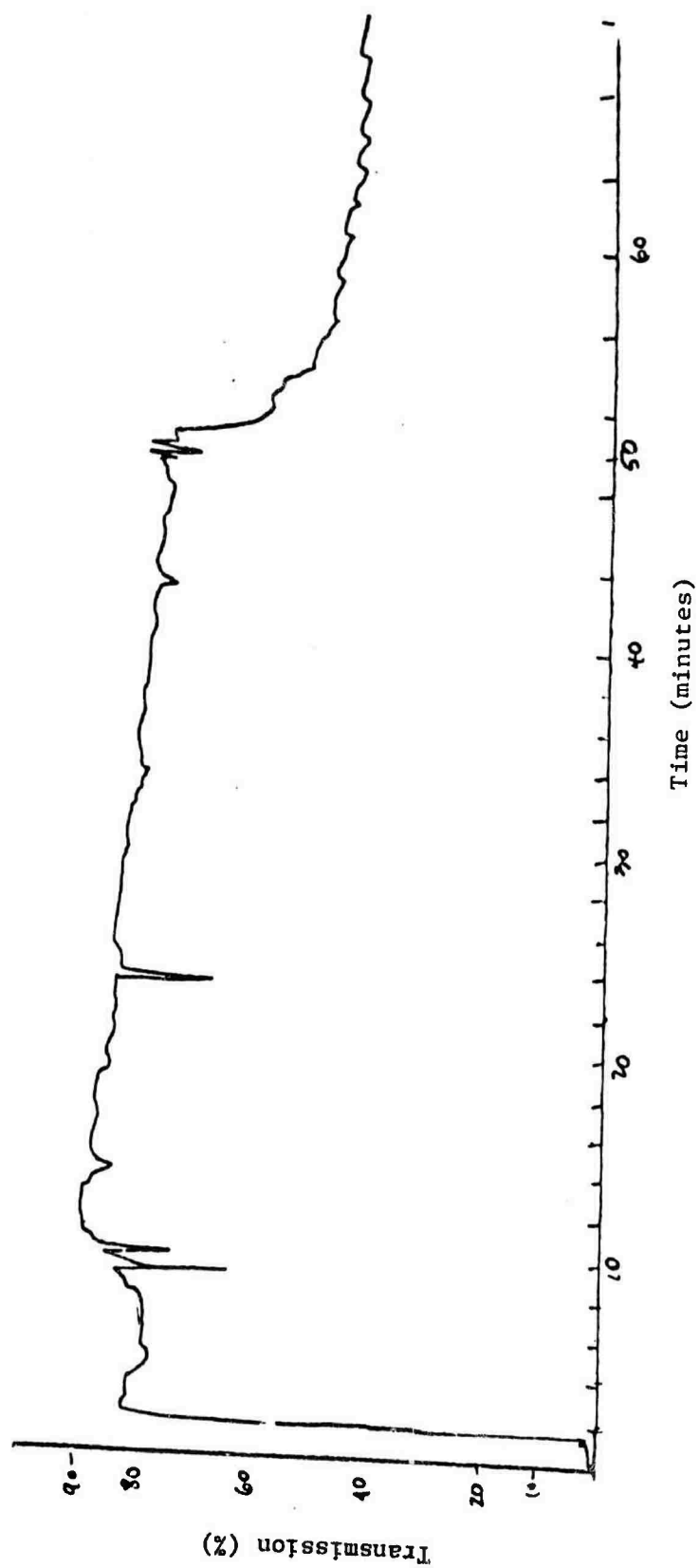


Figure 7. Sealing Curves of FFFP (3%) in Air (House Vacuum); 190 cc/min.

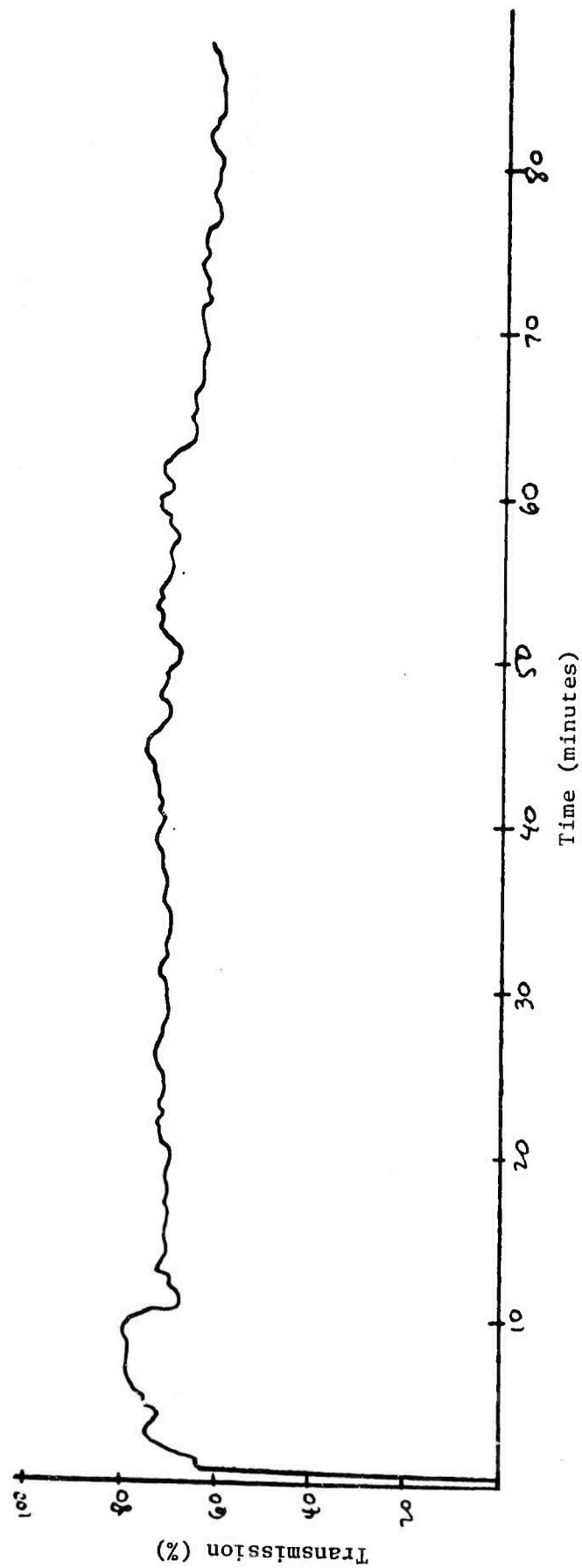


Figure 8. Sealing Curve of AFFF (3%) FFP (.75%) SW (.05%)

TABLE 4. FILM FORMING CHARACTERISTICS OF COMBINATIONS OF AFFF, FFFP,
AND STICKY WATER.

<u>Exp #</u>	<u>Agent</u>	<u>Sealing(%)</u>	<u>Time* (sec)</u>	<u>Remarks</u>
1	Neat AFFF(3%)	76.3	21	Kept max. seal 5 min.
2	Neat AFFF(3%)	74.1	22	Kept max. seal 8 min.
3	Neat AFFF(3%)	79.4	21	Kept max. seal 6 min.
4	Neat FFFP(3%)	89.7	46	Kept max. seal 30 min.
5	Neat FFFP(3%)	92.4	46	Kept max. seal 45 min.
6	Neat FFFP(3%)	96.3	45	Kept max. seal 27 min.
7	AFFF(3%)+Sticky Water(.03%)	81.0	26	Min seal: 56%
8	AFFF(3%)+Sticky Water(.03%)	78.4	29	Min seal: 50%
9	AFFF(3%) + FFFP (1.5%)	80.0	12	Kept max. seal 12 min.
10	AFFF(3%) + FFFP (1.5%)	76.0	13	Kept max. seal 15 min.
11	AFFF(3%) + FFFP (.75%) + Sticky Water (.017%)	83.6	10	Kept seal 40 min.
12	AFFF(3%) + FFFP (.75%) + Sticky Water (.017%)	83.6	11	Kept seal 85 min.
13	AFFF(3%) + FFFP (.75%) + Sticky Water (.017%)	81.5	10	Kept seal 50 min.
14	AFFF(3%) + FFFP (.75%) + Sticky Water (.017%)	80.4	11	Kept seal 70 min.
15	AFFF(3%) + FFFP (.75%) + Sticky Water (.017%)	86.8	10	Kept seal 50 min.

* The time required to cover the fuel surface.

d. Conclusions & Recommendations

The highly expandable starch polymers seem to be able to form a very thin gel-sheet in conjunction with fluorosurfactants and perhaps, necessarily another, smaller water structuring polymer such as a protein in F³P. On its own, however, albumin apparently facilitated the water to drop through the fuel, and thereby reduced the percent seal and lifetime of the AF³ film (Figure 4). Adding a starch grafted copolymer to a mixture of AF³ and protein-fluorosurfactant produced a film (Figure 8) far superior to that produced by the combination of AF³ and protein alone.

The mode of action of a water-structuring reagent in practical application would be to structure the aqueous film as it drains from a foam. Therefore, we caution against putting too much significance on the failure of "water thickeners" to promote a toughened gel-sheet film (Table 4). This "film" was applied dropwise to the surface of the

The results of our studies suggests that the combination of a highly active water structuring polymer, e.g., "sticky water" with a mildly active one, such as protein (or other biological polymers) as found in the F³P, may produce a toughened but still rapidly moving aqueous film draining from the foam. Compositions to be evaluated as foams which include combinations of the best of the highly or even mildly active water structuring polymers are therefore of great interest. It is recommended that these be evaluated in small field tests where the form and method of application will influence the efficacy. From our studies, however, it is very likely that the addition of small amounts of starch-grafted copolymer into a water stream (~0.01 - 0.02 percent w/v) may significantly enhance burnback efficacy of AF³.

2. Fuel Gelling Additives

a. General Considerations

Western Company (Reference 31) 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.

The evaporation rate of a fuel affects its combustion or burning rate, since combustion of fuel is only possible 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 vary in the napalm, elastomer and soap gels. All start as if unthickened, but the elastic systems rapidly skin over with a drastic reduction in evaporation rate. The soap acts as a wick for a time, then forms a skin. 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 that of evaporation, except when a thinning causes a change in lump configuration; this speeds up the rate.

In general, such tests have shown flame spread rates to decrease by a factor of 60 to 150, as compared to the unthickened fuel.

Therefore, it appears that thickening the JP-4 fuel spill will reduce its evaporation, and thereby, its combustion or burning rate, enabling 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 vaporize at a much slower rate, giving time for the fire to be extinguished in the critical minutes (or seconds) after the fire starts. Tests comparing vaporization rates (Reference 31) of gelled and ungelled fuel confirmed that gelled fuel vaporizes much more slowly than liquid fuel.

Figure 9 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. There is much slower vapor release by the gelled fuels. The curves shown in Figure 9 also indicate that increasing the gelling agent concentration does not produce a corresponding reduction in vaporization rate.

The time range within 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 9 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 10 shows a graph of burning times for 160-cc samples of fuel with different concentrations of Westco gelling agents. This figure shows a slight decrease in burning time for the one percent gel, compared to the liquid fuel. This variation is within experimental error. Note that this gel is actually a viscous liquid at a 1 percent concentration, while the higher concentrations give more or less rigid gels.

The Western Company (Reference 31) test showed that gelling the fuel can reduce the vaporization rates and burning rates 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.

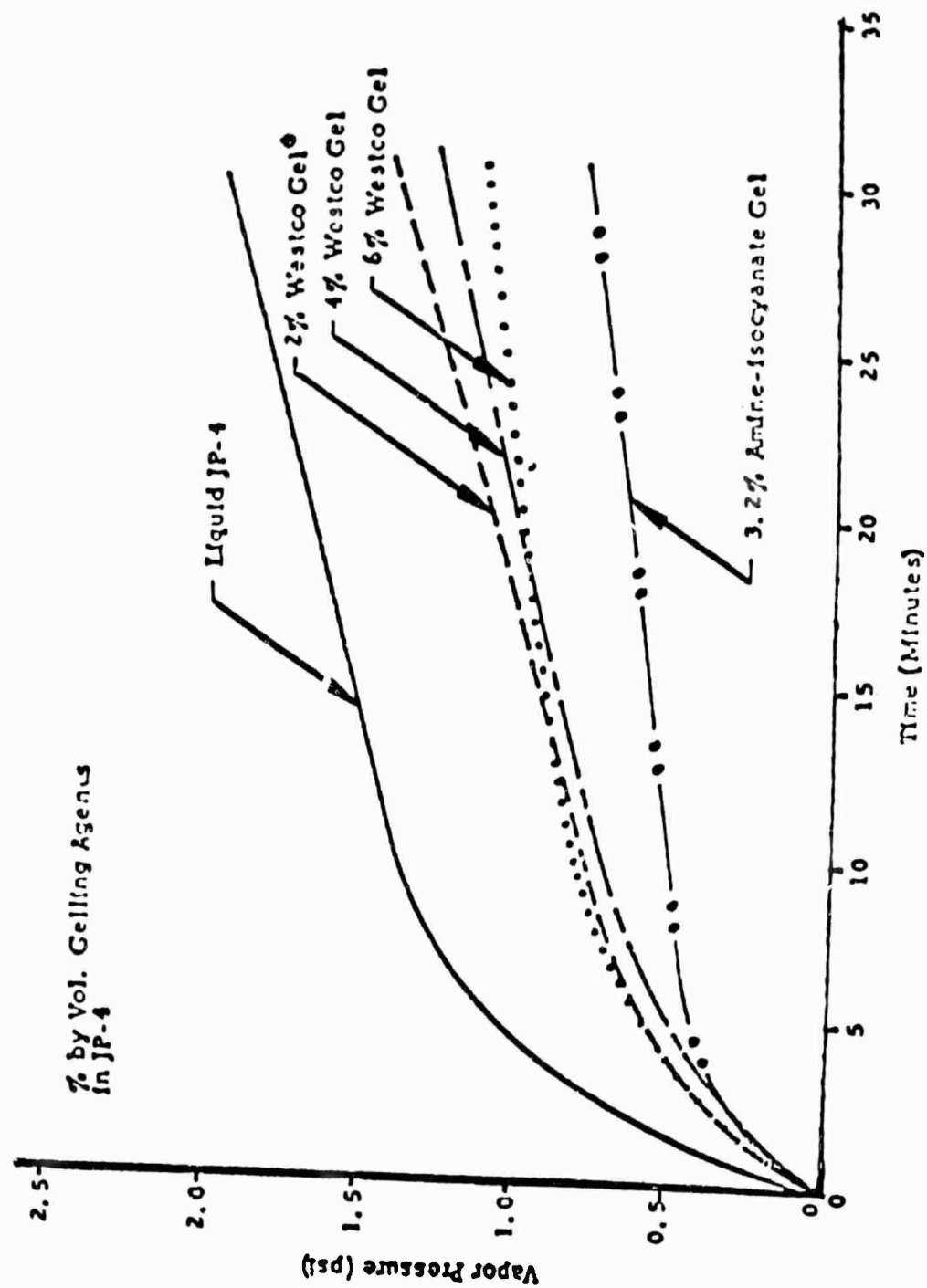


Figure 9. Vapor Pressures Over Time of JP-4 Gels (Reference 31)

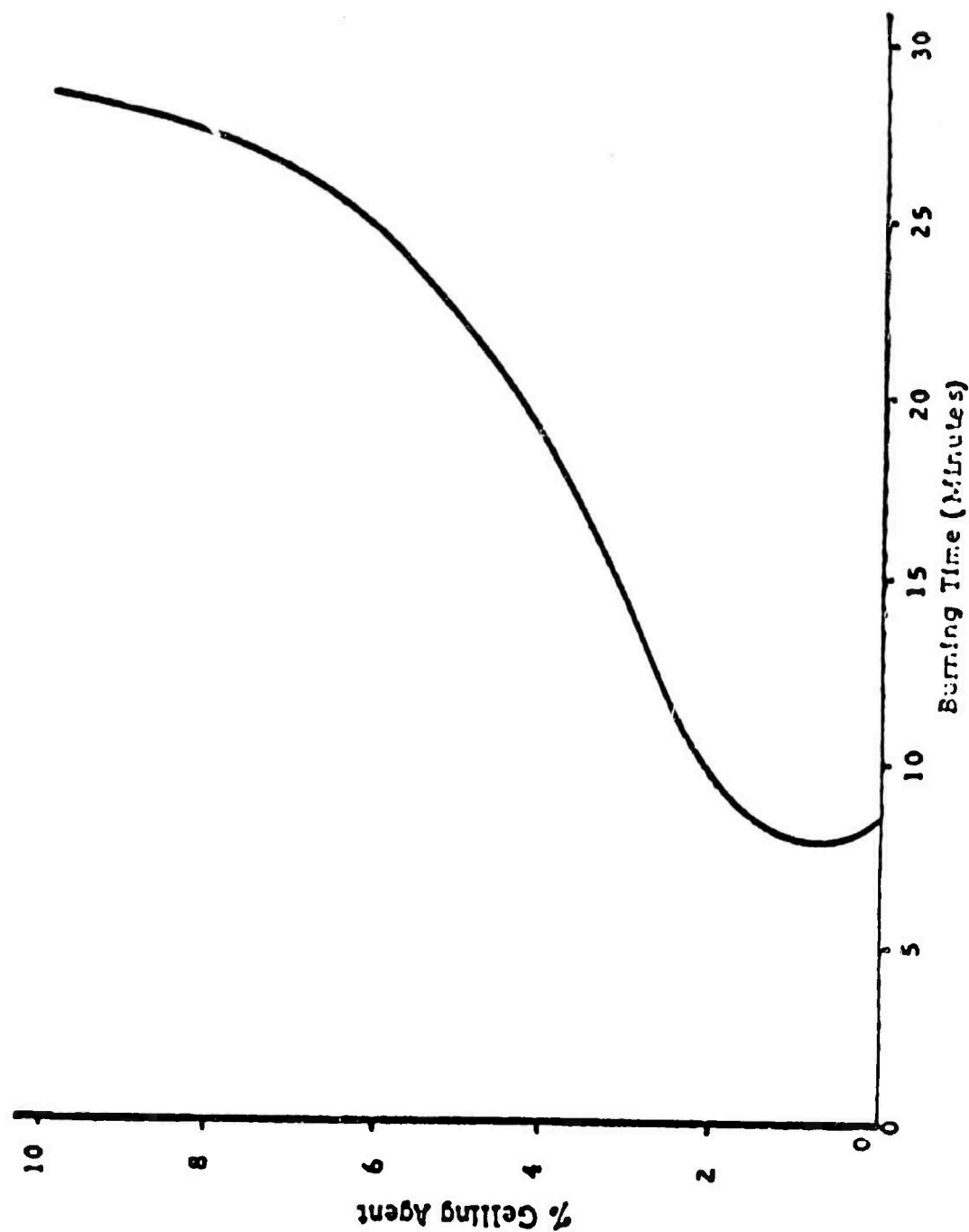


Figure 10. Gel Burning Time vs. % Gelling Agent (Westco)
(Reference 31)

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 32) 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, these results are shown in Figures 11 and 12. Both of the modified fuels offer a substantial reduction of the flame duration time. 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 32) 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 13 and 14 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 Schaeckel (Reference 33) report on measurements of relative flame velocities across liquid and emulsified fuel surfaces at 25°C conducted in a miniature trough, 46 cm 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 33) that weathering effects 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. Flame velocity measured by other investigators may have been caused by the formation of a skin on the surface of the JP-4 thereby limiting diffusion of the JP-4 vapors to the surface. The validity of the relative flame speeds obtained (Reference 33) 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 34) performed a fire hazard evaluation of thickened aircraft fuels at the Bureau of Mines. They

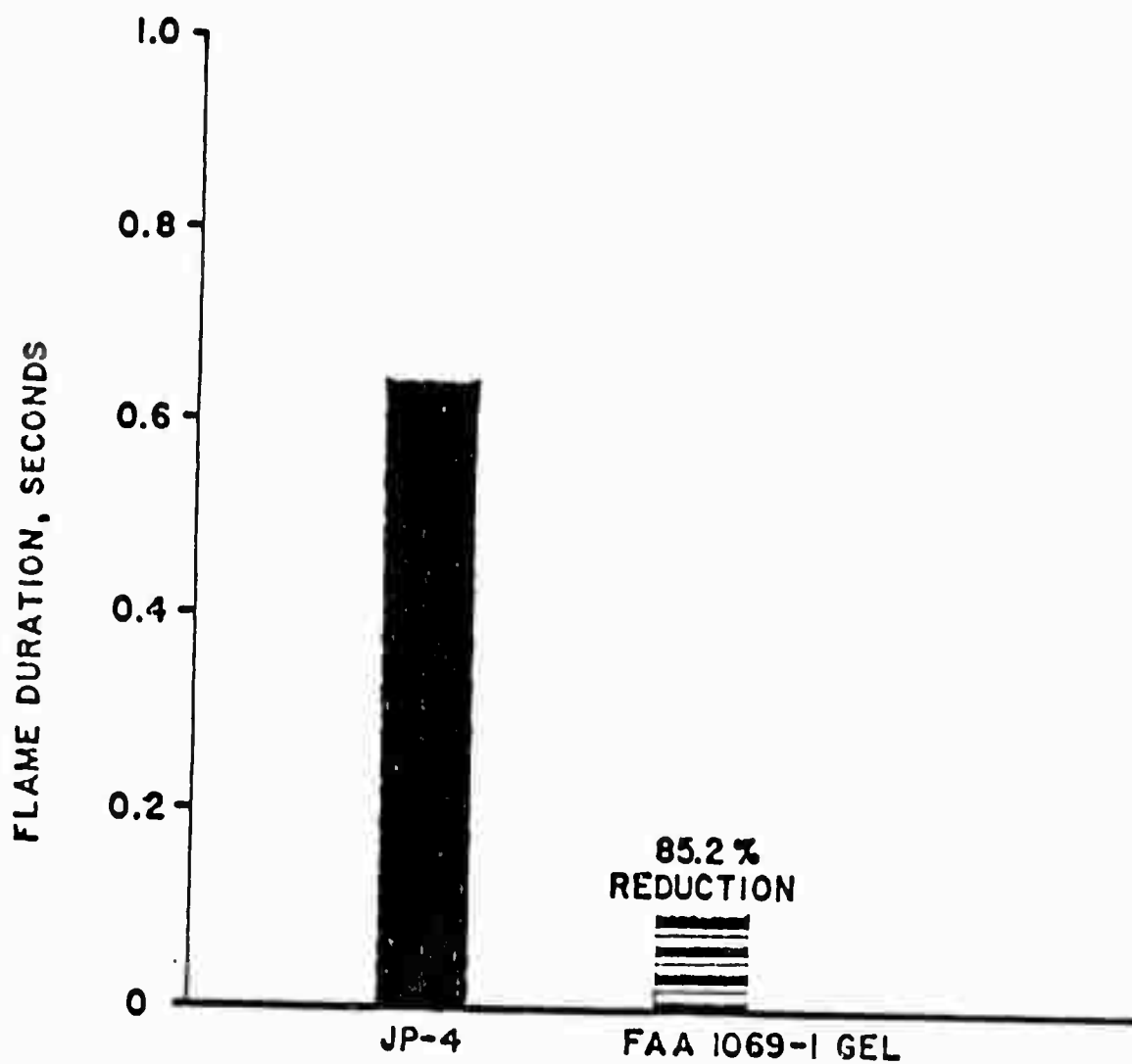


Figure 11. Flame Duration JP-4 versus FAA 1069-1 Gel.
(Reference 32)

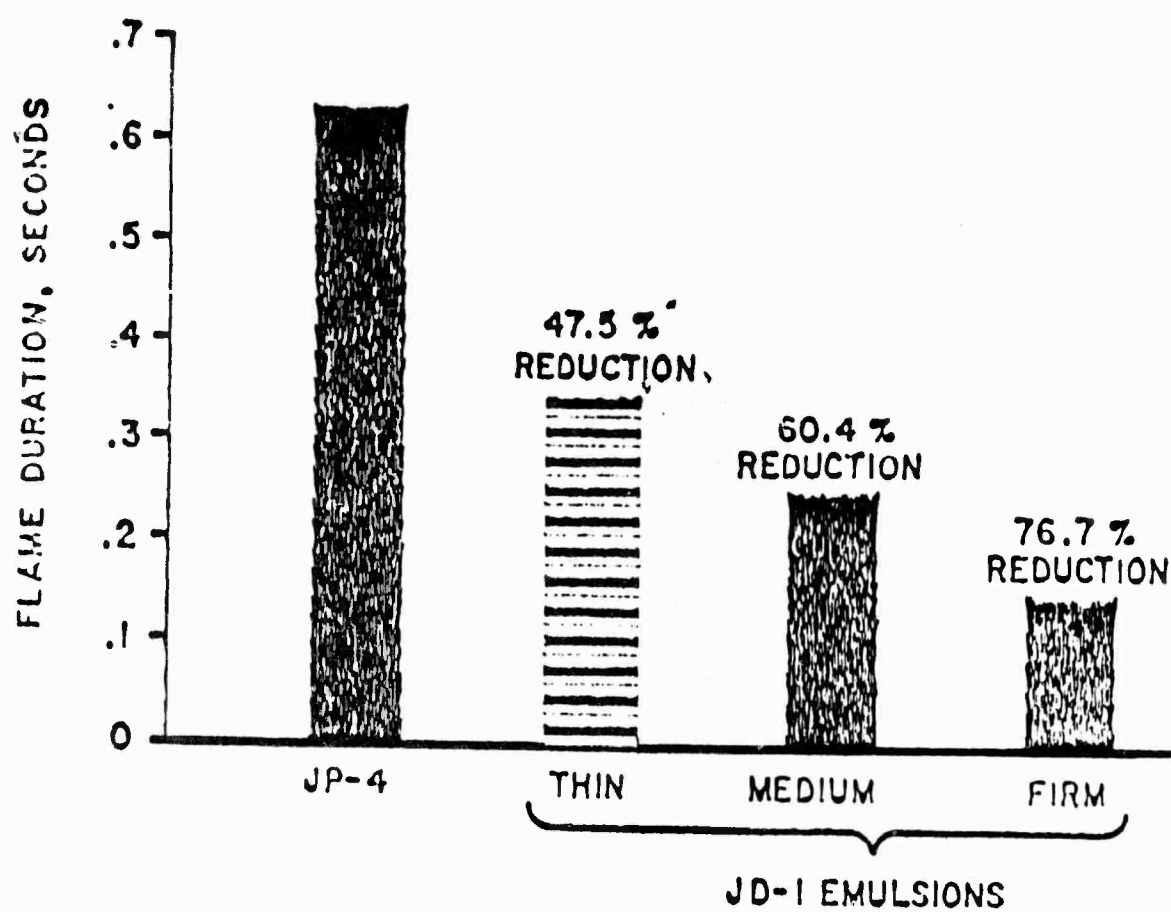


Figure 12. Flame Duration JP-4 versus JD-1 Emulsion. (Peference 32)

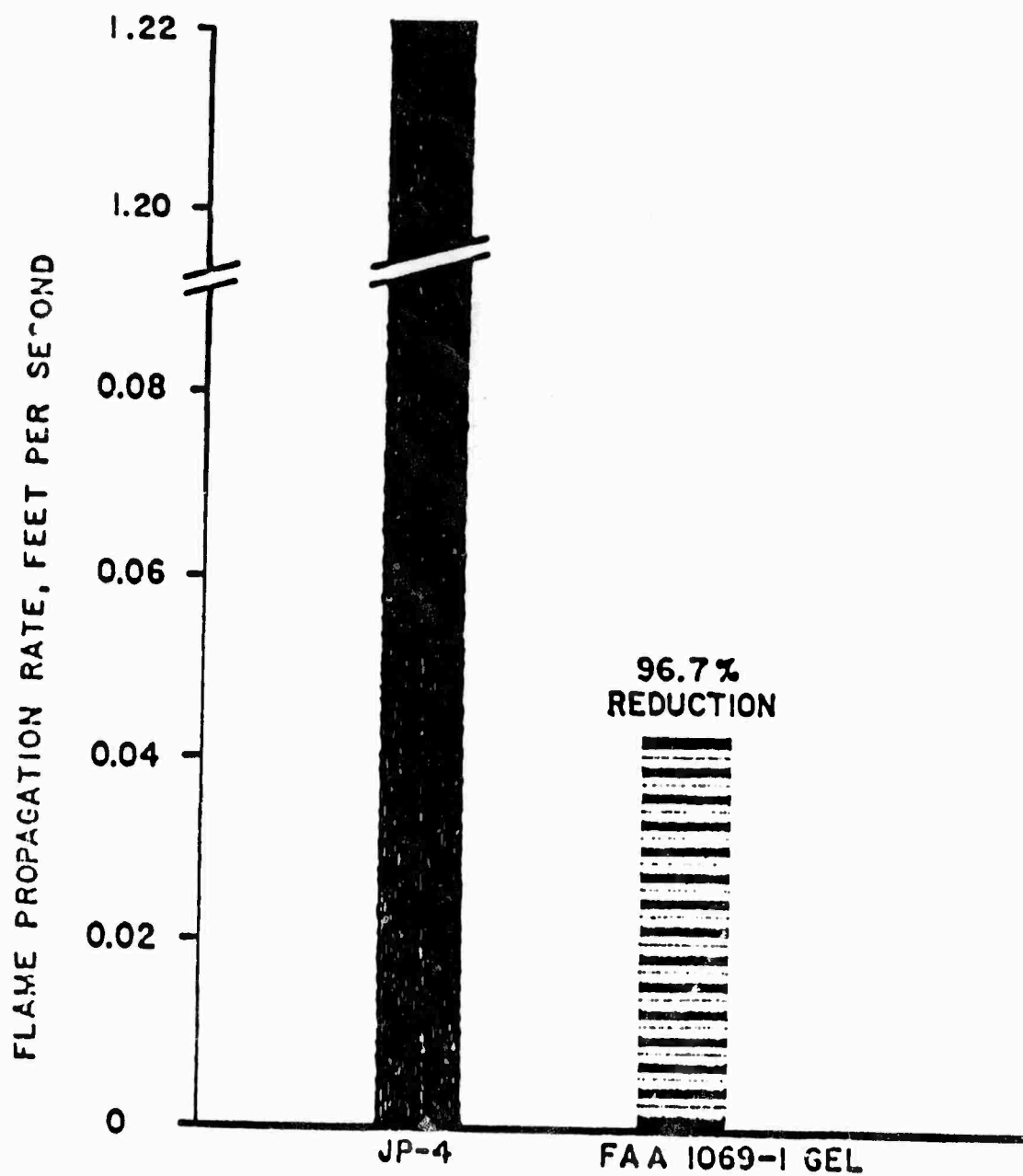


Figure 13. Flame Propagation Rate JP-4 versus FAA 1069-1 Gel. (Reference 32)

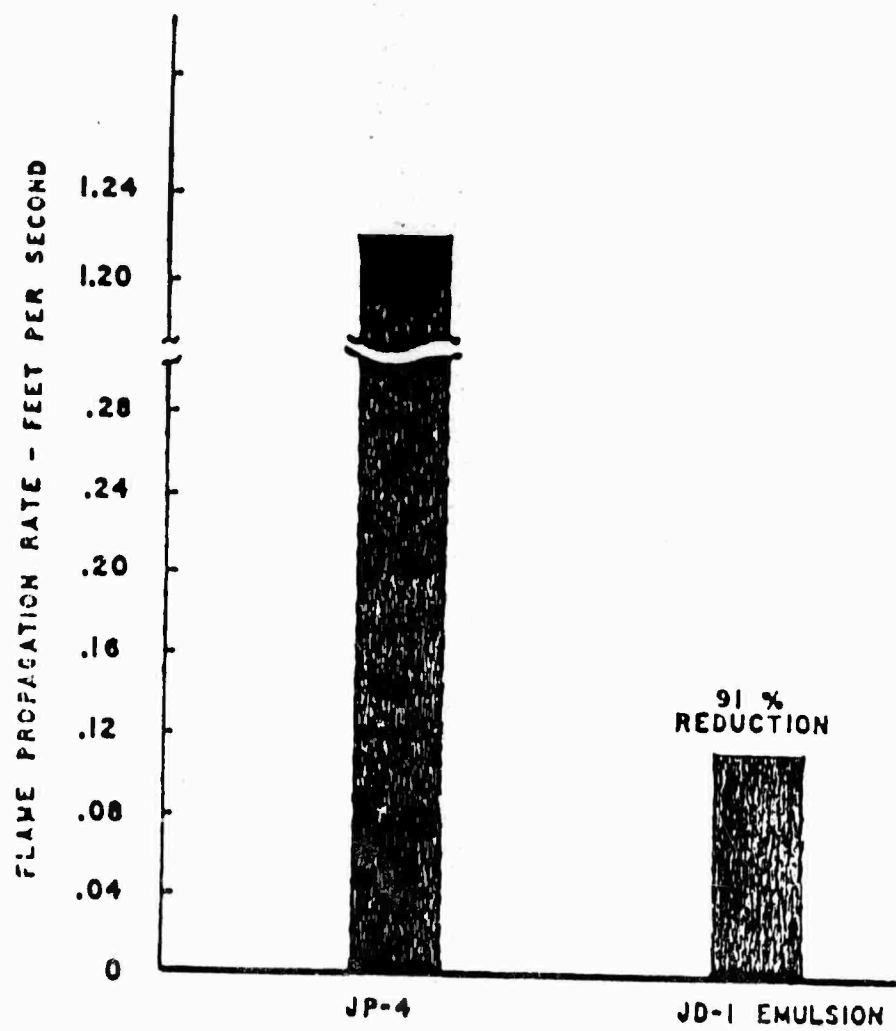


Figure 14. Flame Propagation Rate JP-4 versus JD-1 Emulsion. (Reference 32)

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 34) also measured the rates of horizontal flame travel by burning the fuels in 4-foot long, V-shaped metal troughs. 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. Flame spread rate under static conditions should give an estimate representative of the reduction in vaporization as a result of 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 34):

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 15 compares the vapor pressure versus time curves for two emulsified fuels and their base fuels. Vapor formation from JP-4 is reduced substantially by the addition of the emulsifying agent, which increases the viscosity. Results for JP-4 presented in Figure 15 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 31), 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 35) 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- to 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

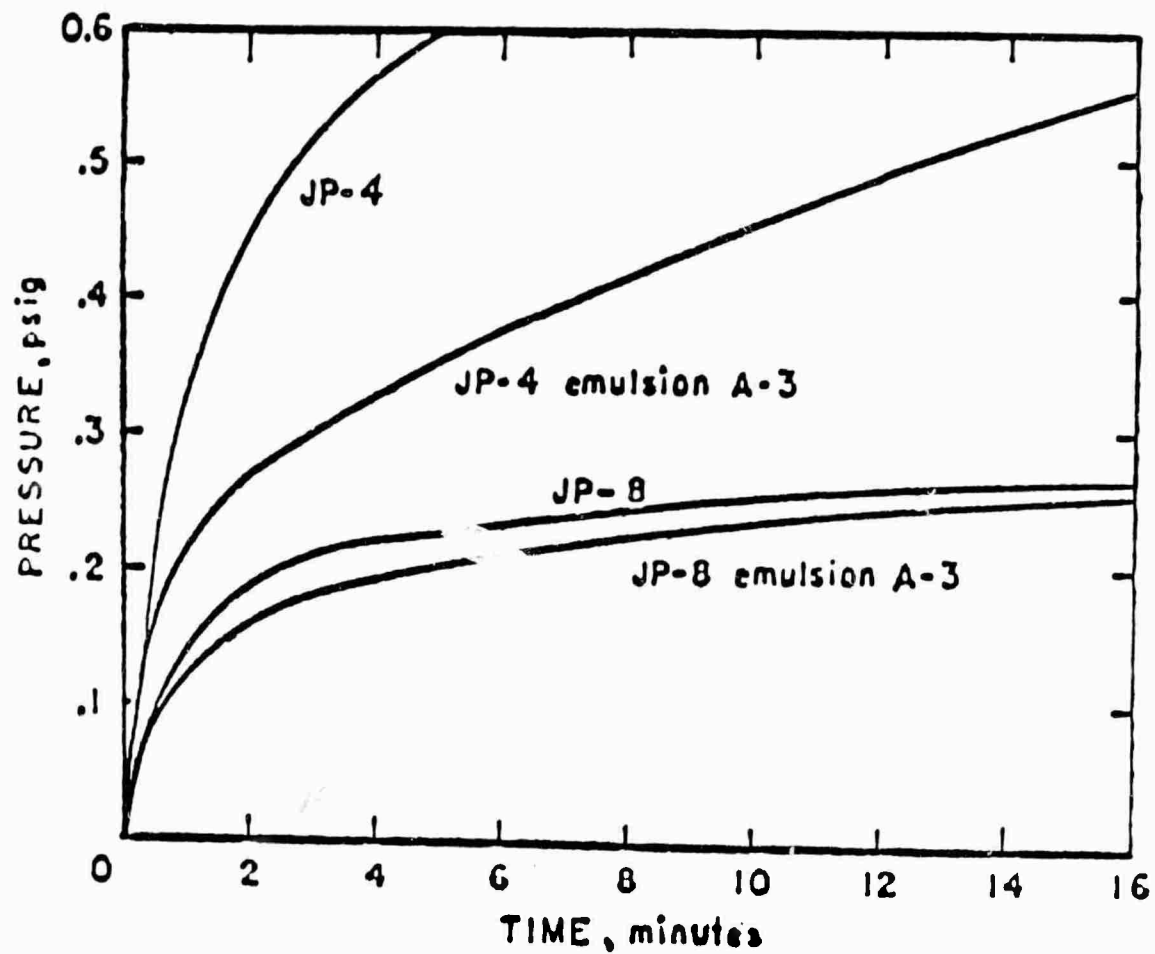


Figure 15: Vapor Pressure Versus Time for Liquid and Emulsified Fuels by Modified Reid Vapor Pressure Method. (Reference 34)

bottom of the trough. Lissant found that the rate of propagation of flame along the trough containing the JP-4 was approximately 5 feet per second and containing EF4-101 was approximately 0.083 feet per second. These results approximately agree with those measured in Reference 34 and indicate that JP-4 liquid has a flame propagation velocity approximately 60 to 150 times faster than JP-4 emulsions with 2.7 - 3 percent water as the external phase.

b. Observations and Results

A number of hydrocarbon gelling agents were obtained and tested for efficacy in simple weight to volume ratio blends, as additives to JP-4. These ratios are expressed as percent weight per unit volume (percent w/v), such that 1 percent w/v is equivalent to 1 gram of additive per 1 milliliter of fuel. Materials obtained for testing included Western 907 (Westco), Hylen TM-65, Armine 12 (Armour Chemical Co.), Alamine 21D (General Mills), amine isocyanates and alkyl-anides (Aldrich Chemical Co.) and polyisobutylene (Polymer Research Laboratory, Fed. Rep. Germany). In every case except the last, polyisobutylene (PIB), the amount of dry chemical required to gel fuel (at 5 mm thick, 150 mm across) was anywhere from 2-10 percent w/v. In the case of the PIB however, gelling sufficient to "freeze flow" occurred at about the 1 percent (by weight) level and perhaps lower. PIB powder is available as "Elastol" (General Technology Applications) a nonagglomerating form in which the granules are coated with water insoluble $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ salt to promote homogeneous spreading. The PIB settles through the surface of the JP-4, and then dissolves. At this low concentration, however, the viscosity of JP-4 will increase very slowly without agitation. Even with agitation, 1 percent levels (10,000 ppm) were seen to take up to an hour to noticeably increase the viscosity of JP-4.

c. Conclusions and Recommendations

A commercially available polymer, with outstanding hydrocarbon gelling capability has been identified and tested. The range of efficacy, given agitation and sufficient time is 0.2 - 1 percent by weight or $2 - 10 \times 10^3$ ppm. Quantitative determination of the increase in viscosity of JP-4 under varied conditions was not undertaken however, due to the unreasonably long gelling time of the products available. In the context of application in the field, an improved form of this material could be applied to a nonburning spill or pool. This will allow for more effective neutralization by AFFF because of both the increased ability to contain the fuel spill and the decreased volatility of the spill. Since the vaporization rate is reduced, the time required to reach an explosive range of vapor pressures will be extended.

To be of use to the Air Force for field application, the powder would have to be made to dissolve and form a gel more quickly and with little or no agitation. The chemistry of the coating may be altered or the powder may be suspended in propylene glycol or other agent to promote dispersion. The Polymer Research Laboratory, (BASF Aktiengesellschaft, Ludwigshafen/Rhein, Fed. Rep. Germany) would probably develop such a specific product if asked to. The gelled fuels do burn easily, and the "neutralization" achieved with these powder agents would be only to the extent of enhancing the efficacy of an extinguishing foam. We

did not pursue development of these agents further and could not locate any commercially available copolymers comparable to the starch-based water-gelling agents.

Synthesis of such copolymers as a subsection of this study was impractical. Such synthesis would constitute an independent research project. By analogy however, fuel-gel polymers, with an order of magnitude greater gelling speed and weight ratio than the PIB family, can probably be made from copolymers of perhaps polyethylene or polypropylene oxide and polystyrene, or other long alkyl chain (50 - 100 carbon links) additionally copolymerized with another long aliphatic chains having some aromatic groups. Crosslinking, to the extent of about 1/2 percent might be affected by lauryl peroxide or polyglycol ether. If such a copolymer could be rapidly extracted from a hydrocarbon solvent in which it is infinitely soluble, and which has been chosen because its chain length is comparable to the dominant species in the fuel of interest (e.g., JP-4 or JP-5, etc.) then a practical hydrocarbon gelling agent probably could be developed.

If the Air Force is interested in pursuing the development of a practical hydrocarbon gelling agent, either by improving the PIB or crafting a copolymer tailored to a fuel of interest, the adaptation of current delivery systems in the field may perhaps be straightforward to permit application of a slurry or powder.

B. COOLING OF REACTION ZONE

1. General Consideration

Theoretically any inert coolant which can absorb heat from the reaction zone can promote extinguishment. Product development efforts oriented toward practical field application, however, had to consider compatibility with the existing extinguishant delivery equipment systems. We did not therefore explore the efficacy of quasi sol-gels, treated silicon dioxides, pellets of dry ice or other novel, potentially effective coolant agents. Our primary focus in this approach was on the water, and its emulsification into the fuel with low mixing energy to render the fuel in an extinguished or nonburning spill "neutralized." To this end, many emulsifiers were obtained and tested, in crossblends and an increasingly larger scale, for "instant" for "self-mixing" performance with JP-4 and then for flammability of the resulting emulsion. Water is a primary coolant used to extinguish fires not only because it is so widely available and inexpensive but primarily because it has such a high specific heat and high latent heat of vaporization. A single gallon of water can absorb 9,280 BTUs of heat as it increases from 25°C (77°F) room temperature to steam at 100°C (212°F).

Water is, of course, more dense (specific gravity 1.00 g/cc) than most hydrocarbon fuels (e.g. 0.8 g/cc) and is immiscible as well. Foam, or, in a sense "shampoo" chemistry, has been used to permit the water to form an effective cover to aid in extinguishing hydrocarbon fires. What we proposed was to explore "laundry" chemistry in which the maximum amount of water can be emulsified with minimum mixing energy, into the JP-4, making a nonflammable "pea soup" (fuel in water) emulsion. We were well aware at the onset of this program of the potential negative effects of

emulsion surfactants on the film-forming capacity of AFFF. Emulsion surfactants can lower the interfacial tension, thereby promoting interdispersion and miscibility of water and JP-4. This is in opposition to the properties of the fluorosurfactants used in AFFF which are to spread an aqueous layer over the fuel. Therefore, the functions of the two types of surfactants will be at odds.

We therefore studied the sealing characteristics of AFFF on emulsified fuel and built emulsifier blends of water and JP-4 which were dramatically "self-mixing." We then screened these blends to determine which were nonflammable in bench tests to prepare for field tests. The water structuring compounds were also added to some of the final blends in the belief that the right mixture of components might permit a somewhat toughened water film to form as water drains from a foam. This film, it was imagined, would seal off the hydrocarbon vapor while other water, also draining from the foam, would become intermixed with the fuel, thereby cooling the reaction zone.

2. Emulsification - Background

Emulsion chemistry is a highly developed empirical science which has grown out of the practical needs of several industries: textile, paint, industrial and consumer equipment and product cleansing and drug and cosmetics.

Generally speaking, the continuous phase of a stable emulsion is that which is the stronger solvent, the oil or the water, for the emulsifying agent. Also, the relative abundance of one solvent over the other influences that phase becoming the continuous one. In laundering, for example, the ratio of water-detergents to oily soil is very high, which favors the formation of the oil-in-water emulsion. With the limited amounts of water deliverable to a flaming JP-4 spill, however, we focused on the hydrophilicity, or degree of solubility in water, of various emulsifiers.

Figures 16 and 17 summarize the meaning of hydro- and lipophilicity as used by emulsion chemists. Broadly speaking, there are only two basic types of liquid-solvents on earth: water -- polar because of the ionic charges on the oxygen and hydrogen, and oil -- nonpolar because it is comprised of carbon chains and rings in which the electric field is highly delocalized. All surfactant molecules are composed of polar and nonpolar parts, soluble respectively in water and oil phases, to form a continuous water or oil phase depending upon the predominant character.

A surfactant locates and arranges itself at an oil-water interface, as schematically shown in Figure 16. 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 the 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 35) which has been tested and proven empirically true over the years.

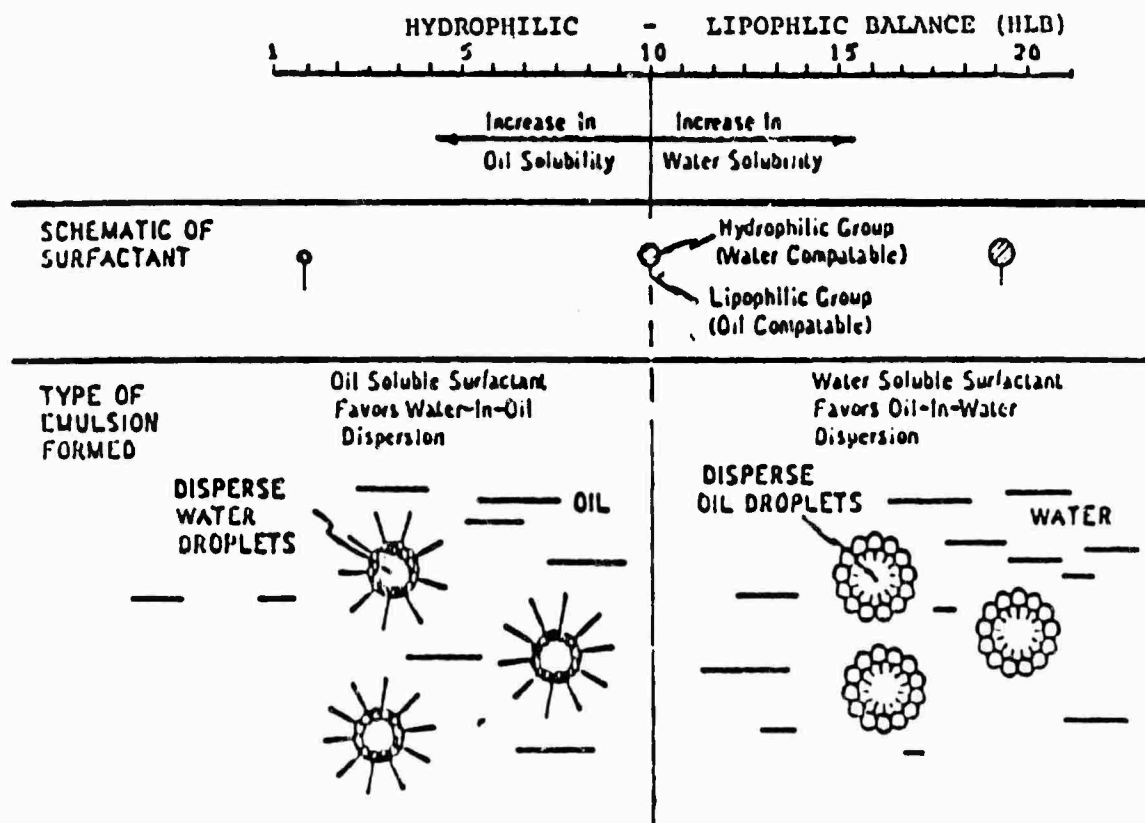


Figure 16. Influence of Surfactant Structure on Type of Dispersion

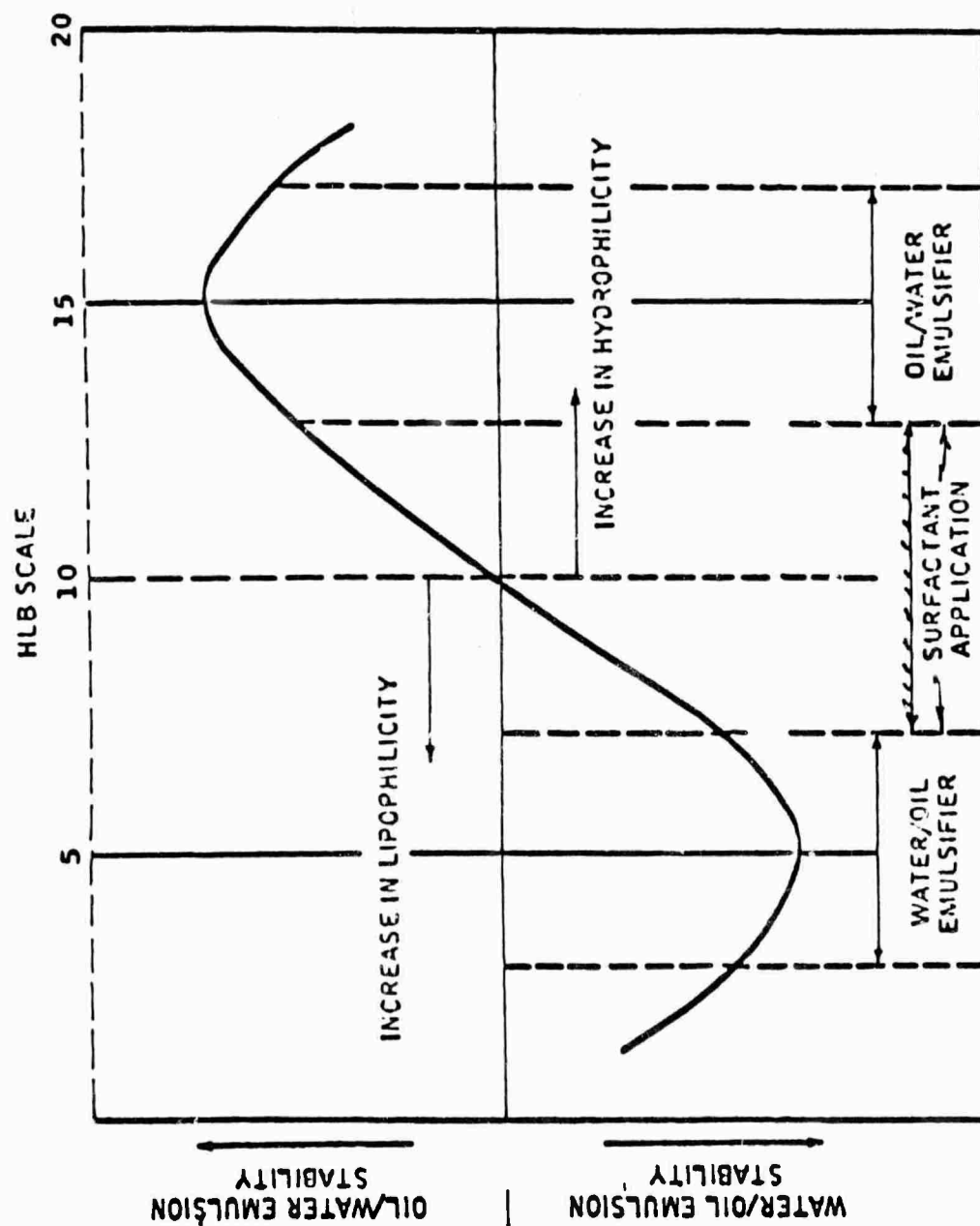


Figure 17. Relationship Between Hydrophilic Lipophilic Balance and Emulsion Type

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 which is sometimes referred to as HLB (Hydrophilic - Lipophilic Balance) by Becker (Reference 36). This relationship between the molecular structure of the surfactant and the emulsion type is also shown in Figure 18 and the physical concept behind Bancroft's Law may be appreciated. For example, for a more water-compatible surfactant, the physical location of the larger hydrophilic group on the outside of the dispersed oil droplets may result 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 37).

The relationship between mixing energy required to make an emulsion and the interfacial area and interfacial tension can be expressed by:

$$W_k = A_{o/w} \gamma_{o/w}$$

Where:

W_k mixing energy, ergs

$A_{o/w}$ interfacial area, cm^2

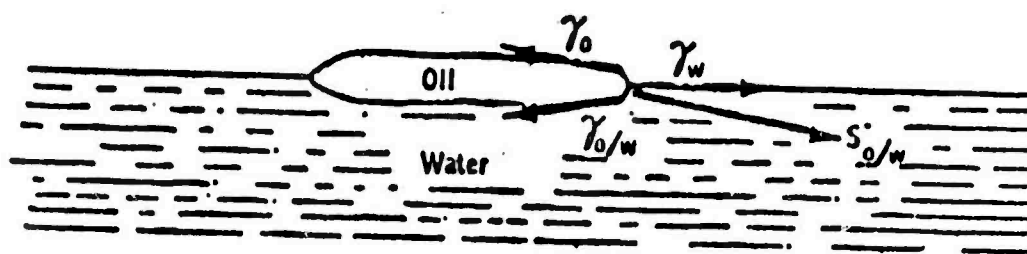
$\gamma_{o/w}$ interfacial tension, dynes/cm

Thus, for the same amount of mixing energy, a reduction of $\gamma_{o/w}$ will result in a corresponding increase in $A_{o/w}$. The mechanisms of intermixing have been described in detail, in studies of application of chemical dispersants to oil slicks at sea (References 38, 39, 40 and 41).

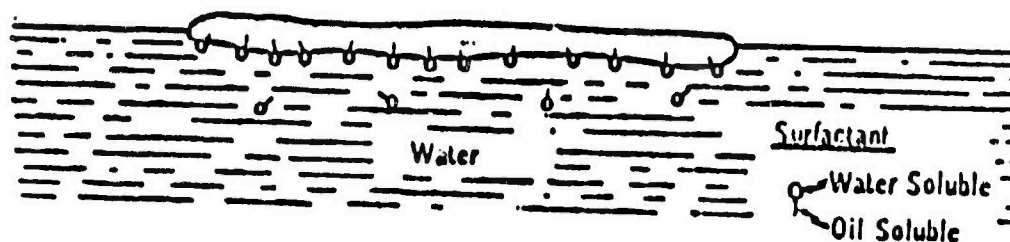
3. Emulsification - Experimental

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. Gerald P. Canevari, in the proceedings from the 1975 Conference on The Prevention and Control of Oil Pollution (Reference 42) wrote about the feasibility of self-mixing dispersants which, if perfected, could reduce the problem of supplying mechanical energy. Theoretically, therefore, it should be possible to devise an emulsifier blend which is "self-mixing" upon addition in water to JP-4. A "blend" is required because one component may be able to reduce the interfacial tension dramatically and incorporate a maximum amount of water into the fuel, and another component may be able to stabilize the fuel-water intimate mixture for a long time.

a) Oil Spill



b) Dispersant Reduces Interfacial Tension



c) Agitation Readily Forms Oil Droplets

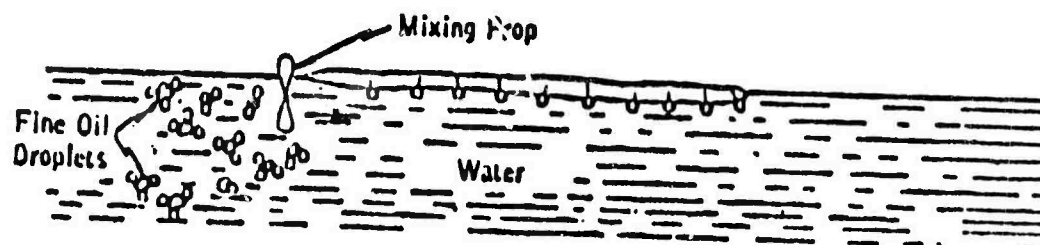


Figure 18. Dispersant Enhances Droplet Formation

The effectiveness of a surface active agent or "surfactant" as an emulsifier depends upon its ability to lower interfacial tension and on solubilizing and dispersing properties. These abilities are often not found in the same molecule. Rapid emulsification, such as is required in our system, results from precipitous lowering of interfacial tension. Experience has shown that for rapidity of wetting, the surface tension of fresh surfactant should be below 35 dynes per cm. The stability of an emulsion depends upon the solubilizing and dispersing characteristics of the surfactant which are themselves determined by the length and polarity of chains, linkages and subgroups within the surfactant molecule. These considerations, combined with our need to make a rapidly formed, fairly stable continuous (JP-4 oil-in-) water phase approaching a microemulsion, using a minimum amount of water and a nontoxic biodegradable surfactant system, guided our selection of chemicals and the design of the tests we carried out.

a. Chemicals and Sources

The chemicals obtained for testing are listed in Table 5 by trade names and grouped by functional group character. For ease of experimental records and to run blind tests on the same chemical from different suppliers, Beltran assigned internal numbers to most of these.

b. AFFF on Emulsified Fuel

As described above, the effectiveness of surface active agents as emulsifiers is based on their ability to lower interfacial tension, and on their solubilizing and dispersing properties.

Rapid emulsification obtained with a surface active agent is the result of its ability to lower interfacial tension. Once the emulsion is formed the stability will be imparted by other characteristics of the agent, such as solubilizing and dispersing properties.

High foam-producing surface-active agents have been employed in applications such as flotation of ores and entraining air in concrete, in addition to firefighting. A primary factor in a surfactants' effectiveness as a foaming agent is its ability to lower surface tension, but a number of other factors also affect the amount and stability of the foam. These are:

- (1) Type of surface active agent used; i.e. nonionic or anionic.
- (2) Concentration of agent.
- (3) Amount and type of salts present.
- (4) Temperature of water.
- (5) Presence of acids or alkalies.
- (6) Amount of air whipped into solution per unit of time.

In industry the volume and persistence of foam produced has been on occasion increased by the addition of "water-soluble" gums such as Gum Tragacanth, Locust Bean, Karaya starches, and synthetic materials such as methyl cellulose, and polyacrylamide.

TABLE 5. CHEMICAL NAMES AND SOURCES OF EMULSIFIERS.

(Registered trademarks are listed in Trademark Notice)

<u>TRADE NAME</u>	<u>CHEMICAL</u>	<u>COMPANY</u>
<u>Sulfonates</u>		
Siponate A246-LX	Alpha olefin sulfonate	Alcolac
Witconate AOS	Alpha olefin sulfonate	Witco Corp.
Marasperse N-22	Sodium lignosulfonate	Reed Lignin
Marasperse 52CP	Sodium lignosulfonate (high m. wt.)	" "
Marasperse B-22	Sodium lignosulfonate	" "
Marasperse OF	Sodium lignosulfonate	" "
<u>Diethanolamides (DEA)</u>		
Sipomide 1500	Cocodiethanolamide	Alcolac Ltd.
Clindrol 101CG	Cocodiethanolamide	Clintwood
Clindrol 210CGN	Cocoamide DEA	Chemical Co.
Clindrol 202CGN	Cocoamide DEA	" "
Clindrol 206CGN	Cocoamide DEA	" "
<u>Ethoxylates (alkyl aryl polyether alcohols)</u>		
Rexol 25/6	Nonyl phenol polyethylene glycol ether	Hart Chem. Co.
Rexol 25/9	Nonyl phenol polyethylene glycol ether	" " "
Rexol 25/20	Nonyl phenol polyethylene glycol ether	" " "
Rexol 25/407	Nonyl phenol polyethylene glycol ether	" " "
Rexonic P-1	Polyalkylene glycol ether	" " "
Witconol SN-90	Ethylene oxide adducts straight chain fatty alcohols	Witco Corp.
Witconol NP-80	Nonylphenol ethylene oxide (8)	" "
Witconol TD-80	Tridecyl ethylene oxide (8) ether	" "
Siponic E-10	Polyoxyethylene cetyl/stearyl alcohol	" "
Neodol-25	C12-C15 linear primary alcohol ethoxylate	Shell Chem. Co.
Igepal	Methoxylated nonylphenol in ethylene oxide, 1:10	GAF
Triton X-35	Octylphenol ethylene oxide (3)	Rohm and Haas
Triton X-45	" " " (5)	" " "
Triton X-114	" " " (7-8)	" " "
Triton X-100	" " " (9-10)	" " "

TABLE 5. CHEMICAL NAMES AND SOURCES OF EMULSIFIERS (concluded).

(Registered trademarks are listed in Trademark Notice)

<u>TRADE NAME</u>	<u>CHEMICAL</u>	<u>COMPANY</u>
<u>Diethanolamide of oleic acid</u>		
Clindrol 200-0	Oleamide DEA	Clintwood Chem.
Schercomid OLA	Oleamide DEA	Scher Chem.
<u>Thioethers</u>		
Siponic 218	Polyoxyethylene thioether	Alcolac, Ltd.
Siponic 260	" "	" "
Siponic SK	" "	" "
<u>Sulfosuccinates</u>		
DV1875	Sodium dioctyl sulfosuccinate	Alcolac, Ltd.
Aerosol OT-70FG	Sodium dioctyl sulfosuccinate	Am. Cyanamid
Aerosol AY-100	Sodium diamyl sulfosuccinate	" "
Aerosol MA-80	Sodium dihexyl sulfosuccinate	" "
Arylene M-75	Sodium dioctyl sulfosuccinate	Hart Chem. Co.
Arylene M-60	Sodium dioctyl sulfosuccinate	" " "
M070R	Sodium dioctyl sulfosuccinate	Mona Chem. Co.
<u>Monooleates</u>		
Witconol H-31A	Polyethylene glycol (400) monooleate	Witco Chem. Co.
Span 80	Sorbitan monooleate	ICI America
Tween 80	Polyoxyethylene sorbitan monooleate	" "
<u>Sulfates</u>		
Witcolate 1259	Alcohol ether sulfate	Witco Chem. Co.
Witcolate 1276	Alcohol ether sulfate	" " "
Witcolate A	Sodium lauryl sulfate	" " "
Witcolate SE-5	Sodium alcohol ether sulfate	" " "
<u>Proprietary Mixtures</u>		
Atlox 3404	Alkylaryl sulfonate (blend)	ICI
Corexit 9527	Surfactant Esters	Exxon
Corexit 9550	" "	"
Corexit 7664	" "	"

In this series of experiments good foam forming surfactants were selected and combined with AFFF to study the sealing characteristics of the resultant film in the apparatus described in Section III A.1.a. The observations are summarized in Table 6. For the most part, the effective emulsifiers either dramatically reduced the efficacy of the film's "vapor cap" (percent seal) or the durability of the film, or both. Clindrols and Neodols were exceptions and are discussed in connection with Figures 22, 23, 24 and 26. A number of other sealing curves are collected here, Figures 19 - 33, each chosen to permit comments on some usual or unusual aspect of the study, which comments follow.

In Figure 19, the durability of the 3 percent film of F^3P , as measured in our apparatus can be seen to vary from 18 minutes to 40 minutes. Throughout our measurements there was generally more reproducibility in the film-spreading speed and percent sealing numbers than in the time the film lasted. The F^3P was seen to take about twice as long as the AF^3 to spread over the JP-4. The measurements by our apparatus therefore confirmed field experience of slower spread and knockdown by F^3P compared with AF^3 .

A number of emulsifiers tried completely cancelled sealing by AFFF at or above the 1 percent final concentration level. In Figure 20, AF^3 (3 percent) is combined in three trials with Sipomide 1500 at 1 percent (w/v) and in one trial with Sipomide 1500 at 0.5 percent. Figure 21 shows three repeat trials with Sipomide 1500 at the 0.5 percent level, permitting 51-70 percent sealing.

The Clindrol series of compounds is nearly identical or closely related to Sipomide 1500 (see Table 5) and at 0.25 percent showed small and perhaps tolerable effect on percent seal achieved by AF^3 , Figure 22. In Figure 22, both Clindrol 210 (Charts a and b) and Clindrol 202 CGN (Chart c), however, exhibited an interesting and reproducible recovery of the vapor-locking or sealing capacity after the initial loss of sealing which occurred at anywhere from 5-10 minutes. Clindrol 206, Figure 23, and 101 CG, Figure 24, also exhibited this profile. We believe this capacity may last 90 - 100 minutes, which was what we observed in the Clindrol 101 CG (0.25 percent) experiment, Figure 24.

Other chemicals exhibited a similar "vapor-lock" capacity kicking in after 5 - 10 minutes, during which time we imagine the low boiling volatiles are being removed by the N_2 gas sweep. These include Corexit 9550, Figure 25 and Neodol-25, Figure 26. A long chain alcohol (similar to Neodol-25 but not ethoxylated), Siponic E-10, caused some enhancement of the action of AF^3 initially, compare Figure 27 with Figure 3, but did not produce a "vapor-lock." The curve within the curve shows the repeat experiment in which a bubble burst, releasing hydrocarbon (fuel) vapors, which were resealed.

None of the four commercially available dioctylsulfo-succinates tested as additives to AFFF exhibited this recovery of sealing capacity at either .05 or .25 percent concentrations, see Figure 28 (OT70-PG), Figure 29 (MA-80), Figure 30 (AY-100) and Figure 31 (DV1875). The

TABLE 6. SEALING CHARACTERISTICS: WITH EMULSIFIER AND AF³.

<u>Exp. No.</u>	<u>Agent</u>	<u>Sealing (%)</u>	<u>Time to Seal (sec)</u>	<u>Time Seal Maintained</u>
1	AF ³ (3%) only	81.5		18
2	"	74.8		20
3	"	77.8		20
4	F ³ P(3%)	92.5	44	40 min. kept sealing 80-95%
5	"	81.9	40	18 min. kept the sealing
6	"	94.2	44	50 min. kept 80-90% sealing
7	Clindrol 210 (0.25%) &	83.5	22	5 min. kept 83.5% sealing
8	"	67.8	AF ³ (3%)	18
9	"	66.0		22
10	Neodol-25 (0.25%) &	80.8	22	30 min. kept 80% sealing
11	"	77.9	AF ³ (3%)	21
12	"	77.7		25
13	Corexit 9550 (0.25%) &	32.5	105	Maintain seal few minutes
14	"	44.3	AF ³ (3%)	58
15	"	26.3		81
16	Corexit 9550 (0.05%) &	80.6	26	Very short or few minutes
17	"	80.9	AF ³ (3%)	23
18	"	85.0		-
19	OT-70-PG	75.6	16	Very short time
			(0.25%) & AF ³ (3%)	
20	"	75.6	14	"

TABLE 6. SEALING CHARACTERISTICS EMULSIFIER AND AF³ (CONCLUDED)

<u>Exp. No.</u>	<u>Agent</u>	<u>Sealing (%)</u>	<u>Time to Seal (sec)</u>	<u>Time Seal Maintained</u>
21	OT-70-PG (0.05%) & AF ³ (3%)	82.2	13	Very short time "
22	"	76.5	14	"
23	"	73.5	14	"
24	MA-80(0.25%) & AF ³ (3%)	77.2	18	"
25	"	79.9	17	"
26	AY-100 (0.25%) & AF ³ (3%)	81.7	15	"
27	"	79.1	19	"
28	"	79.2	18	"
29	"	74.1	17	"
30	AY-100 (0.05%) & AF ³ (3%)	57.9	15	"
31	"	78.2	20	"
32	AY-100 (0.05%) & AF ³ (3%)	80.4	17	"
33	"	74.7	19	"
34	RT-61 (0.25%) & AF ³ (3%)	71.6	27	"
35	"	69.6	17	"
36	"	73.3	31	"
37	RT-61 (0.05%) & AF ³ (3%)	66.1	15	"
38	"	79.0	16	"
39	"	81.5	16	"

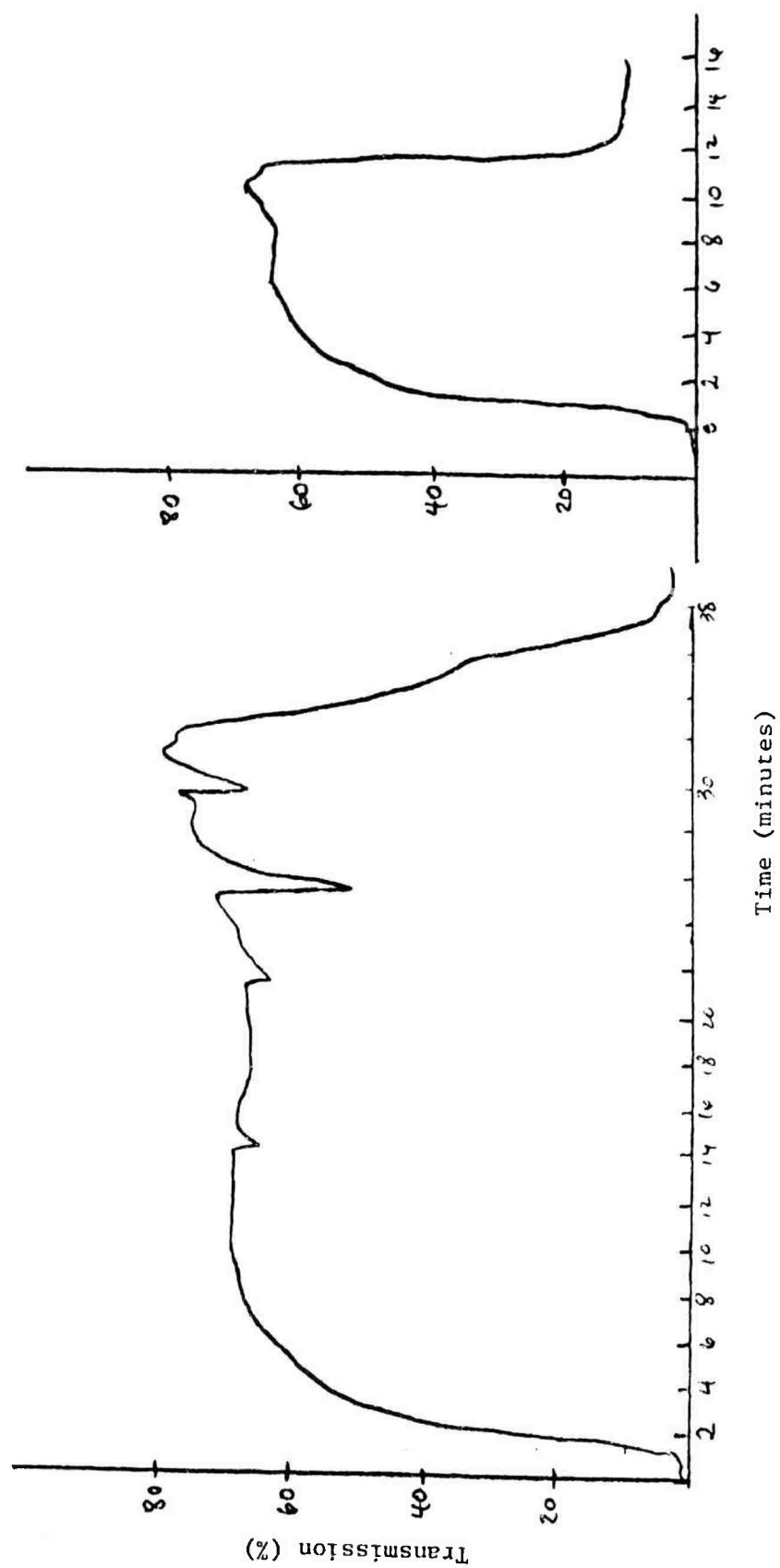


Figure 19. Sealing Curves of F^3P (3%)

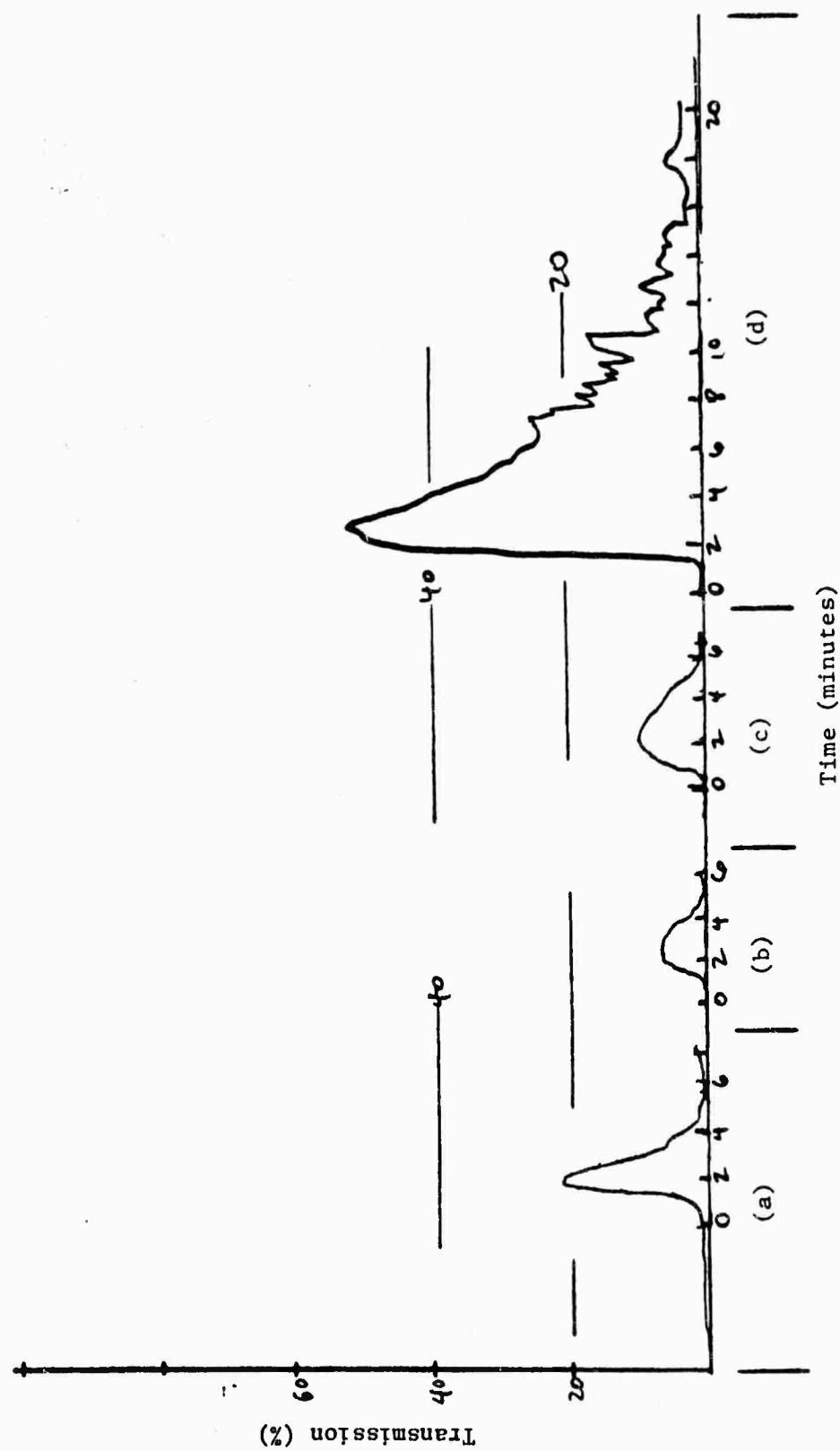


Figure 20. Sealing Curves Sipomide 1500: AF3 (3%), a, b, c (1%), d (0.5%)

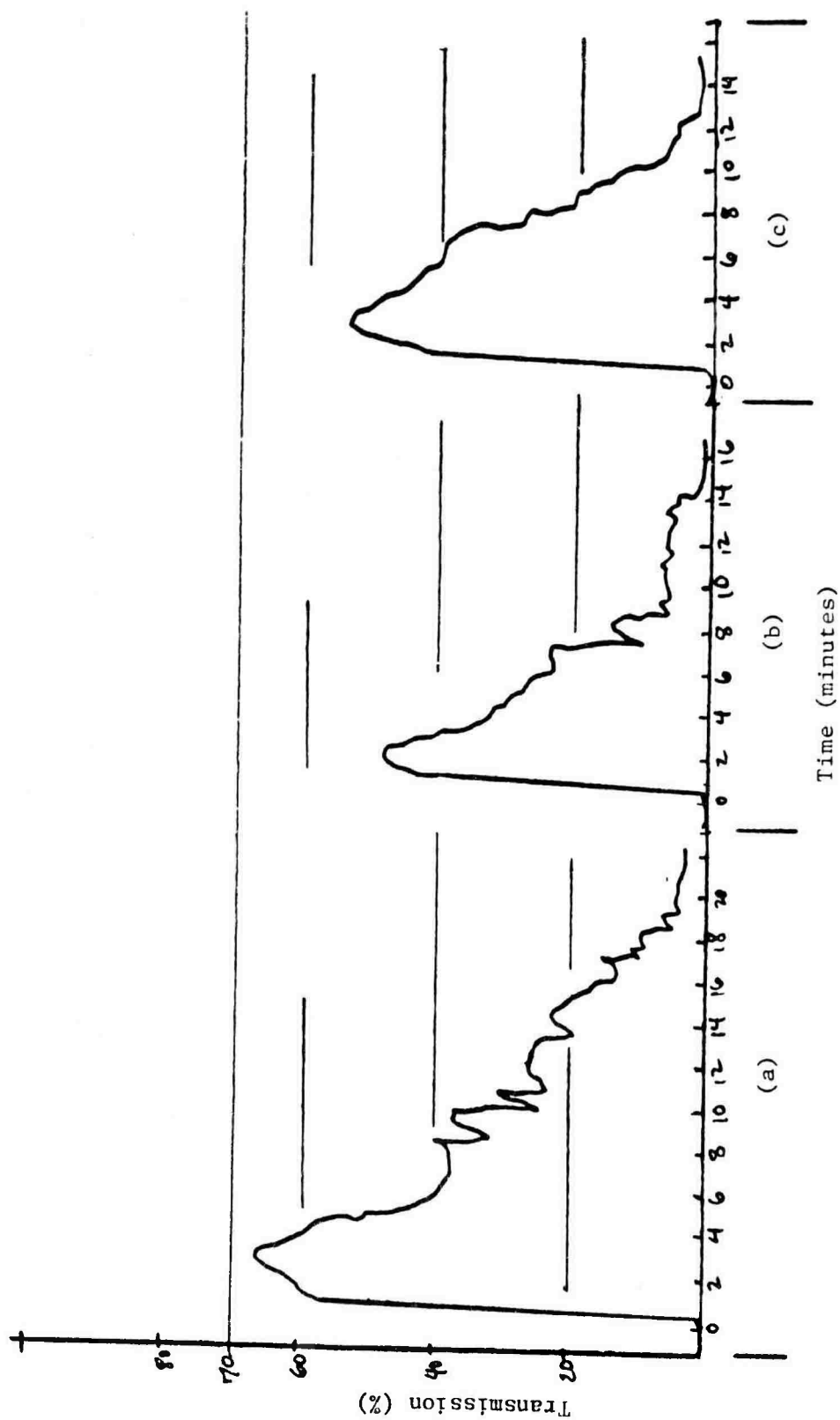


Figure 21. Sealing Curve Sipomide 1500 (0.5%) / AF3 (3%)

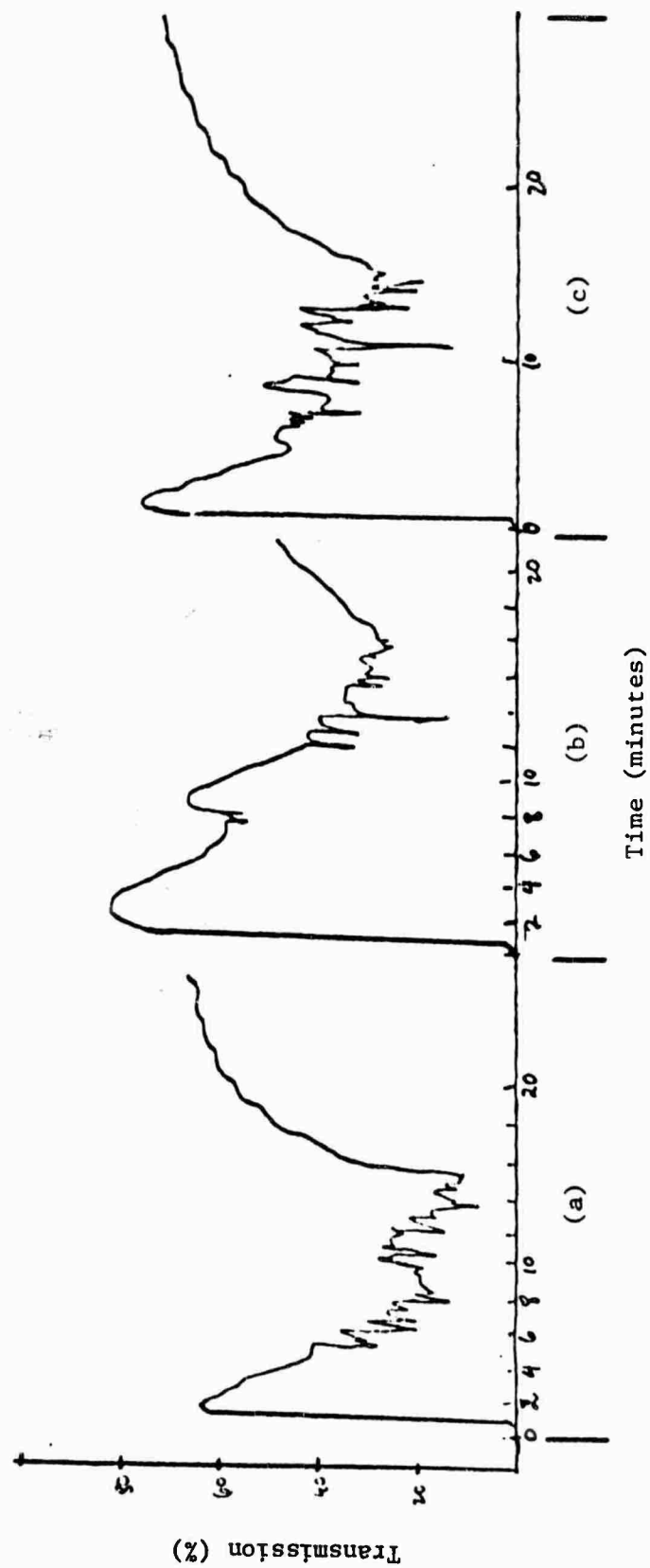


Figure 22. Sealing Curves: a) and b) Clindrol 210 (.25%)/AF³ (3%)
c) Clindrol 202 CGN (.25%)/AF³ (3%)

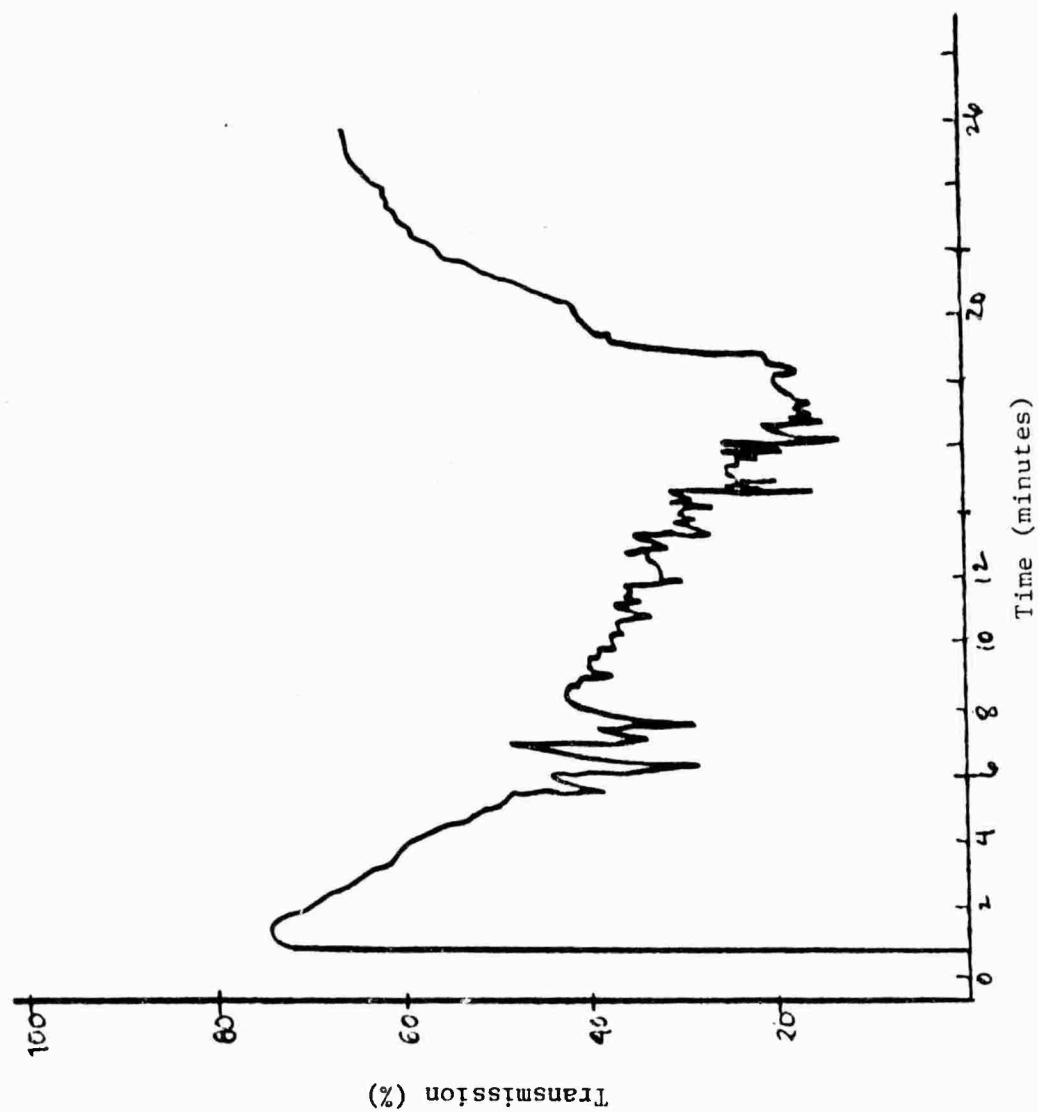


Figure 23. Sealing Curve Clindrol 206 (0.25%)/AF3 (3%)

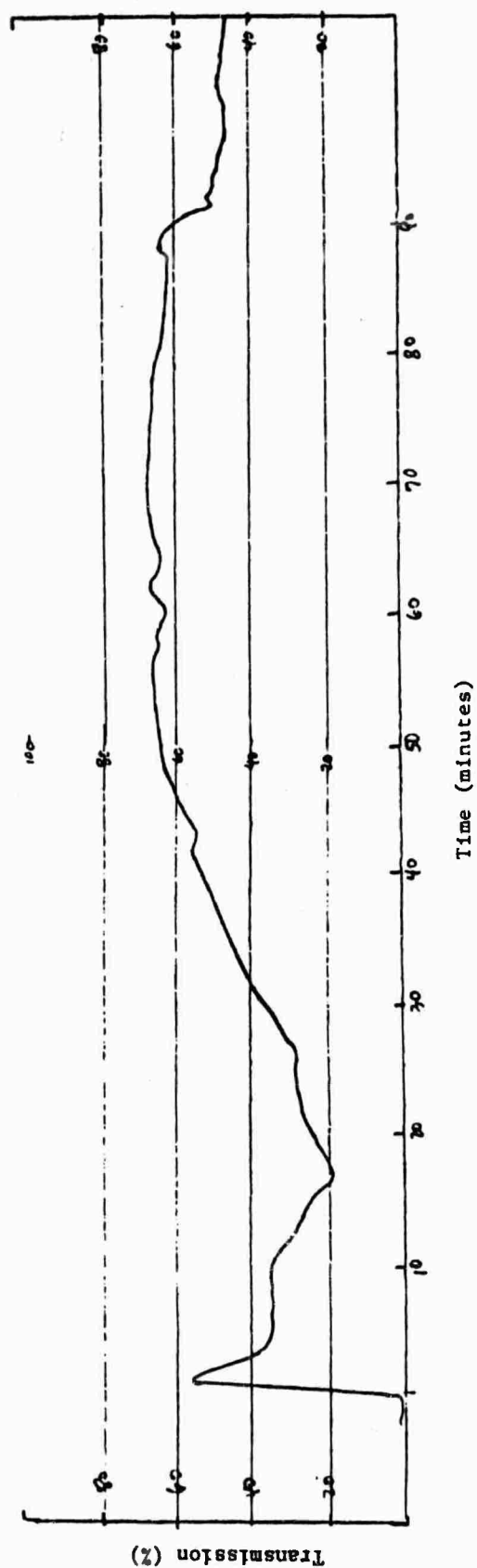


Figure 24. Sealing Curve Clindrol 101 CG (0.25%)/AF³ (3%)

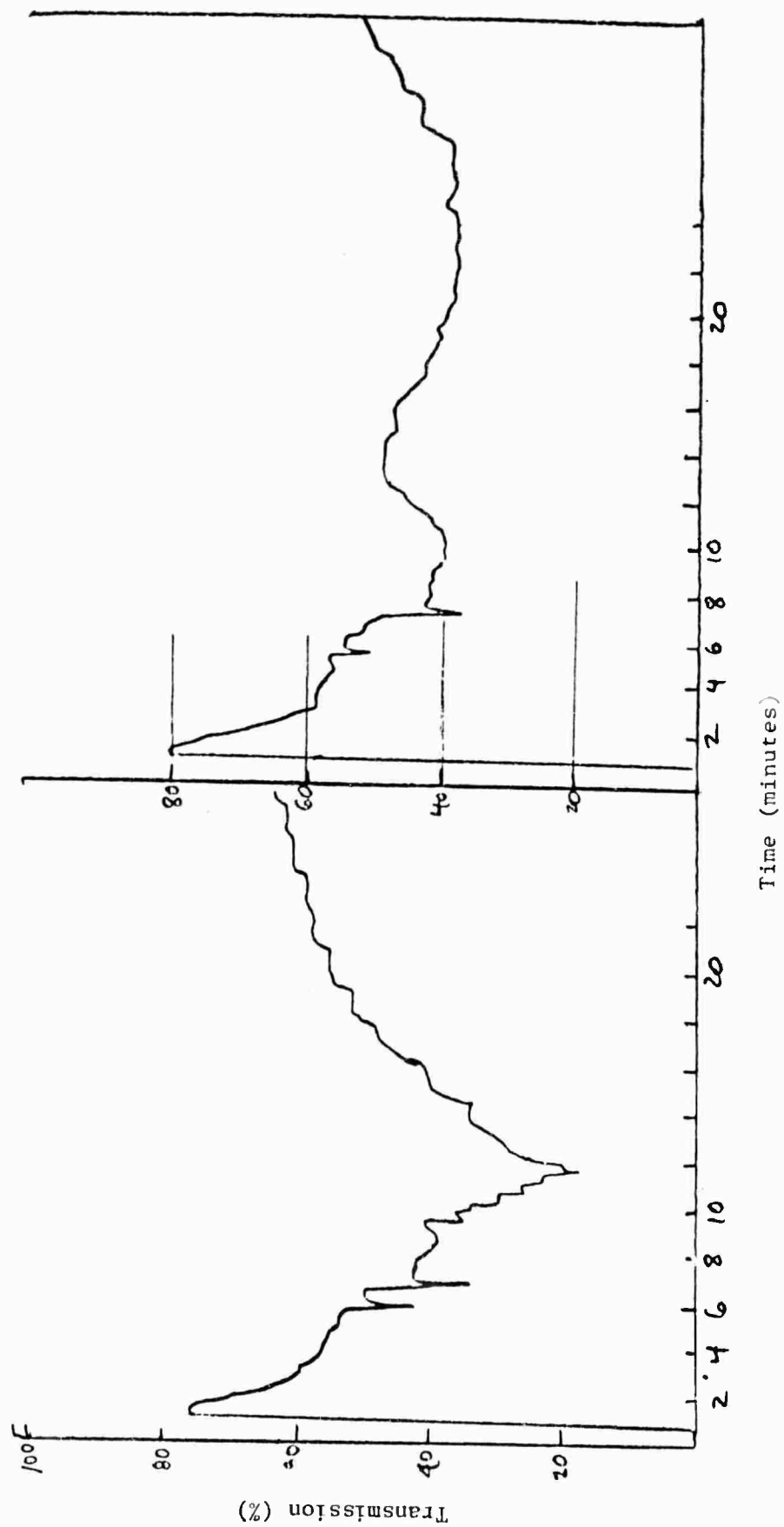


Figure 25. Sealing Curve Corexit 9550 (0.05%)/AF³ (3%)

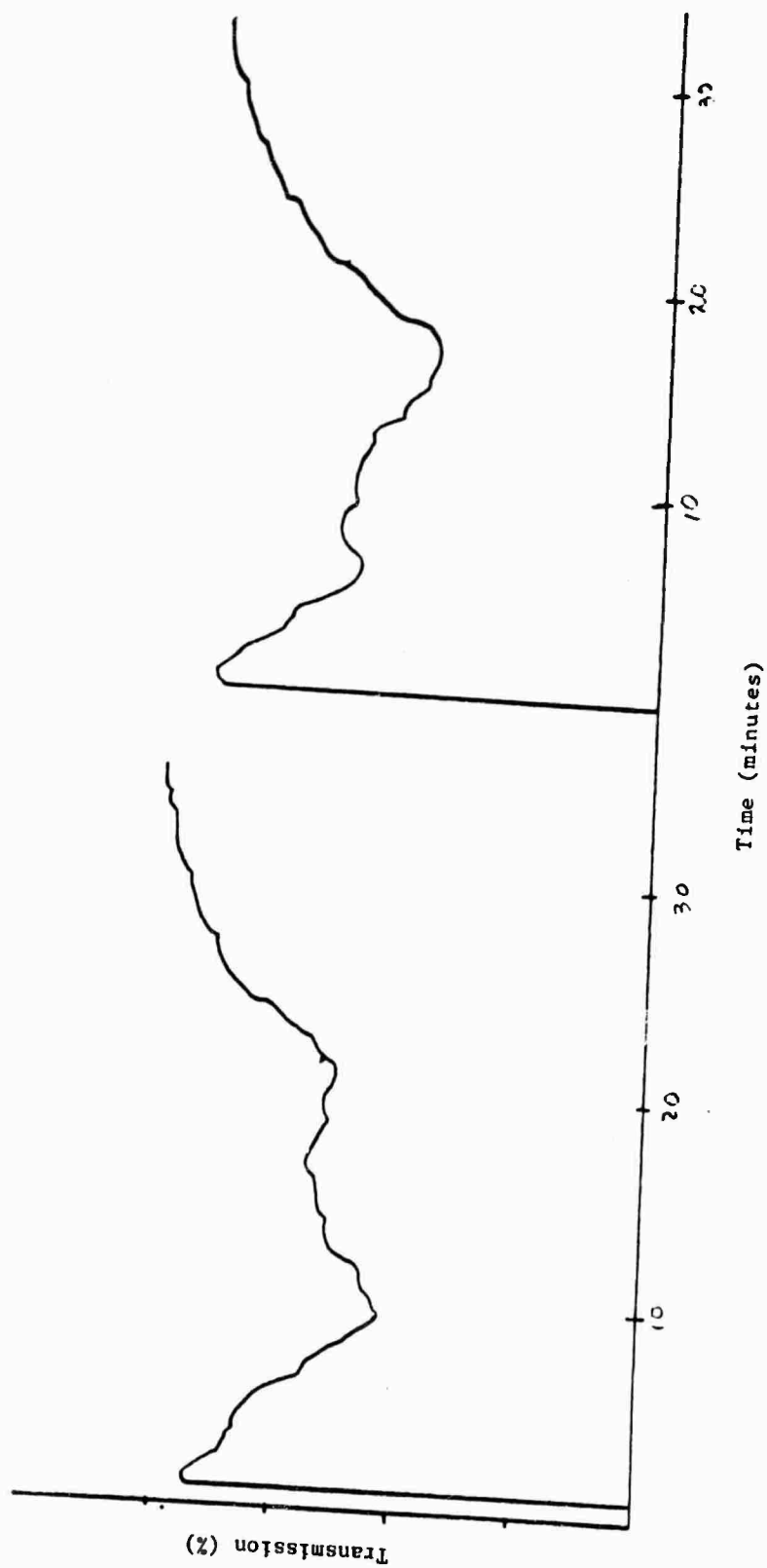


Figure 26. Sealing Curve Neodol-25 (0.25%)/AF3 (3%)

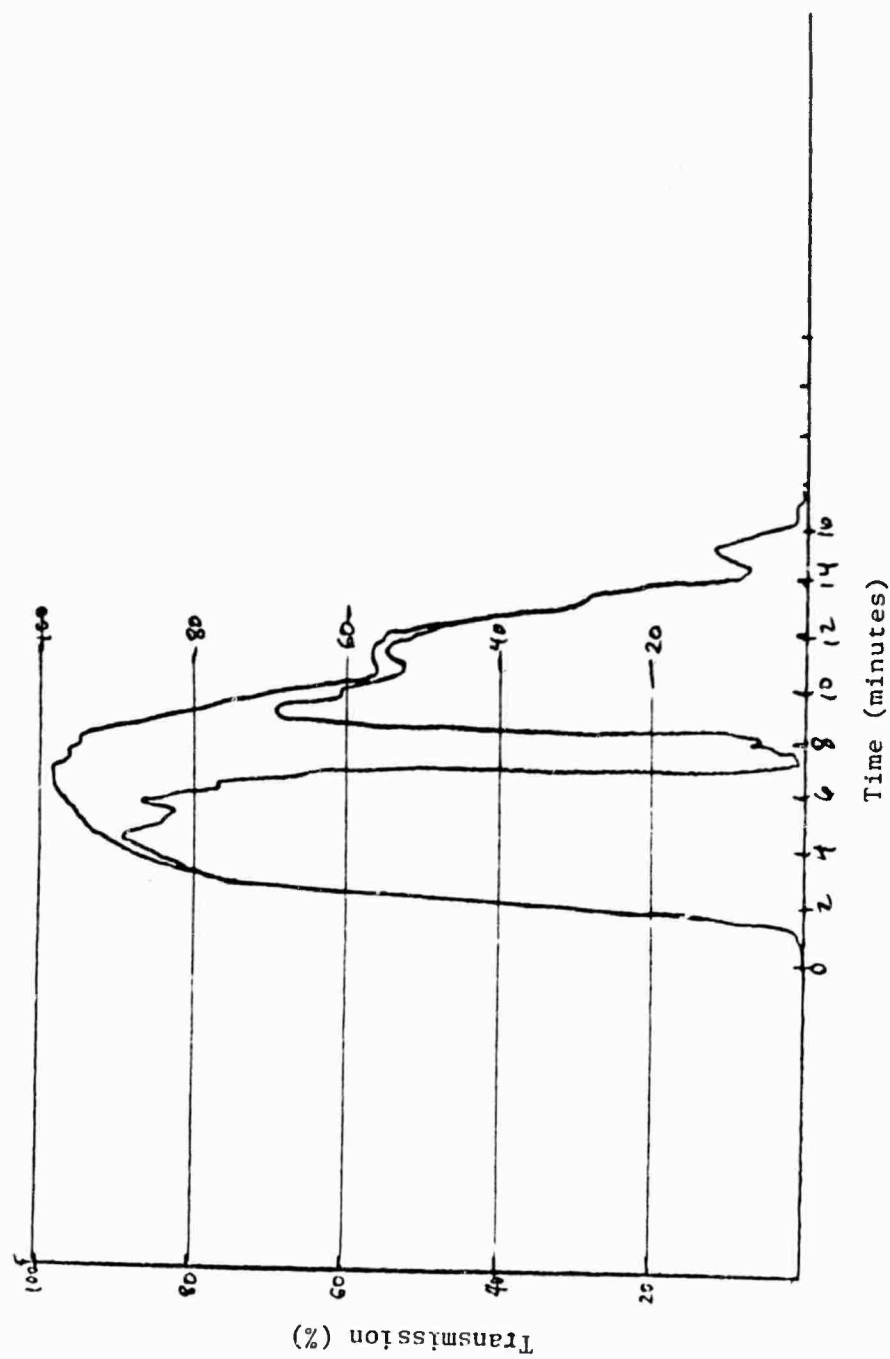


Figure 27. Sealing Curve Siponic E-10 (0.5%)/AF³ (3%)

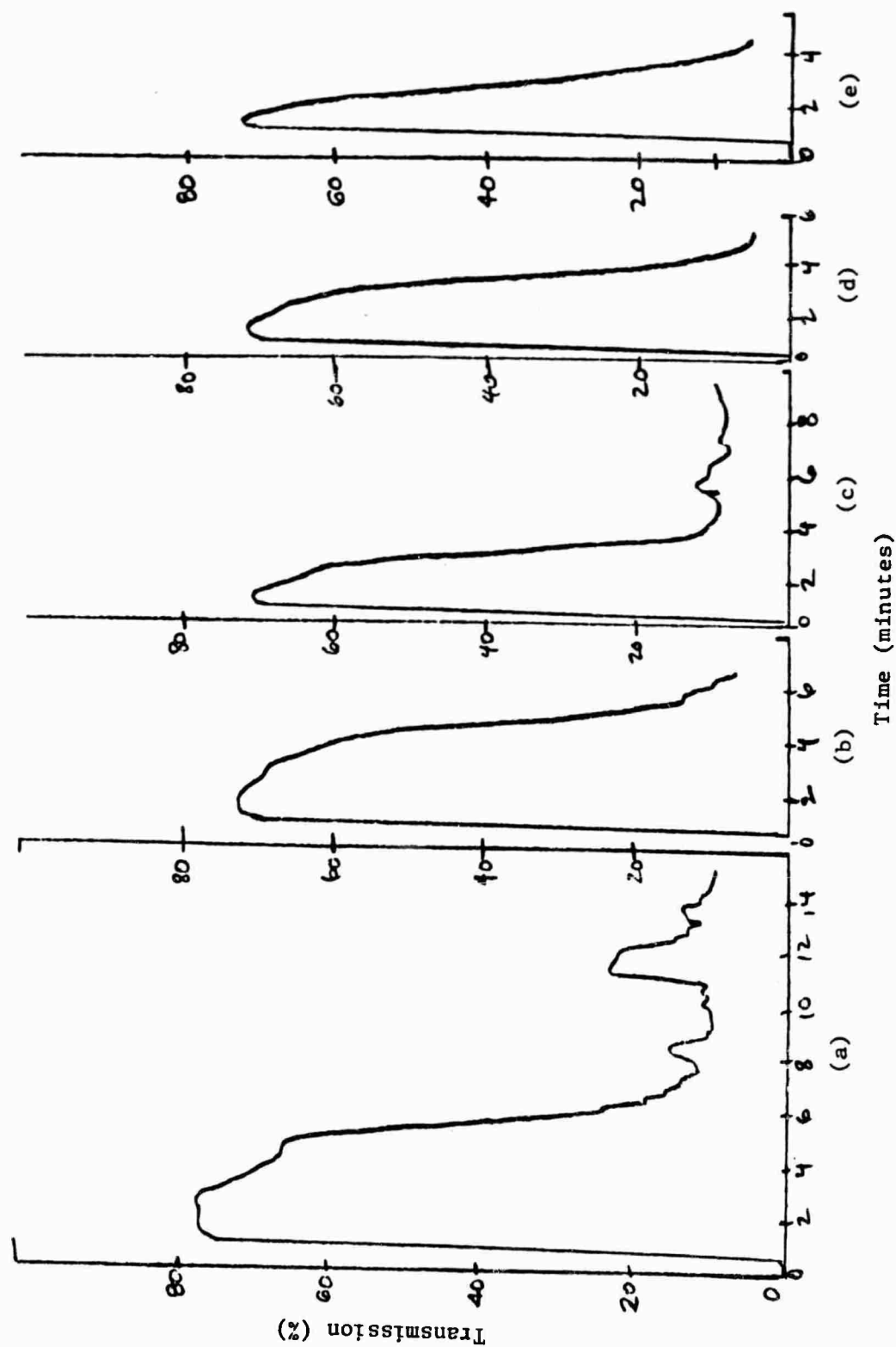


Figure 28. Sealing Curve OT70-PG: (a) and (b) 0.05% AF³ (3%), (c), (d) and (e) (0.25%)/AF³ (3%)

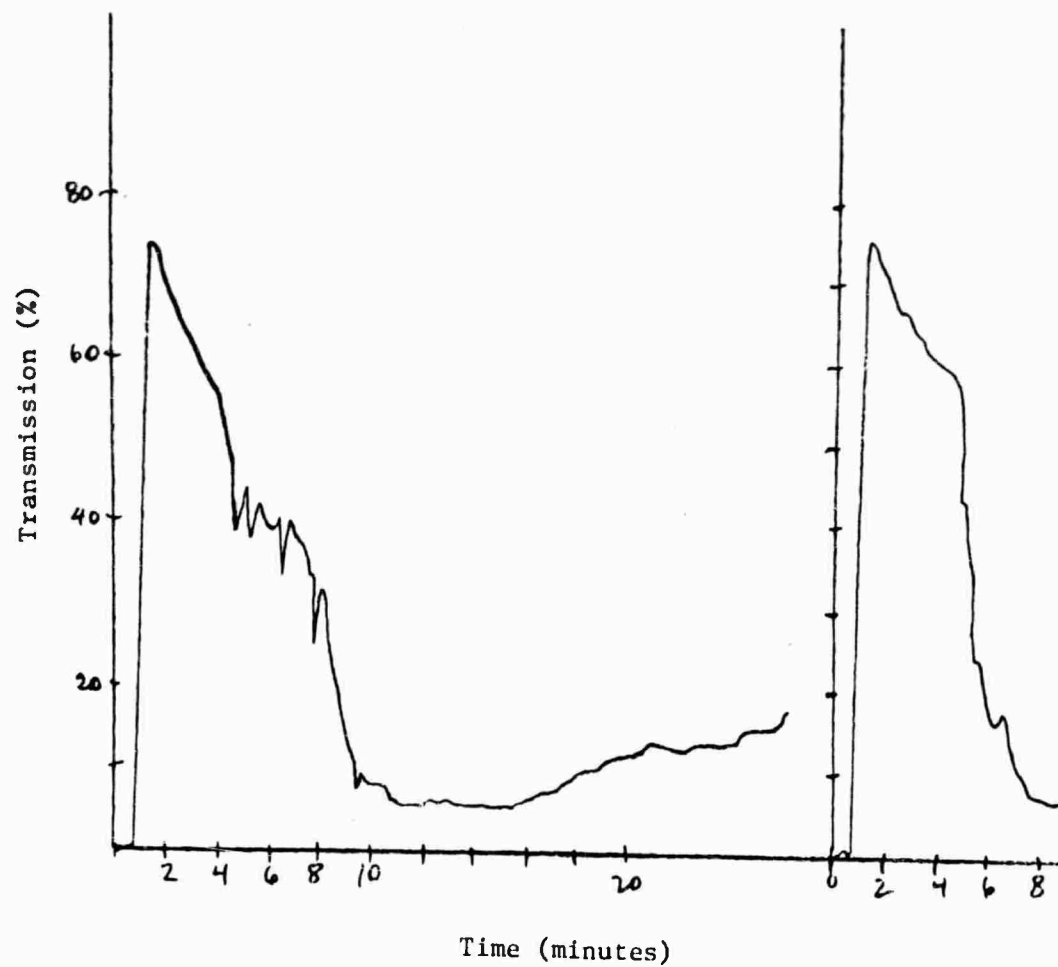


Figure 29. Sealing Curve MA80 (0.25%)/AF³ (3%)

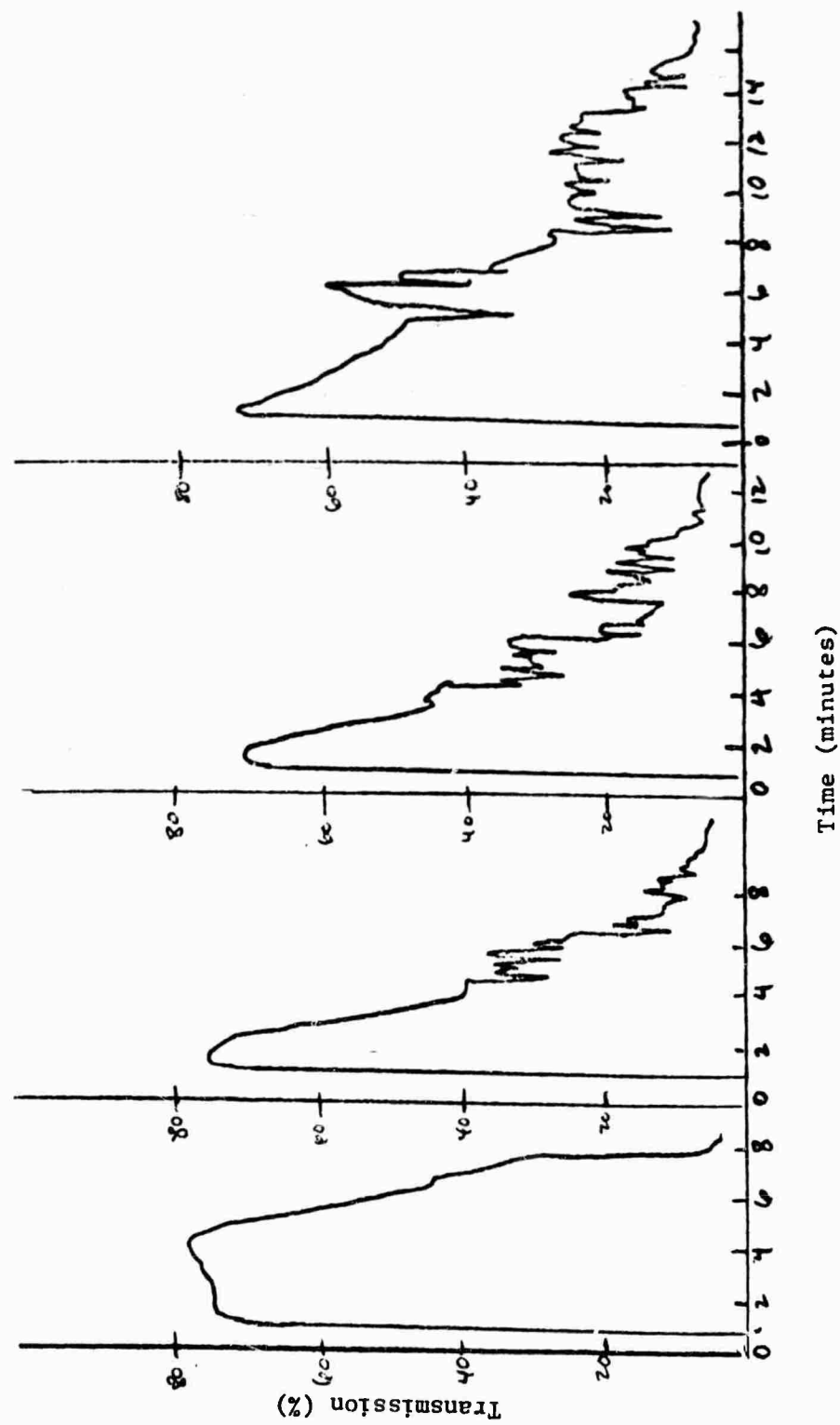


Figure 30. Sealing Curves AY100 (.025%) / AF³ (3%)

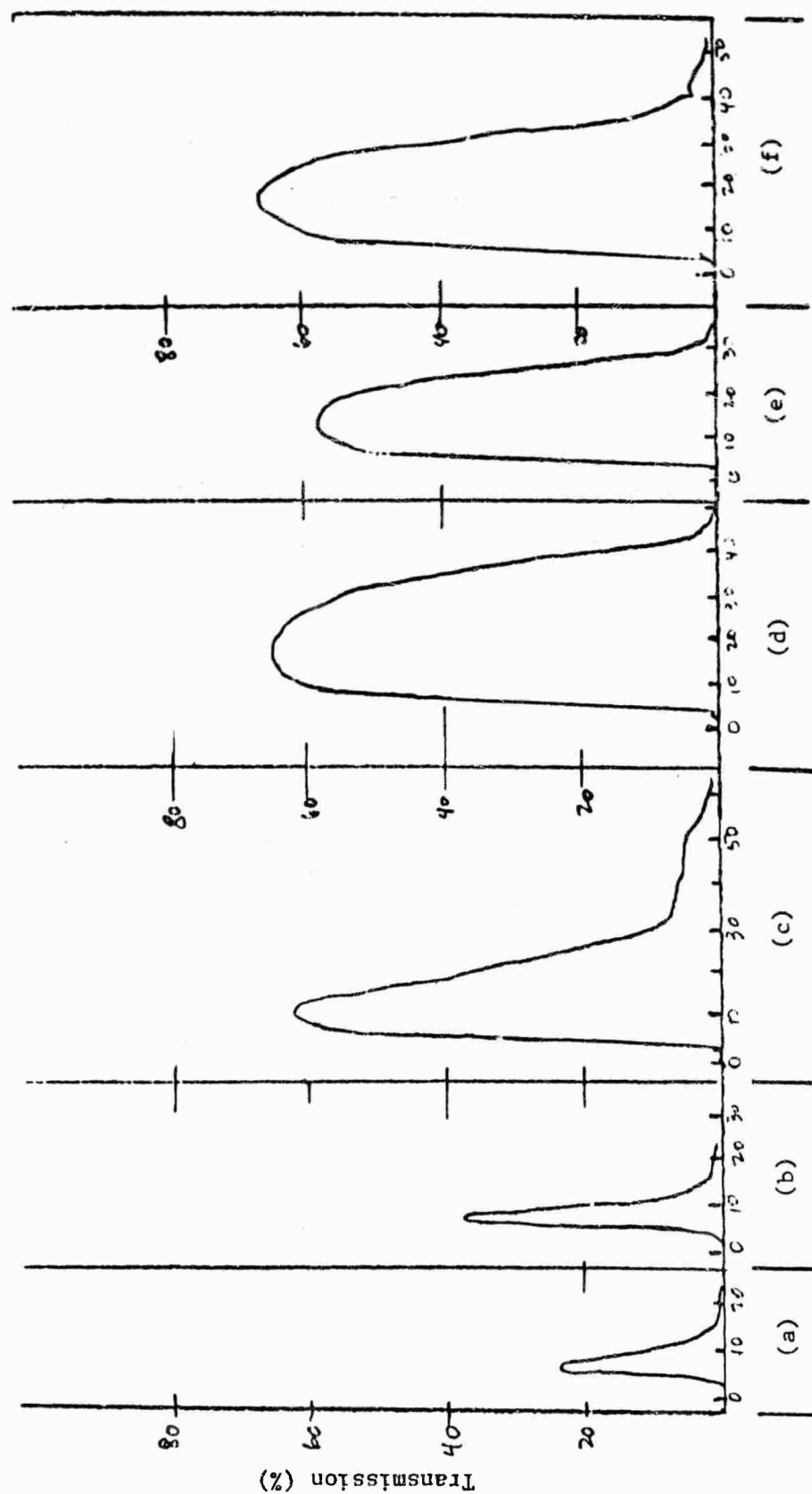


Figure 31. Sealing Curves DV1875: a & b (1%) / AF³; 3
c, d & e (0.5%) / AF³ (3%); f (0.25%) / AF³ (3%)

differences among these chemicals lie primarily in solvent media which disposed some to form bubbles, which broke and show as spikes, e.g., see Figure 30. The effect of concentration of emulsifier at or above 1 percent (w/v) on AFFF can be seen again in Figure 31.

We also studied the "sealing" achievable by 3 percent AF³ on JP-4 which had been emulsified 1:1 with a surfactant solution. Figure 32 is fairly representative of these observations, in which sealing by AF³ was seen to be extended over a very long time but the extent or percent seal was much reduced, to about 1/2 of that in AF³ controls. In Figure 33, the hydrocarbon concentration above neat JP-4 (Curve 1) is compared with that over JP-4 emulsified with AF³ 3 percent (Curve 2) and Atlox 3404 at 0.25 (Curve 3) and 0.5 percent (Curve 4) levels.

This was to be expected as the mechanism of sealing by AFFF depends upon the integrity of the aqueous film on the surface of the fuel, while the mechanism of cooling by water incorporation depends upon chemically assisted low-energy or "self-mixing" emulsification of the water into the fuel. The true tests of efficacy of a "self-mixing" emulsifier could only be small-scale, benchtop burn tests. If a great amount of water could intermix with the fuel, spontaneously, the fuel would tend to resist reignition.

We therefore shifted our attention to determining a blend of "self-mixing" emulsifiers to incorporate a maximum amount of water into the JP-4 with the least mixing energy. Our trial-and-error search was guided at first by determining the hydrophilic, lipophilic balance, HLB, of JP-4, then screening surfactants for emulsifying properties alone with JP-4 and then in combinations. The best of these were then tested in small-scale burn tests.

c. HLB Determination

Hydrophilic-Lipophilic Balance (HLB) system was introduced by a private chemical company (Atlas Chemical Industries) in the late 1940s. This system permits industrial chemists to blend emulsifiers for specific tasks in an orderly way. The chemical structural source of hydro or lipophilicity and the effect on the kind of emulsion formed were described in Section III B.2.

The HLB number was determined by combining mixtures of Tween 80 (HLB 15) and Span 80 (HLB 4.3). These are industrial names for two different derivatives of polyoxyethylene (20) sorbitan monooleates (ICI Americas Inc.), which are hydrophilic (Tweens) or lipophilic (Spans) respectively. Blends of specific HLB numbers were made as shown in Table 7, and Figures 34 and 35. The HLB value of JP-4 was determined to be approximately 11.

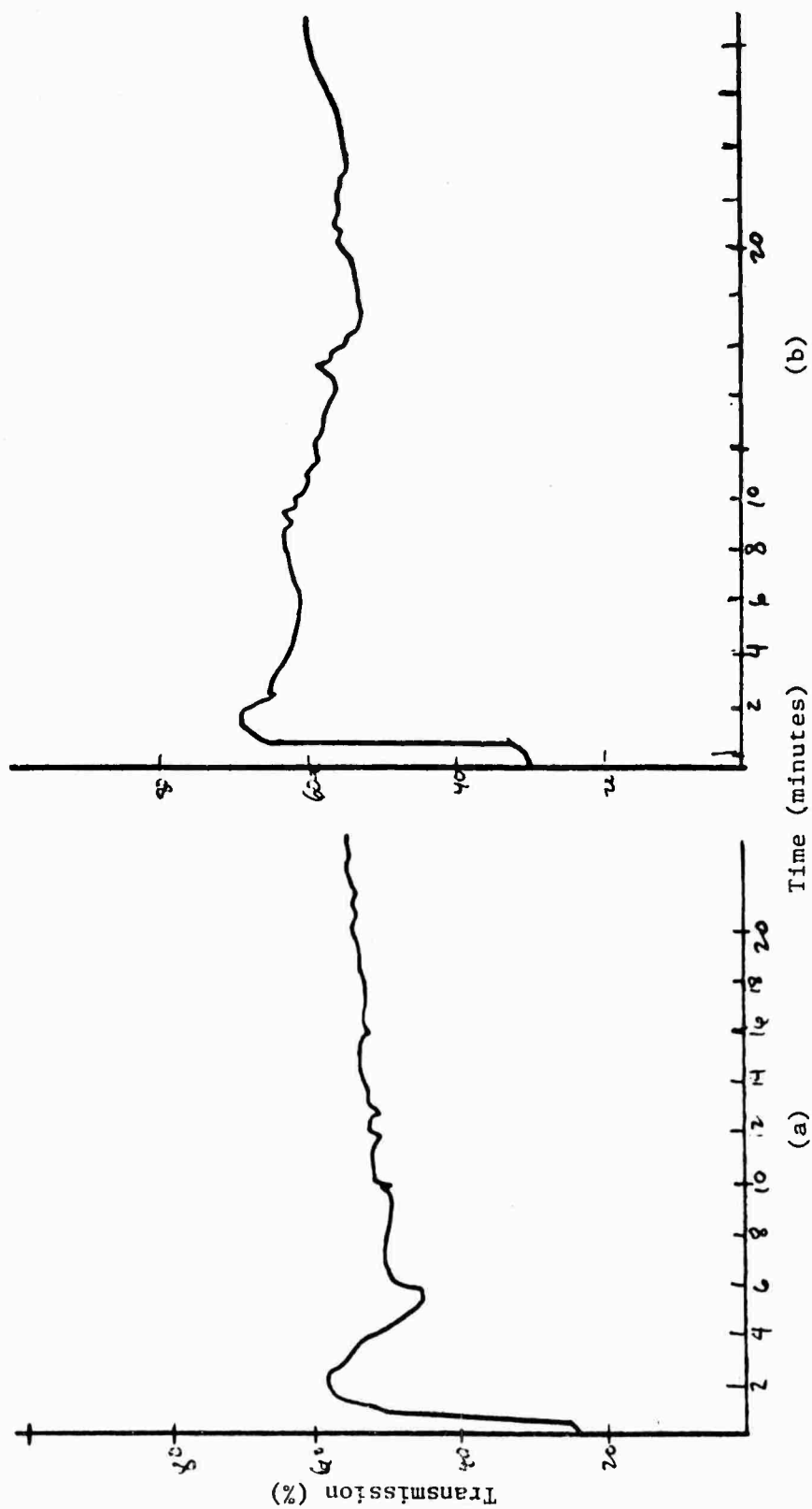


Figure 32. Sealing Curve Atlox 3404 with JP-4 (1:1):
a) 0.25%/AF3 (3%); b) 0.5%/AF3 (3%)

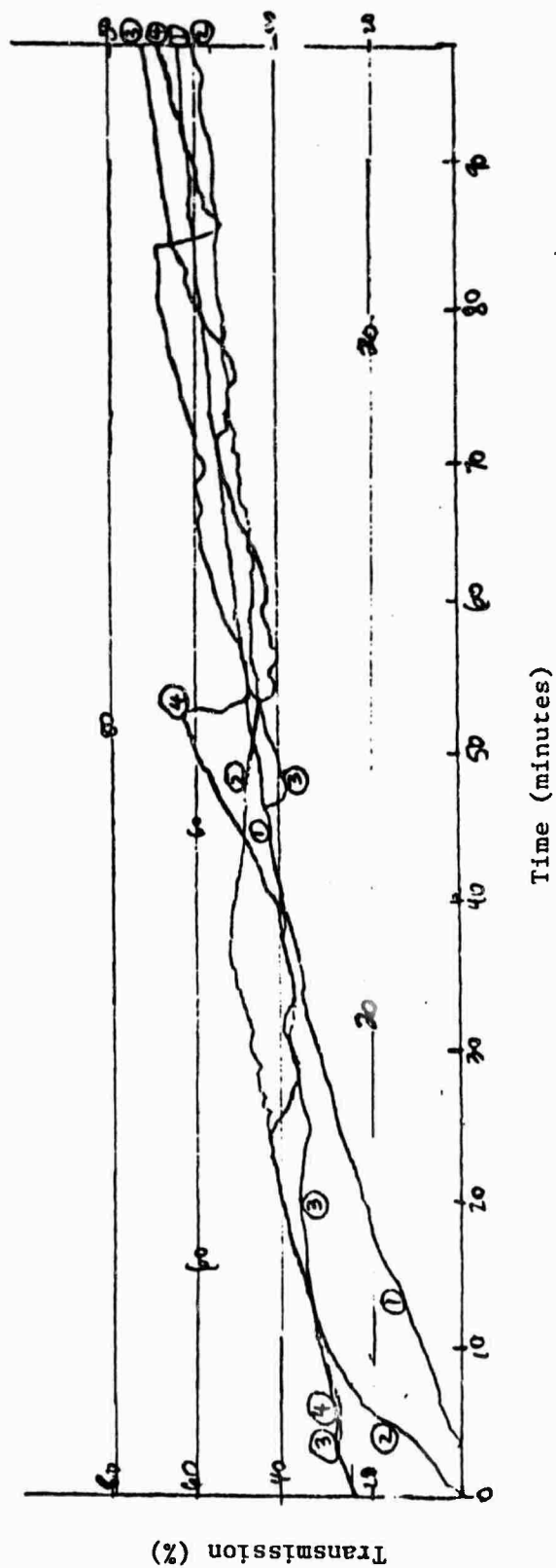
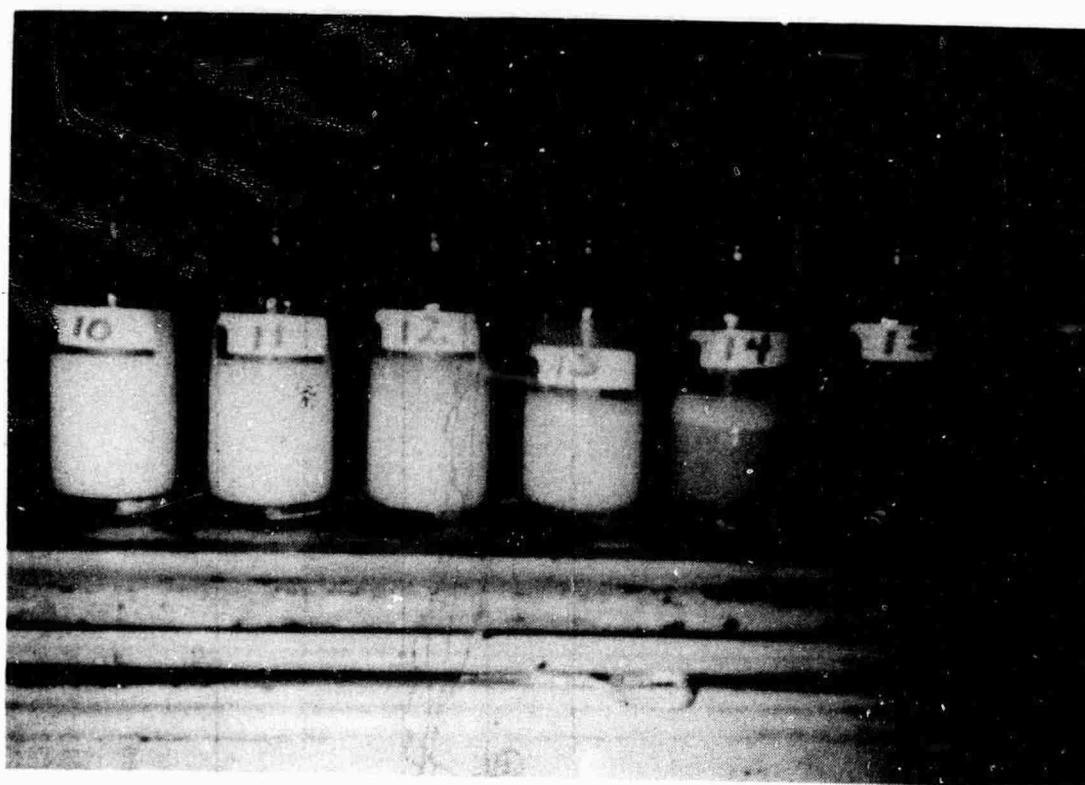
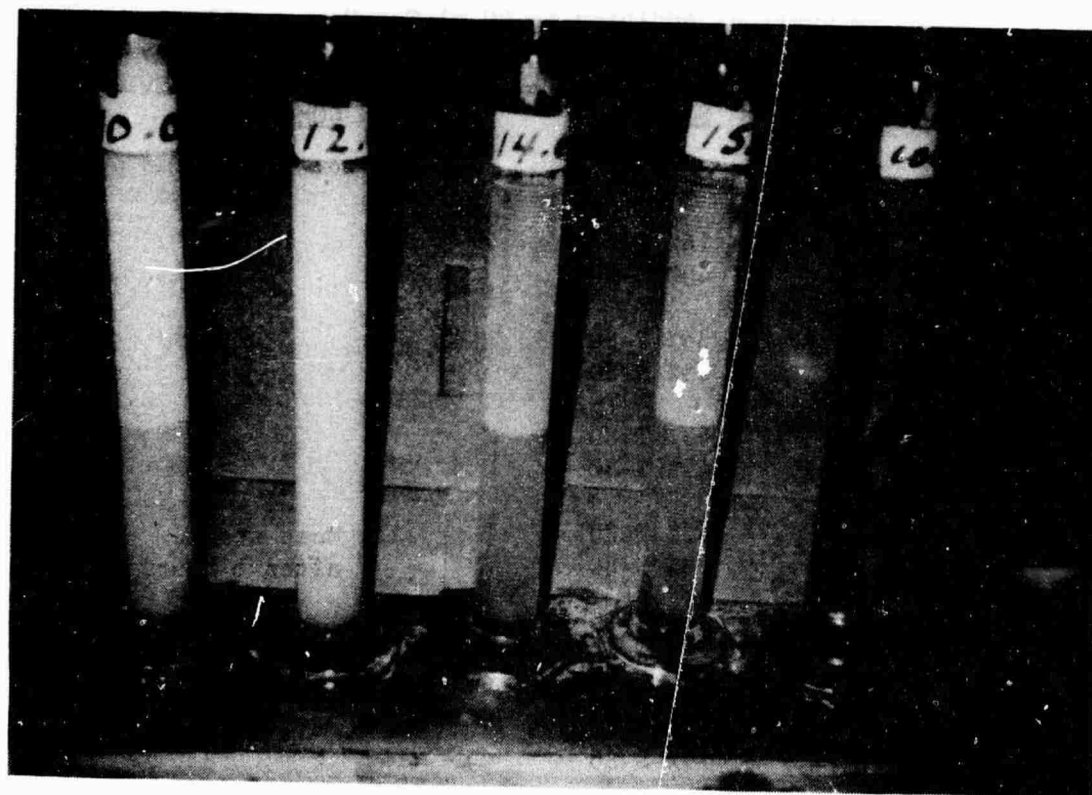


Figure 33. Sealing Curves of (1) JP-4, (2) JP-4/AF3 (3%), (3) JP-4/Atlox 3403 (.25%) and (4) JP-4/Atlox 3404 (0.5%)



10 11 12 13 14 15

Figure 34. HLB Scan to Investigate HLB 10 → HLB 15
50 ml JP-4 + 50 ml Tap Water +
4% Surfactant



10

12

14

15

Control

Figure 35. Initial HLB Scan
50 ml JP-4 + 50 ml H₂O + 4% Surfactant
100 ml Graduate

TABLE 7. HLB SCAN BASED ON SPAN 80 AND TWEEN 80.

(~ 4% Chemical Addition to 50 ml Tap Water + 50 ml JP-4)

<u>HLB</u>	<u>SYSTEM</u>	<u>COMMENTS</u>
4.3	Span 80	
6.0	16% T-80 40% S-80	
8.0	35% T-80 65% S-80	
10.0	53% T-80 47% S-80	
11.0	62% T-80 38% S-80	Most stable after 1 hour.
12.0	72% T-80 28% S-80	
13.0	81% T-80 19% S-80	
14.0	90% T-80 10% S-80	
15.0	Tween 80	

In Table 8, two systems were seen to form emulsions with JP-4 which were stable after 1 hour. These were Triton X-45/Triton X-100 4:1 (i.e. 2.4 ml : 0.6 ml in 50 ml) and Renex 36 alone. Figure 36 shows the photographs of these samples. Even though all of these blends had HLB values close to that of JP-4, most did not form stable emulsions and the ones which did needed to be shaken to be formed. Even though the HLB value above 10 is an indication of correct predominance of water-loving groups, disposing the emulsion with JP-4 to be an oil-in-water emulsion, the efficiency of the emulsifier, i.e., the mixing energy and stability of the emulsion is related to the chemical structure of both the surfactant and the oil or fuel to be emulsified.



Span 80	Triton X-45		G-1096	
+	+	Tween 85	G-1096	+ Renex 36
Tween 80	Triton X-100		Renex 36	

Figure 36. Generic Surfactant Scan at HLB II
 50 ml JP-4 + 50 ml H₂O + 3 ml Surfactant

TABLE 8. GENERIC SURFACTANT SCAN AT ~ HLB 11.0.
(3 ml Addition to 50 ml Tap Water + 50 ml JP-4)

	<u>SYSTEM</u>	<u>COMMENTS</u> - After 1 hour
1.	Span 80 + Tween 80 HLB 11.0 (Base case)	Broke
2.	Triton X-45 + Triton X-100 4 parts 1 part	Stable
3.	Tween 85	Broke
4.	G 1096 (HLB 11.4)	Broke
5.	G 1096 (HLB 11.4) + Renex 36 (HLB 11.4)	Starting to Break
6.	<u>RENEX 36</u> (HLB 11.4)	Most Stable

d. Screening for Self-Mixing

Single surfactants were then combined with JP-4, each representative of a functional subgroup found within the 10.6 - 11.4 range HLB Index of McCutcheon's "Emulsifiers and Detergents" 1988. These chemical families included: alkylaryl sulfonate, polyoxyethylene (POE) ether, nonyl phenol, ethoxylated alcohol, POE esters, polyethylene glycol (PEG) esters, POE ether alcohol, ethoxylated oleic acid, alkyl phenol ethoxylate and ethoxylated alkyl acids. Intimate mixing of water into the fuel, or emulsification to produce a more water-continuous phase layered below the foam was believed to offer the most promise. The challenge was to find an emulsifier which, when added to a stream of water, and applied to hot fuel, would form a fairly stable dispersion of the hydrocarbon fuel in a water phase. A sufficiently low mixing energy is required. Emulsifiers were screened in these qualitative tests for both extent and stability of emulsification of JP-4 into water. Small graduated cylinders, fitted with magnetic stirrers and constant aliquots of fuel and water had varied emulsifiers added, with the amount and lifetime of the emulsified layer measured in each case. Each emulsifying agent was tested on its own and combined with others for ability to integrate the most water into JP-4, the most quickly and stably. The experiments were done in two stages. The huge numbers of screening trials were carried out in 24 ml graduated cylinders. Approximately 6 ml of fuel and 6.5 ml aqueous-phase (containing surfactant) were stirred for 1 minute (on low) with a magnetic stirring bar. The time-to-phase separation (t_{ps}) from when the stirring stopped, was measured, along with the volumes of the aqueous, mixed and fuel phases at that time and again 5 minutes (300 seconds) later. Surfactant concentrations for these trials were either 0.1 percent w/v or 0.5 percent

w/v. Results, averaged from 2-3 tests each, from representative trials are presented in Table 9. Roman numerals indicate chemical families and Arabic numerals indicate the specific compositions, either purchased or blended by Beltran. The key relating number to structure and trade name are given in Table 9.

Before carrying out Burn Tests, as described in the next section, a series of tests was carried out to determine the effect of varying both volume of the water phase and concentration of emulsifiers in the water phase on neutralization of the fuel. Both the volume of water incorporated into the JP-4 and the ease of directly igniting the emulsified fuel were measured for each series of tests on each of four candidate emulsifier blends.

This series of experiments was carried out with 100 ml graduated cylinders fitted with ground glass stoppers. Surfactants or blends of surfactants which had demonstrated the longest times to phase separation and the greatest total volume of emulsified fuel after 5 minutes, or the complete incorporation of fuel or water into an emulsified stage (i.e., volume aqueous phase [Vaq], or volume oil phase [Vol] after 300 sec. was essentially zero), were selected from the extensive preliminary screening trials. The concentration of a surfactant, or of each surfactant in a blend, was then adjusted to maximize incorporation of water with a minimum of "mixing energy."

We inverted the graduated cylinder once and began timing to phase separation, measuring volumes immediately and again after 5 minutes. In addition to varying the concentration of components, we varied the ratio of JP-4 to aqueous phase between 1:1 and 2:1. Figures 37 and 38 show a typical series in which concentration and proportion are varied for one system. The fuel is the yellow phase on top and the water is the translucent layer below the opaque one on the extreme right in both photographs.

All tests were carried out, in duplicate for each blend, in graduated cylinders to determine the effect of the volume amount and then the concentration of emulsifier on the total volume of water incorporated into the JP-4. Burn tests were also carried on every resultant aliquot of emulsified fuel (V_{E-F})

Tables 10 and 11 show results typical of an experimental series in which the volume of the water phase (containing emulsifier blend) was varied. Tables 12 and 13 show results typical of series in which the concentration of emulsifier was varied and the volume of fuel to water was kept constant (Table 12), or also varied (Table 13). The Key to items in these tables is given following Table 13.

These tests were carried out for each of four emulsifier blends up to total volumes of 50, 75, and 100 ml.

TABLE 9. SCREENING EMULSIFIER BLENDS FOR HYDROPHILICITY.

(NOTE: Starting aqueous volume (Vaq) was 6.5 ml, and starting oil phase volume (Vol) was 6.0 ml in all samples.
All emulsifiers were 0.1% w/v concentrates, except those marked by an asterisk, "**", which were 0.5% w/v.

Sample	t _{ps}	aq.	Vat t _{ps}		V after 300"		
			mix.	ol.	aq.	mix	ol.
I. <u>Ethers</u> (nonyl phenol polyethylene glycol ether (65-80%) ethylene oxide.							
Rexol 25/9	210"*	2.0	10.5	0.0	2.5	10.0	0.0
"	immed.	5.0	3.0	4.5	6.4	1.2	4.9
" 25/6	Phase separated right after stopped stir						
" 25/20	23"*	3.0	9.5	0.0	5.8	6.7	0.0
"	immed.				6.1	3.9	3.5
" 25/407	immed.*				5.5	6.5	0.5
II. <u>Corexit</u> : Exxon proprietary oil dispersant							
Corexit 9527	*Phase separated right after stopped stir						
" 9550	*						
" 7664	*						
III. <u>Diethanolamide of oleic acid</u>							
Clindrol 200-0	*Phase separated right after stopped stir						
Schercomid ODA	*						

TABLE 9. SCREENING EMULSIFIER BLENDS FOR HYDROPHILICITY (CONTINUED).

Sample	t _{ps}	aq.	Vat t _{ps}		V after 300"	
			mix.	ol.	aq.	mix
IV. <u>Witco alcohol ether or olefin sulfates (anionic)</u>						
W-1276	20"	3.0	8.5	1.0	6.0	4.5 2.0
W-A	*Phase separated right after stopped stir					
AOS	*		"		6.2	2.8 3.5
W-1259	*		"		6.1	1.9 4.5
SE-5	40"				5.6	6.9 0.0
"	immed.				6.1	1.4 5.0
V. <u>Witco (neutral) Ethoxylates - polyethylene glycol (40%)</u>						
W-SN-90	65"	4.0	8.5	0.0	5.6	6.9 0.0
"	immed.				6.3	0.5 5.7
W H-31A	Phase separated right after stopped stir					
VI. <u>Proprietary mixtures</u>						
Atlos 3404	*No phase separation throughout the experiment					
	210"	2.0	10.5	0.0	3.0	9.5 0.0
" 1087	Phase separated right after stopped stir					
Tween 80	140"	3.5	9.0	0.0	4.0	8.5 0.0
"	30"				6.0	4.5 2.0
Span 80	Phase separated right after stopped stir					

TABLE 9. SCREENING EMULSIFIER BLENDS FOR HYDROPHILICITY (CONTINUED).

Sample	t _{ps}	aq.	Vat t _{ps} mix.	ol.	V after 300"	aq.	mix	ol.
VII. <u>Sulfosuccinates</u>								
DV-1875	180"* 40"	0.0 0.0	12.5 12.0	0.0 0.5	2.9 6.0	9.6 2.5	0.0 4.0	
OT70PG	240"* 120"	5.5 3.0	7.0 9.5	0.0 0.0	5.5 6.0	7.0 3.0	0.0 3.5	
AY-100	*Phase separated right after stopped stir							
MA-80	*Phase separated right after stopped stir							
M-60	240"* immed.	1.5 0.0	11.0 12.0	0.0 0.5	2.2 6.3	10.3 1.2	0.0 5.0	
VIII. <u>Ethoxylated thioethers</u>								
Siponic 218	120"* immed.	5.0	7.5	0.0	5.7 6.3	6.8 1.2	0.0 5.0	
" 260	30"*	3.0	6.0	3.5	6.0	2.5	4.0	
" SK	Phase separated right after stopped stir							
IX. <u>Olefin Sulfonates</u>								
Siponate A246-LX	45"*	4.0	8.5	0.0	5.6	6.9	x	
"	immed.				6.4	0.6	5.5	
Marasperse N-22	Phase separated right after stopped stir							
M52CP	"							
MB-22	"							
M-OF	"							

TABLE 9. SCREENING EMULSIFIER BLENDS FOR HYDROPHILICITY (CONTINUED).

Sample	t _{ps}	aq.	Vat t _{ps}		V after 300"		
			mix.	ol.	mix	ol.	
<u>X. Cocoamide DEA's</u>							
Clindrol 101CG	90**	5.5	5.5	1.5	6.1	2.2	4.2
Sipomide 1500	170**	2.0	10.5	0.0	3.0	9.5	0.0
"	50"	3.0	9.5	5.5	5.4	7.1	0.0
Clindrol 210CGN	*No phase separation throughout the experiment immed.				0.5	7.0	5.0
Clindrol 202CGN	30**	0.0	12.0	0.5	6.0	2.0	4.5
Clindrol 206 CGN	15**	6.1	1.4	5.0		same	
<u>XI. Alcohol Ethoxylates</u>							
Neodol-25	150** immed.	4.5	8.0	0.0	6.1	same 2.9	3.5
Siponic E-10	Phase separated right after stopped stir						
Igepal	immed.*	4.5	4.5	3.5	6.4	2.1	4.0
RT-61	75**	3.2	9.3	0.0	5.0	5.0	2.0
Rexonic P-1	Phase separated right after stopped stir						
Acrysol ICS	Phase separated right after stopped stir						

TABLE 9. SCREENING EMULSIFIER BLENDS FOR HYDROPHILICITY (CONTINUED).

Sample	t _{ps}	aq.	Vat t _{ps} mix.	ol.	V after 300"		ol.
					aq.	mix	
XII.							
Ansulite AFC 5A "	200**	2.0	10.5	x	3.5	9.0	x
	60"	2.0	10.5	x	4.9	7.6	x
Ansulite AFC 5 "	75**	1.5	11.0	x	4.0	8.5	x
	immed.				6.4	1.6	4.5
AF ³ (3%)	44"	4.0	8.5	x	5.5	7.0	x
FFFP (3%)	immed.				6.0	6.5	
AF ³ (0.1%)	immed.	6.5	1.5		6.1	2.9	4.5
FFFP (0.1%)	immed.		x		6.0	1.0	5.5
<u>Mixture with emulsifier and AF³</u>							
AF ³ (3%) & Atlox 3404 (0.1%)	180	3.0	9.5	x	4.0	8.5	x
AF ³ (3%) & AFC 5A	180	4.5	8.5	x	5.0	7.5	x
AF ³ (3%) & Sipomide 1500	240	3.0	9.5	x	4.0	8.5	x

TABLE 9. SCREENING EMULSIFIER BLENDS FOR HYDROPHILICITY (CONCLUDED).

Notes:

- a. All emulsifiers are used 0.1% aqueous solution except the AF³ samples.
Aq. emulsifier 6.5 ml and JP-4 6 ml were used.
- b. The time at which a phase separation was observed = T_{ps}.
- c. The volumes were observed at the first phase separation detected after the stirring is stopped.
Aq.: Aqueous solution, (ml).
Mix: Mixture of aq. emulsifier and fuel. vol (ml).
Fuel: Fuel. vol (ml).
- d. The volumes were observed 5 min. after the stirring is stopped. The volumes (ml) of aqueous, mixed and fuel were read from bottom up.

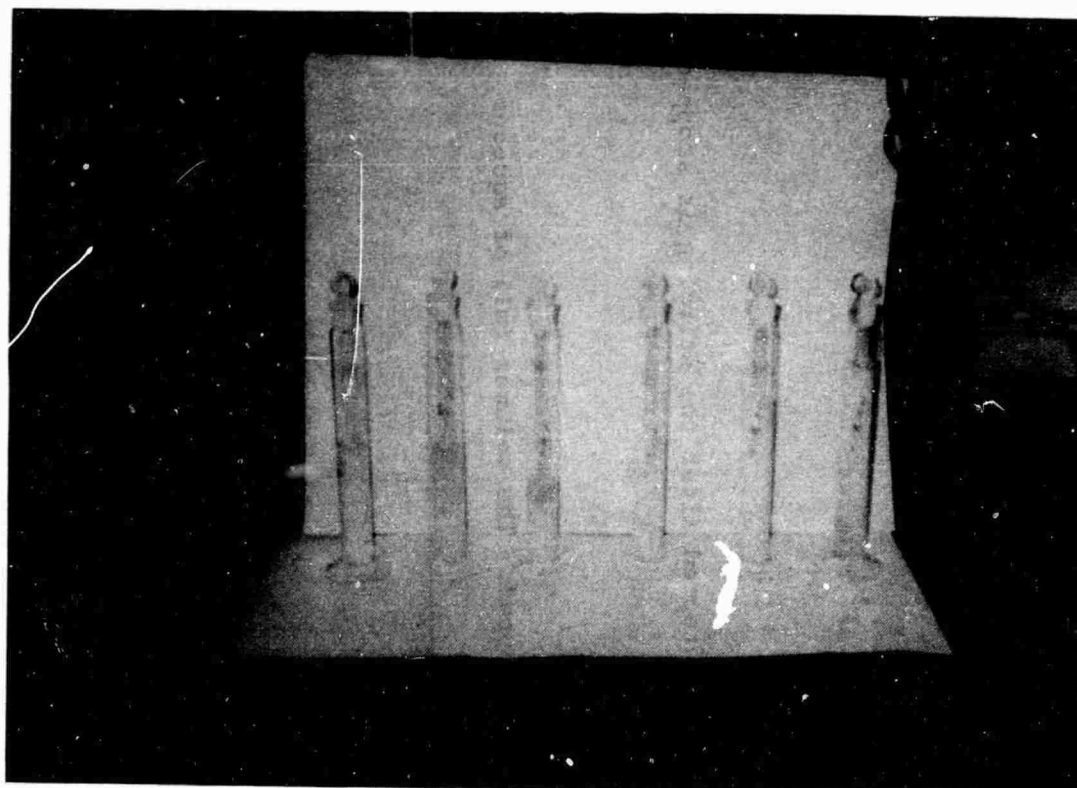


Figure 37. Effect of Emulsifier Concentration on Emulsion Formation with JP-4

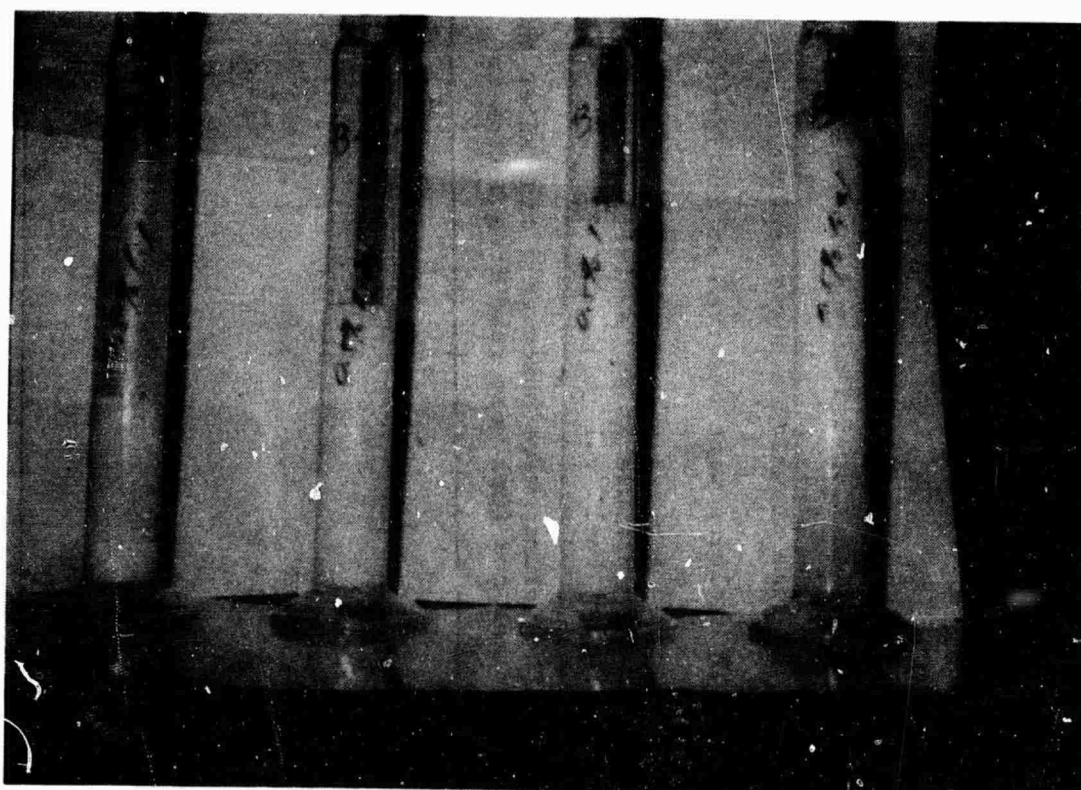


Figure 38. Effect of Fuel/Water Ratio on Emulsion Formation with JP-4

The abbreviations represent the following:

[E] - Emulsifier concentration, percent w/v

[E] - Concentration of emulsifier w/v
as percent in stock solution.

E_{III} - Atlox 3404G Table 13.

E_I - DV1875/TX45 Table 10 & 11.

E_{II} - OT70PG/TX45 Table 12.

V_F - Volume fuel premix

V_E - Volume emulsifier premix

V_{E-F} - Volume pea soup phase postmix

V_A - Volume aqueous below V_{E-F}

V_O - Volume oil above V_{E-F}

Key to Tables 10-13:

V_M - Volume emulsified mixture after 5 hours (ml).

V_A - Volume aqueous phase, below V_M (ml).

V_O - Volume oil or fuel phase, above V_M (ml).

V_E - Volume of Emulsifier.

V_F - Volume Fuel (JP₄) in ml.

In Tables 10 and 11: Emulsifier System was DV1875, in
Table 12: E- OT70 PG/TX45, and in Table 13: E- Atlox 3404G.

The variability from one blend to another was great, on
the order of 5 ml, but the trends were the same within each series.

TABLE 10. EFFECT OF FUEL: WATER VOLUME (ML) ON FUEL NEUTRALIZATION.
(100 ml maximum at 1:1)

	<u>a.</u>	<u>b.</u>	<u>c.</u>	<u>d.</u>	<u>e.</u>	<u>f.</u>	<u>g.</u>	<u>h.</u>	<u>i.</u>	<u>j.</u>
V _F	50	50	50	50	50	50	50	25	25	25
V _E	5	10	15	20	25	30	50	30	40	50
V	5.2	14.5	26.5	58.8	61	56	66	31	30.8	31
V _A	4.8	9.5	14.5	11.2	14	24	34	24	34.2	44
V _O	45	36	24	0	0	0	0	0	0	0

TABLE 11. EFFECT OF FUEL: WATER VOLUME (ML) ON FUEL NEUTRALIZATION.
(50 ml maximum at 1:1)

	<u>a.</u>	<u>b.</u>	<u>c.</u>	<u>d.</u>	<u>e.</u>	<u>f.</u>	<u>g.</u>
V_F	25	25	25	25	25	25	25
V_E	10	15	20	25	30	40	50
V	6.0	31.8	34.8	33.5	31.5	30	30
V_A	10.2	8.2	10.2	16.5	23.5	35	45
V_O	19.1	0	0	0	0	0	0

TABLE 12. EFFECT OF EMULSIFIER CONCENTRATION: ON FUEL NEUTRALIZATION.
(100 ml volume)

	<u>a.</u>	<u>b.</u>	<u>c.</u>	<u>d.</u>	<u>e.</u>
V_F	50	50	50	50	50
V_E	50	50	50	50	50
[E]	0.5	1.0	1.5	2.0	2.5
V	52.4	52.7	56.3	54.0	58.0
V_A	47.6	47.3	43.8	46.0	42.0
V_O	0	0	0	0	0

TABLE 13. EFFECT OF EMULSIFIER CONCENTRATION AND FUEL:WATER RATIO
ON FUE. NEUTRALIZATION.
(60 ml maximum at 1:1)

	<u>a.</u>	<u>b.</u>	<u>c.</u>	<u>d.</u>	<u>e.</u>	<u>f.</u>	<u>g.</u>	<u>h.</u>	<u>i.</u>
V_F	30	30	30	20	20	20	30	30	30
V_E	30	30	30	40	60	80	22.5	15	7.5
V_F/V_E	1:1	1:1	1:1	1:2	1:3	1:4	4:3	2:1	4:1
[E]	2	1	0.5	0.5	0.5	0.5	2.0	5.0	5.0
Burn		X	X	X	X	X		X	X
Not Burn	X (on old JP-4)						X (on old JP-4)		

Observations:

(1) Water to Fuel Ratio

The water:fuel ratio had to be 2:5, Table 10(d) or 1.5:2.5, Table 11(b) or greater than 1:2 (Table 13 a and g) in order to incorporate the maximum volume of water for a given concentration of an emulsifier system. Increasing this ratio by adding more water, e.g. $V_E:V_F$ 2:1, Table 10(j), 11(g) and 13(d) does not increase the incorporation of water into the fuel, at a constant emulsifier concentration or inhibit burning, even when the effective total emulsifier concentration has been increased. For example, in Table 13(f), 80 ml of 0.5 percent emulsifier $V_F:V_E(4:1)$ does burn while 22.5 ml of 2 percent, Table 13(g) $V_F:V_E(1:1)$ does not, in direct torch tests. This observation is not easy to translate to a real fuel-spill burn situation because the local ratio of water to fuel will be determined by the ratio of spill volume to surface area.

(2) Emulsifier Concentration

The concentration of total emulsifier components was generally varied between 0.5 and 5.0 percent w/v. Above approximately 5 percent w/v the emulsifier may become a phase itself.

Increasing the [E] between 1.5-2.5 percent, Table 12, interestingly did not increase the amount of water incorporated into the emulsified-fuel phase. This was misleading however, as observations were made in which the same amount of water was incorporated into the emulsified fuel at two different fuel:water ratios, and in one case the emulsified fuel burned, Table 11(b), and in the other case it did not, Table 11(e). The former had 6.8 ml of water incorporated into the emulsified fuel (31.8-25.0 ml), the latter, which did not burn, slightly less, 6.5 ml (31.5-25.0 ml). The surfactant concentration being greater in the latter case must promote the oil-in-water emulsion required for non-burn.

Although the volume of water incorporated into the fuel varied slightly, with increasing emulsifier concentration in every series, all aliquots of emulsified fuel made with concentrations of emulsifier less than 2 percent in the water premix burned. The surfactant concentration is therefore as critical to neutralizing the fuel as the actual volume of water intermixed with the fuel. In most tests more phase stability and longer periods of neutralization of the fuel (i.e., nonburn after time study) were observed with total surfactant concentration of 3-4 percent.

e. Emulsified Fuel-Flame Tests

The primary goal of our emulsifier formulation effort was to instantly alter the JP-4 fuel to such an extent that it will not burn. We therefore devised a small, simple burn test to be carried out in a laboratory hood, on freshly prepared samples of emulsified fuel. Samples were placed in a large petri dish, sitting on a hot-plate. A small aerosol pump flask containing AF^3 was nearby for extinguishing, as shown in Figure 39. Flame was applied to the emulsified fuel with a hand-held torch, as

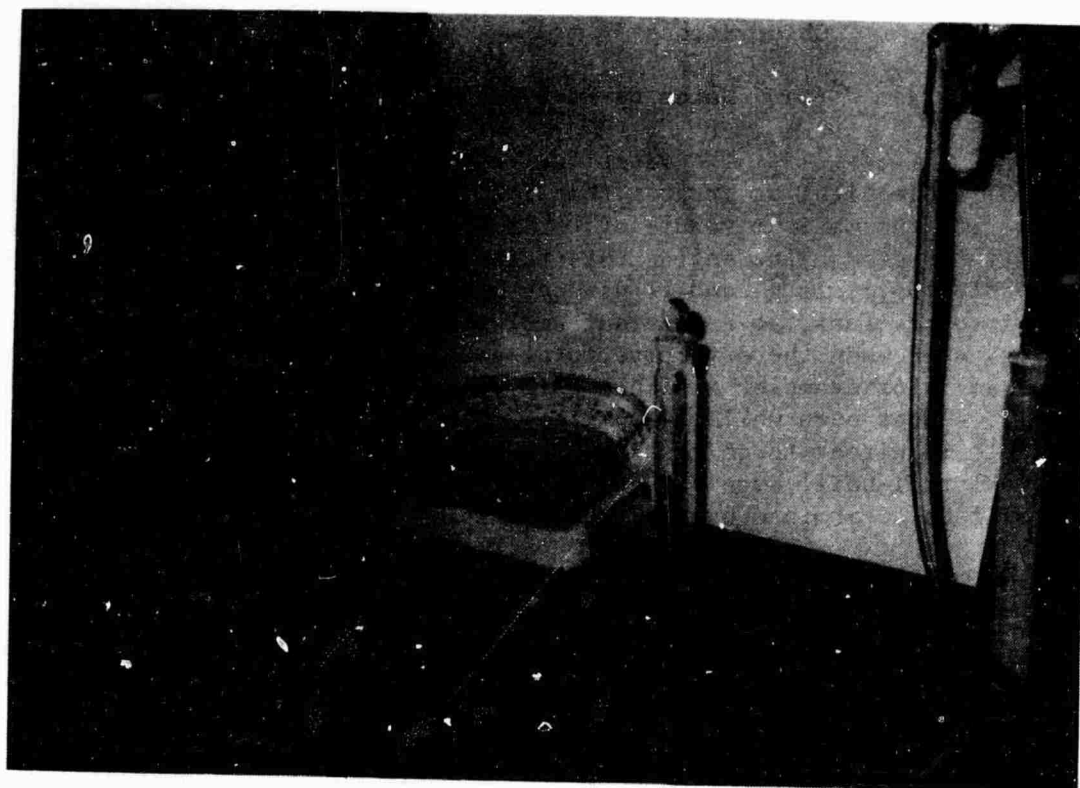


Figure 39. Small-Scale Bench Burn Test Setup

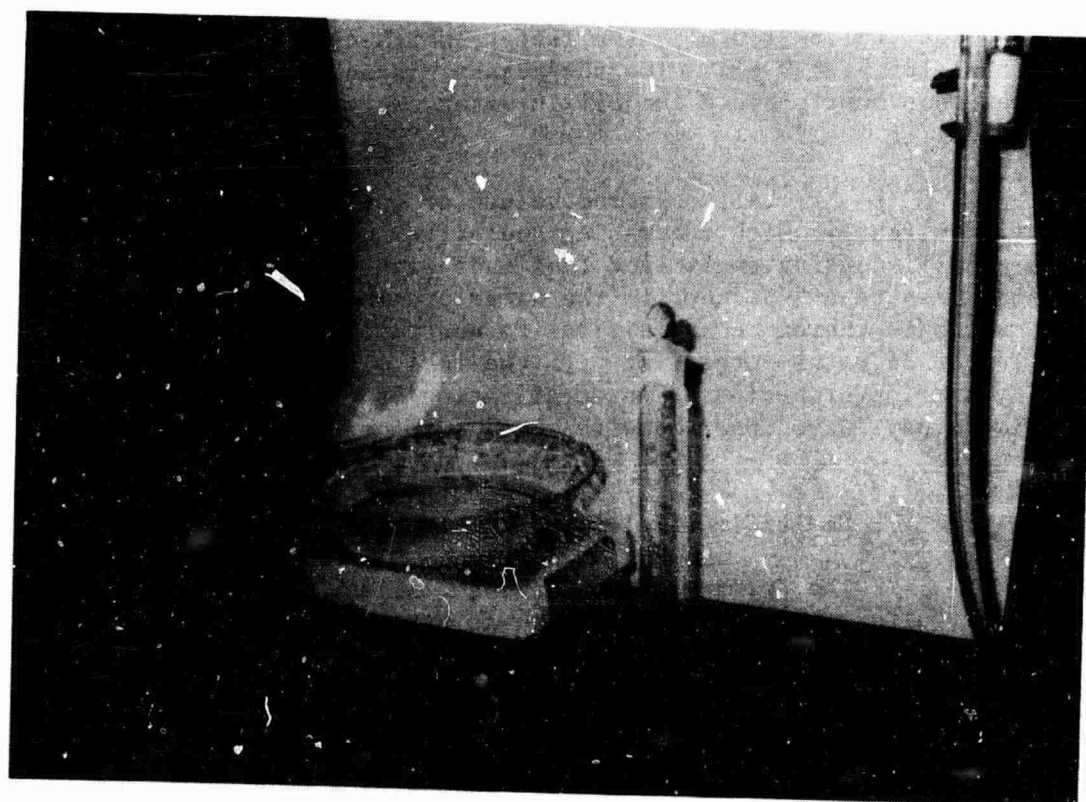


Figure 40. Application of Flame in Small-Scale Test

shown in Figure 40. A record was made of how easily a sample burned, any characteristics of the flame and, in some cases, how many minutes of applied flame passed without ignition of the emulsified JP-4. Figure 41 shows a an emulsified JP-4 sample burning in the petri di-

Initially, sealing curves of various emulsion blends with JP-4 were studied in comparison with hydrocarbon vapor concentration above neat JP-4, in an effort to screen blends before burn tests. Figure 42 represents one such effort in which curve 1 shows the slow-evaporation of low boiling volatiles from JP-4 and the other curves show from 65-75 percent sealing in the emulsified fuels. In burn tests on these mixtures however no correspondence between sealing efficacy and non-ignition, by direct flame in petri dish could be found. For example, compare the burn tests in Table 14 with the curves in Figure 42.

In these mixtures, the final total concentration of emulsifier was 2 percent or 1 percent in a 1:1 mixture with JP-4. Total volumes ranged from 50 to 100 ml. In these trials the mixing energy was extremely varied, i.e., ranging from "needing inversion" to instant emulsification. The ease of emulsion formation however, was not related to reduced ignitability of the fuel.

In fact, our mistaken initial assumption that this could be the case led us, in early efforts, to select surfactants or blends which would most likely form a microemulsion with JP-4. Guided by interfacial tension data for individual components we succeeded in forming "instant" emulsion with JP-4. Fine microemulsions were formed using several systems. Following through to the burn test, however, revealed that the truly "fine" microemulsions all burned quite easily, while the coarser ones did not. There is probably a point at which the increase in the surface area of fuel promotes combustibility through the increasingly thin surrounding aqueous phase of every droplet or micelle. Even the stable emulsions formed after hard shaking, such as the Renex 36 (HLB 11.4) and TX45/TX100 (4/1) of Table 8 were easily flammable. We therefore had to proceed screening blends of these components with others which could promote an easily formed oil-in-water emulsion with JP-4.

TABLE 14. BURN TESTS ON SAMPLES IN FIGURE 42.

<u>Material</u>	<u>Fuel:Water Ratio</u>	<u>Curve #</u>	<u>Burn</u>
JP-4:DV1875/TX45 (2%:2%) emulsion	1:1	2	No
JP-4:OT70PG/TX45 (1%:1%) emulsion	1:1	3	Yes
JP-4:DV1875/TX45 (2%:2%) emulsion	4:3	4	No
JP-4:OT70PG/TX45 (2%:2%) emulsion	1:1	5	No
JP-4 Atlox 3404F (2%) emulsion	1:1	6	Yes

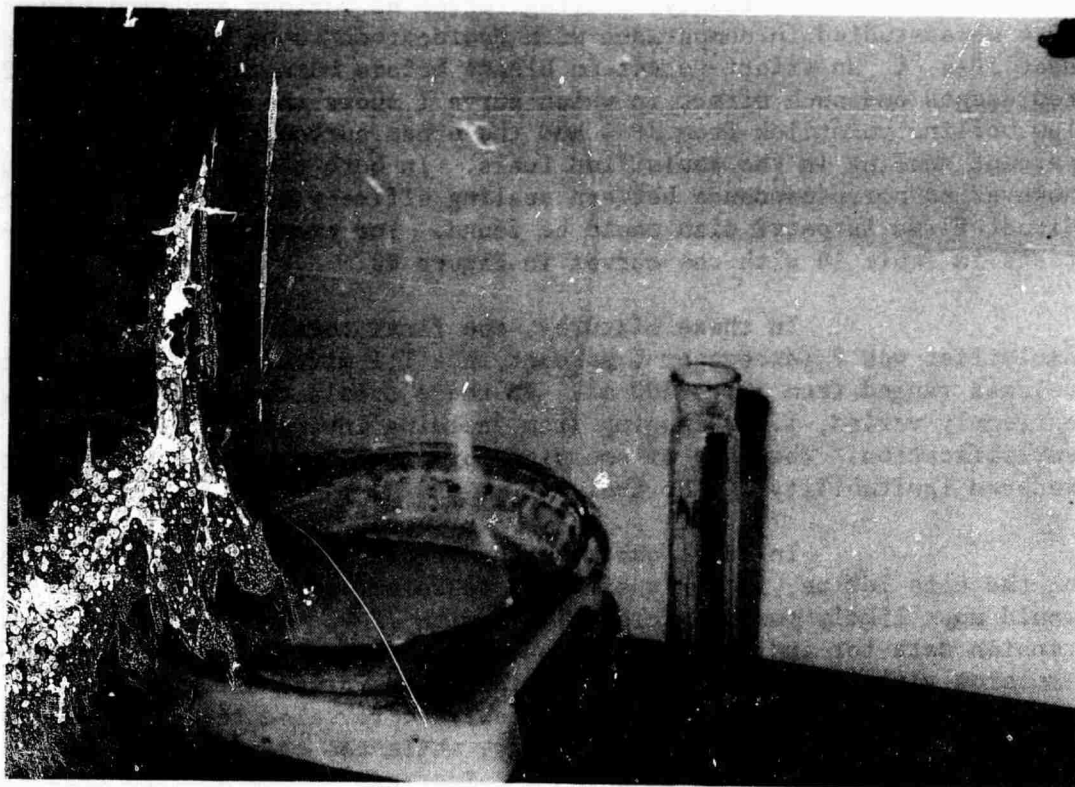


Figure 41. Emulsified JP-4 Burning

T = 22-23°C

1. JP-4 only
2. JP-4 + DV1875/TX45, 2% (1:1)
3. JP-4 + OT70PG/TX45, 1% (1:1)
4. JP-4 + DV1875/TX45, 2% (4:3)
5. JP-4 + OT70PG/TX45, 2% (1:1)
6. JP-4 + Atlox 3404F, 2% (1:1)

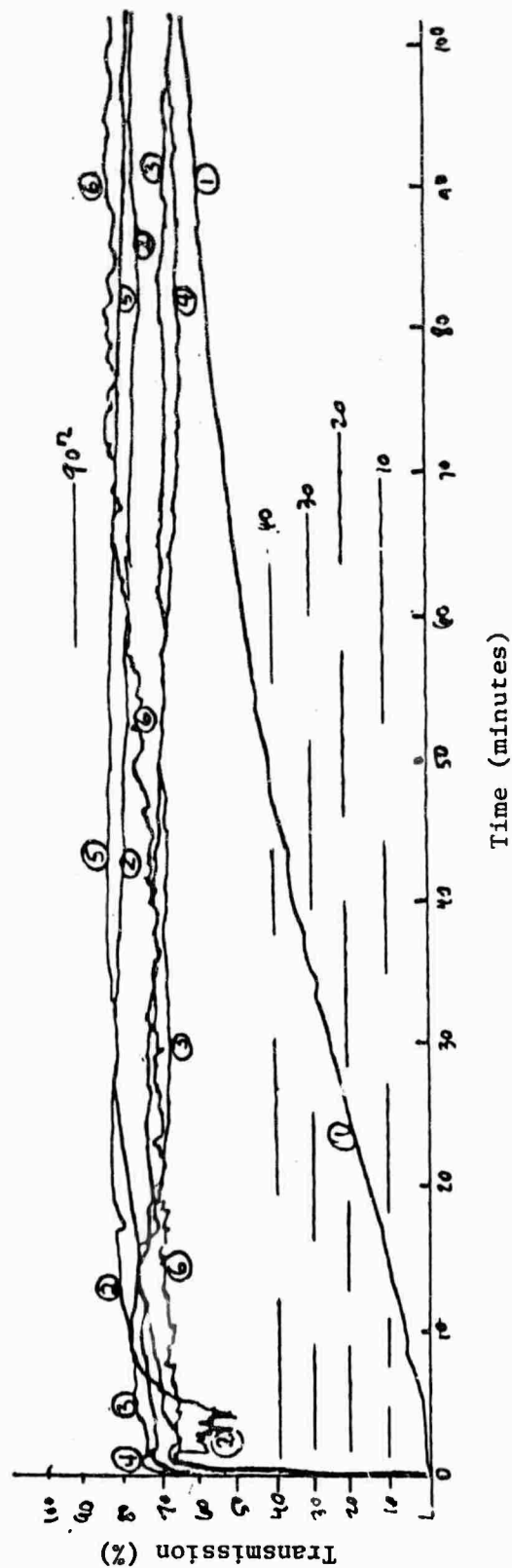


Figure 42. Sealing Curves of Neat JP-4 Compared to Emulsified Mixtures

In considering concentrations with which to work, we were guided by a number of factors already referred to. For micelle and not separate phase formation total emulsifier concentration should be below 5 percent. The economics and practicality of field application further enhanced the 3 percent (w/v) total emulsifier concentration level. In general we observed a decrease in flammability of the emulsified fuel with an increase in emulsifier concentration, with some notable exceptions. In one two-component system a 2 percent total concentration of emulsifier (1 percent of each component) resisted burning better than a 4 percent total concentrate of the same system and as well as a 4 percent concentrate of another two-component system (See Table 15). It will be remembered that DV1875 and OT70PG have the same active surfactant, dioctylsulfosuccinate.

This observation can be explained either by an increased fuel surface area, resulting from increased emulsifier, promoting combustion, or perhaps by combustion of the hydrocarbon surfactant or hydrocarbon solvent or diluent.

There frequently appeared to be a tradeoff between low mixing energy and ease of burning. Most systems which quickly formed good emulsions also burned more easily. This may be related to the presence of a solvent or diluent, such as methyl alcohol or propylene glycol, commonly included in surfactant compositions. On the other hand, this may have been the result of forming a fine microemulsion in which the fuel is more accessible. Atlox, in Table 15 showed no volume aqueous phase and yet burned easily after a half hour.

TABLE 15. VARIED EMULSION CONCENTRATION IN BLENDS.

<u>TX45</u>	<u>Sample</u> DV1875	<u>[E] final</u> [JP4:E 1:1]	<u>Vaq</u> [after 1/2 hr]	<u>Burned t after</u> (min'sec")
2%	2%	2%	7	2'
2%	1%	1.5%	17	30"
1%	2%	1.5%	15	30"
1%	1%	1%	23	20"
	<u>OT70PG</u>			
2%	2%	2%	0	0
1%	1%	1%	0	2'30"
Pyrocap	3%	1.5%	25	0
Pyrocap	6%	3%	25	0
Atlox 3404F	2%	1%	0	0

In conclusion, each system had to be evaluated empirically, with the burn test being applied to all samples of emulsified JP-4 which did not phase separate after 5 minutes. Care had to be taken, however, to use fresh JP-4 in the proofing trials. A number of blends worked very well on JP-4 which had been used throughout the summer and did not work at all on fresh JP-4. The lower boiling fractions had evidently easily distilled away during ordinary handling at summertime laboratory room temperatures.

All of our observations are summarized in Tables 16 and 17. For more interesting compounds, we have included records of combinations with many other compounds in blends which either did not "self-mix" easily or which did burn easily. This is to make most bench work available as a foundation on which to build. In collecting the results of the screening trials in this way, subsequent effort can focus on varying components or concentrations toward greater efficacy. Each set of tests narrowed our own interests in particular compounds as we tried to build an emulsion which was both "self-mixing" and nonburning.

In Table 16, the Triton X series was tested on its own with JP-4. TX-45 showed best emulsification of the fuel, which still ignited immediately. This compound was then tested in combination with many others at a 2 percent (1 percent final in 1:1 mixture with JP-4) and 1 percent (0.5 percent final in 1:1 mixture with JP-4) level for time to phase separation, upon one inversion of the 1:1 mix with JP-4, and time to ignition under direct torch test as described. We also screened 2 percent solutions of Tween 85, 80 and DV1875 in blends as these materials all tended to form emulsions with JP-4 easily.

As can be seen from Tables 16 and 17, several formulas formed good emulsions but burned easily. The compositions of these were as follows:

TX45 2%	OT70-PG 2%	Sipomide-	TX45 1%	DV1875 2%	TX45 2%	TX45 4%
	TX45 2%	1500 2%	DV1875 1%	Clindrol 210	MT80H2W 2%	
		TX45 2%	CMC .5%	CGN 2%		
			PG 1%			

Others did not form emulsions easily, but once shaken hard, resisted ignition very well. These were:

TX45 (2%)	and	TX45 (2%)
MO70 (2%)		MO84R2W (2%)

The two compounds which performed best in both emulsification and nonburning were DV1875 and MO70R. Each of these was then blended with F³P to try to enhance the resistance to burning by including a formulated fluorosurfactant ingredient. This trial is shown in Table 18 and focused attention on two formulas: in one, dioctyl sulfosuccinate (DOSS) is combined, at a 1 percent level with a formulated surfactant mixture with protein similar to F³P and denoted as FM (at 1 percent) and a highly swellable polymer like SW (at .05 percent), and in

TABLE 16. EMULSIFICATION AND BURN TESTS ON TX45 (2%)

BURN TEST I.

All emulsions at 2% w/v final and 1:1 dilution with JP-4 (inverted once) to 100 ml total volume, unless noted in parenthesis (i.e. 2% TX45 + 2% DV1875 at 1:1 with JP-4 yields 2% w/v emulsifier final.)

<u>Triton X Series</u>	<u>Tps. (min'sec")</u>	<u>Time to Burn</u>
TX 35 (HLB 7.8)	0	0
TX 45 (HLB 10.4) 2%	10'+	0
TX 100 (HLB 13.5)	0	0
TX 114 (HLB 12.4)	0	0
<u>TX 45 (2%) 1:1 (JP-4)</u>		
TX 45 (4%)	10'+	0
SDS	0	0
OT70 PG	10'+	2-4'
DV1875	10'+	5-6'
Arylene M60	10"-5'	4'30"
Witconate AOS	35"	40"
MA80	43"	10"
Clindrol 210 CGN	0	0
Siponate A246	40"	0
Siponic 218	0	0
Sipomide 1500	10'+	0
Sipomide 1500 (1%)/TX45 (1%)	0	0
WSE5 (0.5%)/TX45 (0.5%)	0	0
Renex 36	0	0
Tween 85	0	0
MM 80 (dihexyl)	1'	40"
MB 45	0	0
MT 80H2W	5'	0
MO70	0	10'+
MO70R	10'+	10'+
MO84R2W	0	2'50"

TABLE 17. EMULSIFICATION AND BURN TESTS ON TX45 (1%)

BURN TEST I.

All emulsions at 1% w/v final and 1:1 dilution with JP-4 (inverted once) to 100 ml total volume, unless noted in parenthesis (i.e. 1% TX45 + 1% DV1875 at 1:1 with JP-4 yields 1% w/v emulsifier final.)

<u>TX 45 (1%)</u> 1:1 with	<u>Tps. (min'sec")</u>	<u>Time to Burn</u>
M070 (1%)	1'	1'30"
M070R (1%)	2'	3'30"
M070R (1%) PVP(.05%)	2'	1'30"
* M070R (1%) PVP (.5%)	5'+	6'40"
M070R (1%) PG (1%)	3'	2'
* M070R (1%) PG (1%) PVP (.5%)	10'+	5'50"
DV1875 (1%)	0	40"
* DV1875 (1%) PVP (.05%) PG (1%)	10'+	10'+
* DV1875 (1%) CMC (.5%) PG (1%)	10'+	2'10"
DV1875 (1%) SW (.05%)	0	5'
DV1875 (1%) PVP (.5%)	5'	7'
* milky on inversion		
<u>Tween 85 (2%)</u>		
DV1875	5"	0
OT70PG	35"	0
<u>Tween 80</u>		
DV1875		0
DV1875 (1%) TW80 (1%)	10"	0
M 60	15"	0
Renex 36	0	0
<u>DV1875 (2%)</u> 1:1 with		
Rexol 25/9 (1%) DV (1%)	0	0
Tween 80 (1%) DV (1%)	10"	0
Tween 80	4'	0
Clindrol 210 CGN	10'+	1'
TX 45 (1%) PVP (.5%)	10'+	7'20"

TABLE 18. EMULSIFICATION AND BURN TESTS ON FM (1%) BLENDS.

<u>Sample</u>	<u>Tps</u>	<u>Time to Burn</u>
FM (1%) 1:1 with		
SW (.05%)	0	0
DV1875 (1%)	0	50"/2'
DV1875 (1%) SW (.05)	10'+	4'
DV1875 (1%) CMC (.5%)	10'+	0
DV1875 (1%) CMC (.5%) PG (1%)	10'+	2'10"
DV1875 (1%) PVP (.5%)	10'+	30"
TX45 (1%) SW (.05%)	0	0
TX45 (1%) SW (0.5%) PG (1%)	0	2'
MO70R (1%) SW (.05%)	0	10'30"
FM (1%) alone	0	0/0

the other, DOSS is combined with TX45 at a 2 percent level. The best performing dioctylsulfosuccinates were DV 1875 (from Alcolac, Ltd.) and MO70R (from Mona Chem.)

In the next and subsequent series of small-scale bench tests, we recorded the ease of emulsification upon pouring and then upon a single inversion and also the time to first appearance of a self-extinguishing blue flame (halo) and time to ignition with a self-sustaining flame for each sample. Each of these is shown as a column heading in the tables with the early and late events separated by a slash. The code for observations of emulsification was as follows: In a total of 50 ml; 25 ml JP-4 25 ml aqueous emulsifier

- + mixing very good - almost no fuel left on top.
- 0 less than 5 ml fuel left on top.
- 5-15 ml fuel left on top.
- x phase separation immediate - 25 ml fuel on top.

This approach to recording observations is first shown in Table 19, a screen of Clindrols as additives to AF³ (3 percent) to promote its JP-4 emulsification facility. In each case the "time to burn" was measured on a mixture which had been shaken vigorously.

TABLE 19. SELF MIXING AND BURN TESTS ON AF³ BLENDS WITH CLINDROLS.

	Self-Mixing <u>pouring/inversion/shaking</u>	Time to Burn (min/sec) <u>Halo/Self-Sustaining</u>
AF ³ (3%)		
Clindrol 101	x/x/+	0/30"
Clindrol 200	x/x/-	0/15"
Clindrol 206	-/0/0	0/30"
Clindrol 210	-/0/+	0/10"
Clindrol 202	-/0/0	0/10"
+ mixing very good - almost no fuel left on top. 0 less than 5 ml fuel left on top. - 5-15 ml fuel left on top. x phase separation immediate - 25 ml fuel on top.		

In the next series, each of the two commercially available dioctyl sulfosuccinates was studied in blends with JP-4 emulsifiers, water structuring compounds and FM formulated surfactant mixture. Table 20 shows the results for DV1875, and Table 21 for M070R. The numbers in parentheses are all percentages. Abbreviations can be found in Table Key Section in the table legends.

To summarize the highlights of the screening tests from Tables 16-21, TX45 was determined to best promote emulsification of JP-4 with water, after vigorous shaking. As the emulsified mixture burned as readily as fuel (Table 16), other components were sought to promote a more stable oil-in-water emulsion which would not burn. Two screens were then carried out. One at 2 percent TX45 showed the DV1875 and M070R performed best at 2 percent each in combination with 2 percent TX45. Each of these was further tested in Table 17, at a 1 percent level of TX45 and in combination with polymers to promote the structuring of water.

Tables 18 and 19 screened for emulsification in existing fluorosurfactant foaming extinguishants, and while the clindrols did not promote the efficacy of AF³ as an emulsifier (Table 19), the M070R and Sticky Water looked like possible additives to the fluorinated surfactant mixture (FM).

Each dioctyl sulfosuccinate, DV1875 and M070R, was then extensively blended with compounds to promote dispersion, reduction of interfacial tension and structuring of water, to promote a stable, easily formed nonburning emulsion of JP-4 at 1:1 with an aqueous phase. These observations are recorded in Tables 20 and 21, and the most interesting formulas from Tables 16-21 are collected in Table 22.

TABLE 20. EMULSIFICATION AND BURN TESTS ON DV1875 BLENDS.

<u>Sample</u> <u>Surfactants</u>	<u>Water Polymer</u>	<u>Emulsification</u> <u>Pour/Inversion</u>	<u>Time to Burn</u> <u>Halo/</u> <u>Self-Sustaining</u>
DV1875 (1) TX45 (1)	PVP (.5)	x/+	6'/7'
DV1875 (2) TX45 (1)	PVP (.5)	-/+	3'50"/7'20"
DV1875 (1) TX45 (1)	PVP(.2) PG(1)	-/+	10'+
DV1875 (1) TX45 (1)	CMC (.5)	0/+	0/4'40"
DV1875 (1) TX45 (1)	CMC(.5) PG(1)	+/+	0/2'10"
DV1875 (1) TX45 (1)	PAM (.5)	0/+	0/2'
DV1875 (1)	SW (.05)	+/+	0/2'
DV1875 (1) FM (1)	CMC (.5)	+/+	0/0
DV1875 (1) FM	CMC(.5) PG(1)	+/+	0/0
DV1875 (2)		0/x	0/2'
DV1875 (4)		0/+	0/2'
DV1875 (2)	SW (.1)	0/+	0/2'
DV1875 (.5) TX45 (.5)	PG (.5)	x/x	0/2'
DV1875 (.5) TX45 (.5)	AOS(.5) PG(.5)	x/x	0/0
DV1875 (1) TX45 (1)	PVP(.2)PG(1)FC100(.3)	++/+	6-10'+
DV1875 (1.5) FM (1.5)		0/+	50"/2'
DV1875 (1.5) FM (1.5)	SW (.05)	+/+	0/2'10"
DV1875 (1.5) FM (1.5)	PVP (.5)	0/+	1'/2'
DV1875 (1.5) FM (1.5)	PVP (.5) SW (.05)		
DV1875 (1) FM (1)	CMC (.5)	+/+	0/0
DV1875 (1) FM (1)	CMC(.5) PG(1)	0/+	0/2'10"

CMC = Carboxymethyl Cellulose
PG = Propylene Glycol
PAM = Polyacrylamide
FM = Fluorinated Surfactant Mixture

TABLE 21. EMULSIFICATION AND BURN TESTS ON MO70R BLENDS.

<u>Sample</u> <u>Surfactants</u>	<u>Water Polymer</u>	<u>Emulsification</u> <u>pour/inversion</u>	<u>Time to Burn</u> <u>Halo/</u> <u>Self-Sustaining</u>
MO70R (1.5) TX45(1.5)		0/+	2' / 4' 28"
MO70R (1) TX45 (1)		-/0	2' / 3' 30"
MO70R (1) TX45 (1)	PVP (.05)	-/0	1' / 1' 30"
MO70R (1) TX45 (1)	PVP (.5)	x/+	4' 30" / 6' 40"
MO70R (1) TX45 (1)	PG (1)	-/0	1' 20" / 2'
MO70R (1) TX45 (1)	PG(1) PVP(.5)	0/+	4' / 5' 50"
MO70R (1) TX45 (1)	PAM (.1)	-/+	0/15"
MO70R (1) FM (1)	PG(1.25) PVP(.25)	+/+	40" / 1' 40"
MO70R (1.5) TX45 (1.5)	FC100 (.3)	x/0	2' / 4' 30"
MO70R (1) FM (1)		+/+	3' 30" / 5' 40"
MO70R (1) FM (1)	PAM (.5)	+/+	20" / 30"
MO70R (1) FM (1)	PAM (.05)	0/+	50" / 2' 30"
MO70R (1) FM (1)	Renex 36 (1.25)	-/+	10" / 1' 50"
MO70R (1) FM (1)	SW (.05)	+/+	7' / 10' 30"
			4' 40" / 6'
			6' 20" / 8' 10"
MO70R (1.5) FM (1.5)	SW (.005)	+/+	1' 50" / 3' 30"
MO70R (1) FM (1)	SW (.005)	+/+	55" / 2' 30"
MO70R (2) TX45 (2)		-/+	10' +
MO70R (1.5)	Renex 36 (1.5)	-/+	1' 20" / 3'
MO70R (1)	SW (.05)	x/x	5' 10" / 8' 10"
MO70R (1) TX45 (1)	SW (.05)	-/+	4' / 8' +
MO70R (1) TX45 (1)	SW (.05) FC100(?)	-/+	5' 30" / 6' 30"

TABLE 22. SUMMARY OF FORMULA PERFORMANCE: EMULSION AND BURN TESTS.

	1	2	3	4	5	6	7	8	9	10	11
M070			2%								
M070R				2%	1%			1%			1
DV1875	2%					1%	2%		1%	1	
TX45	2%	2%	2%	2%	1%	1%	1%			1	
Sipomide 1500		2%									
PVP					.5	.2	.5			.2	
PG					1%	1				1	
CMC								.5			
SW								.05			.05
F ³ P								1%	1%		1
FC100										.3	
Self-mixing	+	+	0	10+	10+	10+	10+	10+	10+	10+	10
T _{burn}	6'	0	10'	10	5'50"	10	7'20"	10'30"	0	10+	5-10

Seeing the efficacy of Formula 8, we screened blends of the fluorinated surfactant mixture (FM) with emulsifier and water structuring additives and discovered that most of these were unstable over time and the "aged" samples, standing a day or two, made emulsions which ignited more easily (Table 23).

We then screened blends of emulsifier and water structuring polymers in combination with FC100, FC99 and FC135, the proprietary fluorosurfactants from 3M, "Fluorads," (Table 24). The series was designed according to the patent formulations of AF³, so that the ratio of FC 99/FC100 type surfactants should be about 2:1 and the total concentration should vary between .03 and .3 percent.

The best overall performers of this series were Numbers 21 and 2.

M070R 2%	and	DV1875 1%
SW .05		TX45 1%
FC99 .03		PVP .2%
FC100 .06		FC100 .3%
		PG 1%

These were comparable in efficacy to a formulation of M070R 1 percent, SW 0.05, FM 1 percent in both self-mixing and nonburning, and so we used this mixture for our larger-scale bench tests, along with a formulation of AF³ with dioctylsulfosuccinate (DOSS) and polyacrylamide added as a toughened foam which can drain an emulsifier.

f. Large-Scale Bench Tests

As the formulation developed, the DOSS appeared attractive for use in both extinguishment and neutralization formulations. DOSS can be used as an additive to AF³, with a water structuring polymer, to be applied during extinguishment, or it can also be blended with a fluorosurfactant mixture and a water structuring polymer as a neutralizer of non-burning (or extinguished) fuel spills. The following two formulas were therefore tested for extinguishing and burnback properties.

(I)	(II)
AF ³ 3%	Fluorad Mixture 1%
PAM 0.3%	SW .05
DOSS 1%	DOSS 1%

Extinguishment time is defined as in MIL-F-24385. Burnback time is also defined as in MIL-F-24385. This time is a measure of reignition potential of foam by a hot surface.

Securing by Fuel Neutralization is defined as the ability to prevent reignition following extinguishment. Securing ability was measured in our tests as the ability of our agent to prevent reignition by both hot surface exposure and direct flame exposure. Fuel Neutralization is affected by forming a water/fuel emulsion with water as the continuous phase.

TABLE 23. EMULSIFICATION AND BURN TESTS ON FM BLENDS.

<u>Anionic</u>	<u>Water Structure</u>	<u>Mixing on Pouring /Up & Down Once</u>	<u>Time to Burn Halo/Sustained</u>
FM (1.5%)		0/+	1'30"/3'00 (fresh)
M070R (1.5%)		0/+	20'/40' (aged)
FM (1.5%)			
M070R (1.5%)	SW (0.05%)	0/+	-/0 (aged)
		+/+	2'/4'50" (fresh)
		+/+	2'40"/5'30" (fresh)
FM (1.5%)			
M070R (1.5%)	PVP (0.5%)	0/+	-/0' (aged)
		0/+	1'20"/3'10" (fresh)
FM (1.5%)			
M070R (1.5%)	SW (0.05%)		
	PVP (0.05%)	+/+	-/0 (aged)
			40'/1'10' (fresh)
FM (1.5%)			
DV1875		0/+	20"/30" (aged)
			50"/2'00 (fresh)
DV1875			
FM	SW (0.05%)	+/+	0'/40" (old)
			0'/2'10" (fresh)
DV1875			
FM	PVP (0.5%)	0/+	0'/30" (old)
			1'00/2'00 (fresh)
DV1875			
FM	PVP (0.5%)		
	SW (0.05%)	+/+	20"/1'00 (old)
			1'50"/3'50" (fresh)
FM			
M070R (1%)	SW (0.05%)	+/+	4'/40"/6'00 (fresh)
			6'20"/8'10" (fresh)
FM			
M070R (1.5%)	SW (0.005%)	+/+	1'50"3'30" (fresh)
FM			
M070R (1%)	SW (0.005%)		5'20"/8'10"

TABLE 24. EMULSIFICATION AND BURN TESTS IN FLUORAD BLENDS.

Formula:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Compound:																							
M070R	1			1					1				1.25	1.25	1.25	2	2	2	2	2	2	2	2
DV1875		1	1			1	2	1	1	1													
T. 100												0.5											
IX45	1	1	1								2												
Renex 36											3												
FVP		.2									1		.25	.25				.25					.25
PAM						.5	.5	.4	.3	.4													
SW	.05		.05	.05	.05												.05	.05					.05
FC99			.3	.3	.3	.03	.03	.03	.03		.3	.3		.03			.03		.1	.03	.03	.03	.03
FC10	.3	.3			.06	.06	.06	.06					.06	.06	.06		.06	.06	.06	.06	.06	.06	.06
FC135													.06	.03		.1		.03	.03				
PG	1												1.25	1.25				1.25					1.25
Self-mixing-	+	+	+	+	+	0/+	0/+	0/+	0/+	+	0	+	+	+	+	+	+	+	0	0	+	0/+	0
Extng.	0	6/10	7'/9'	4'/5'	4'/5'	9/+	5/11	9/15+	7/12	9/16	5/10	6/10	2/3	3/4	2/3	2/4	4/6	4/6	6/10	3/6	4/7	1/6	6/9
Halo/	8/+																						
sustains	7/+																						

(1) Methodology of Application:

For fire extinguishment, the FN agent is applied in addition to water and AFFF (Air Force standard fire extinguishing agent) as shown schematically as Application Type 1 (Figure 43). The Fuel Neutralization (FN) agent is applied at the same time as AFFF through an aspirating foam making or non-aspirating nozzle. Extinguishment is a result of film and foam formation and spreading, similar to AFFF alone. The time to reignition should be longer than with AFFF alone.

For postfire fuel securing, or to neutralize a non-burning fuel spill, the FN agent is applied to the site as in Application Type 2 (Figure 43). Currently, the best procedure is to use a nonaspirated nozzle with application vigorously and directly upon the fuel or foam blanket surface.

An ICI cocktail soda siphon (980 ml capacity) or a hand-held extinguisher (capacity 5 gallons), each charged to 110 psi, were used to deliver approximately 390 ml/minute.

(2) Results:

Small-scale fire tests were designed and carried out. The tests were done in general accordance with the procedures outlined in MIL-F-24385. The main deviation was in the size of the test apparatus. Due to the need to run many tests and use many agent formulations, the size scale of the testing was reduced. The reduction in scale of the tests also allowed more tests to be run to establish repeatability and statistical trends. Normal data scatter as would be expected from the full-scale MIL F-24385 tests would prohibit running of the number of tests required to rate the effectiveness of the several agent mixtures being considered.

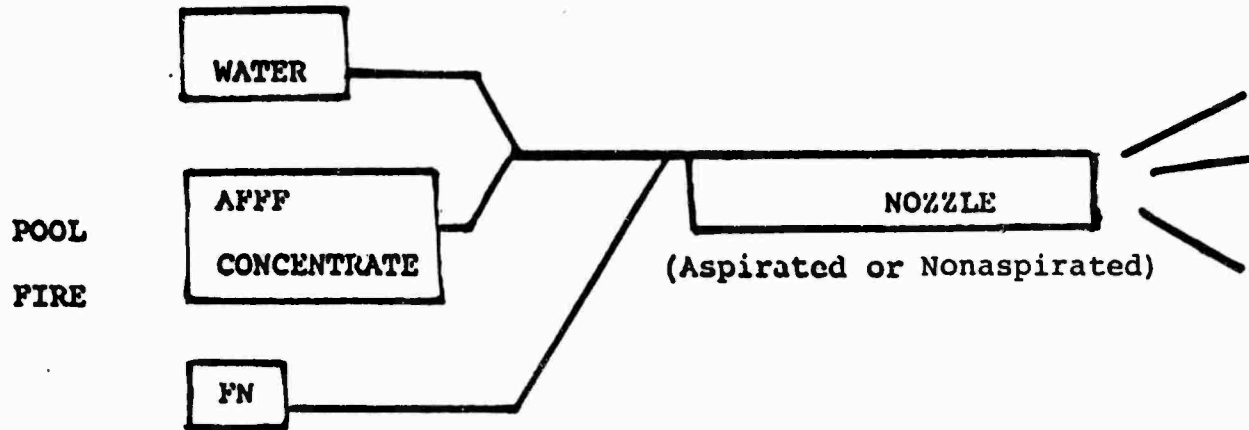
The subscale tests were conducted with round and rectangular pans of various sizes. Most testing was performed in a round pan of 16-inch diameter.

For burnback tests, the area of the reignition pan relative to the total fire area was maintained at the same ratio as in MIL-F-24385.

Specifically, the MIL-F-24385 for fuel fire extinguishment requires application of a liquid agent at a rate corresponding to 3 liters per minute per square meter. A 16 inch circular pan corresponds in area to .13 square meters. The scaled-down application rate is therefore 390 ml per minute for 90 seconds for a total of 585 ml. This closely simulates the small-scale fire tests developed to test extinguishing agents according to the United Kingdom Defense Standards 42-21, 42-22 and 42-24. The correlation between tests on a scale of 0.25 m^2 and those on a scale of 40 m^2 was established in 1978.

APPLICATION TYPE 1

FIRE EXTINGUISHMENT AND BURNBACK PROTECTION



APPLICATION TYPE 2

POST-FIRE FUEL SECURING OR FUEL SPILL NEUTRALIZING

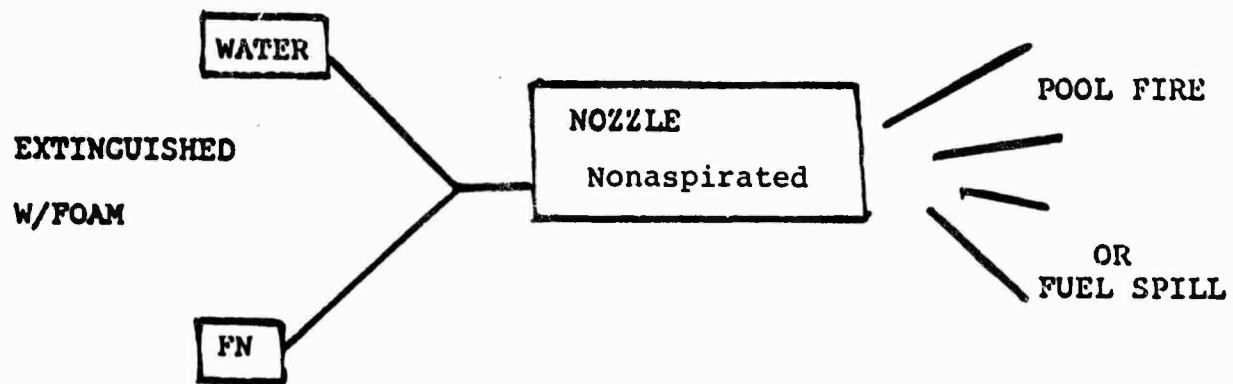


Figure 43. Application Methods of Fuel Neutralization Agent

For extinguishment and burnback tests, the variables have included:

- (a) Size and shape of the pan
- (b) Application rate of the agent
- (c) Application time (total amount of agent applied)
- (d) Initial burn time
- (e) Aspirating (foaming) and non-aspirating nozzles
- (f) Direct or indirect impact of the agent jet upon the burning fuel

For both postfire fuel securing and nonburning fuel spill securing tests, ignition sources of hot surface and direct flame impingement were investigated.

In all cases, the newly developed FN agents were compared with commercial agents AFFF and F³P agents to rate their effectiveness. The results for "Time to Start of Burnback" and "25 percent Burnback" are shown in Figures 44 and 45, respectively. The high density foams (see Tables 25 and 26) of FN-1 added to AFFF outperformed both AFFF alone and FFFP. This comparison in the same apparatus appears to be more useful than rating absolute numbers for tests conducted in other equipment. For fire extinguishment, the application of the best FN agent in conjunction with AFFF and water results in the same extinguishment time as AFFF alone (Table 25).

For hot surface burnback prevention, the film and foam formed by this combination improve the burnback suppression ability beyond that of AFFF alone. The data also compare favorably with FFFP alone (Table 25). The FN agent foam composition was Fluorad Mixture (FM) 1 percent/DOSS 1 percent and SW (.05) (II).

The times to burnback in the FN agent foam run 50 to 120 seconds longer than in the AFFF foam test. This represents a 20 to 30 percent delay before flashback reignition. The time it took for the fire to spread over the foam was only marginally less using the FN agent, 15 to 10 seconds, representing only 1 to 10 percent delay. At a practical foam thickness (.5-1.0 cm) the FN agent had efficacy comparable to FFFP. Foam in time to reignition and 25 percent burnback, while it did not exhibit the delayed knockdown time of FFFP compared to AFFF.

For postfire fuel securing, the water/fuel emulsion formed has resisted ignition by a continuously applied direct flame for nearly 10 minutes. Hot surface ignition tests, conducted in the burnback apparatus, have shown even greater protection potential.

Figures 46 and 47 show testing of levels of PAM in Formula I with respect to the concentration required to maintain phase stability (>0.8 percent w/v) and that required to enhance burnback resistance (>0.5 percent w/v).

COMPARISON OF AFFF, FFFP & FN AGENT TIME TO START OF BURNBACK

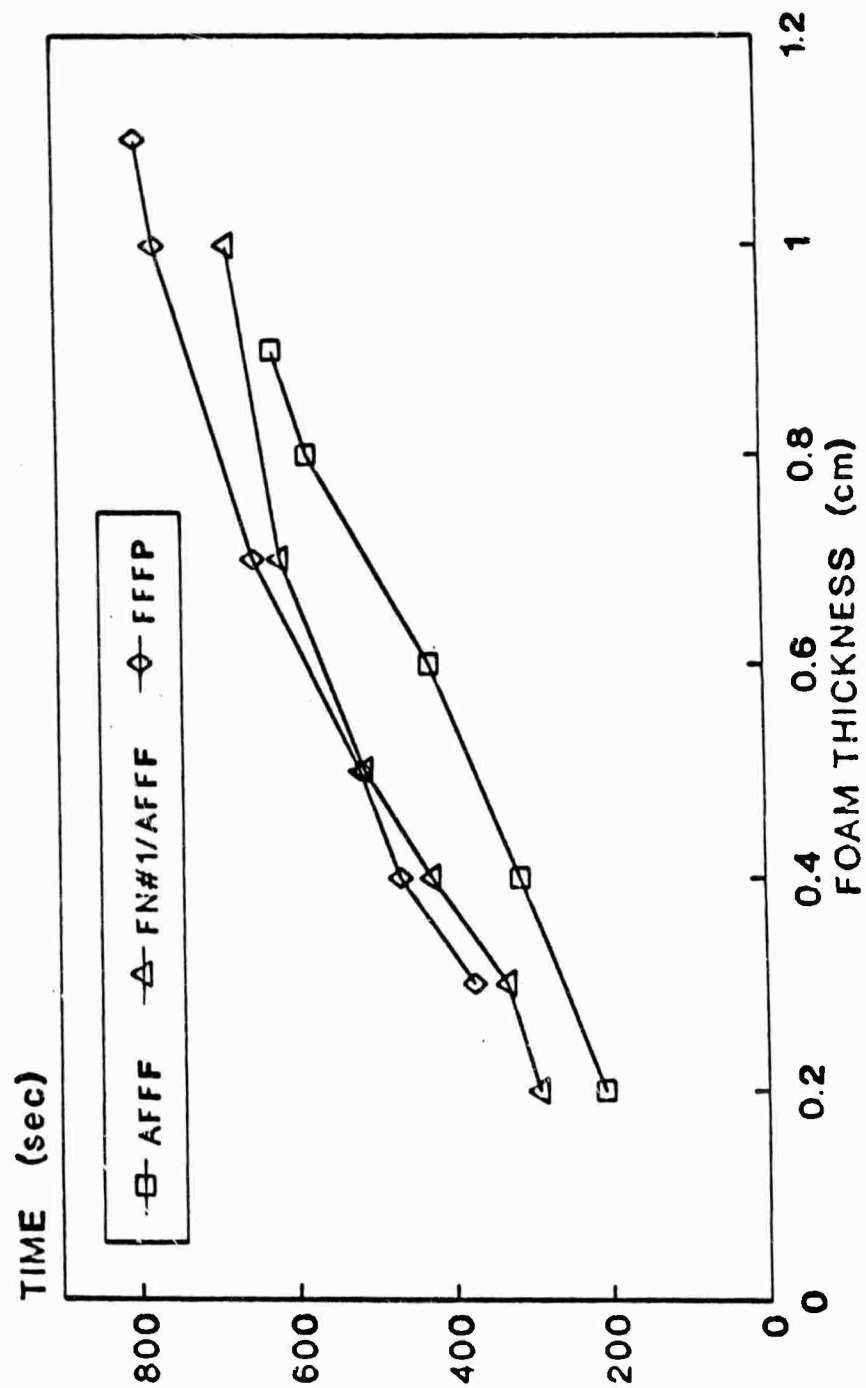


Figure 44. Time to Burnback Starts of AF3, F3P and FN1 Foams

COMPARISON OF AFFF, FFFP & FN AGENT 25% BURNBACK TIME

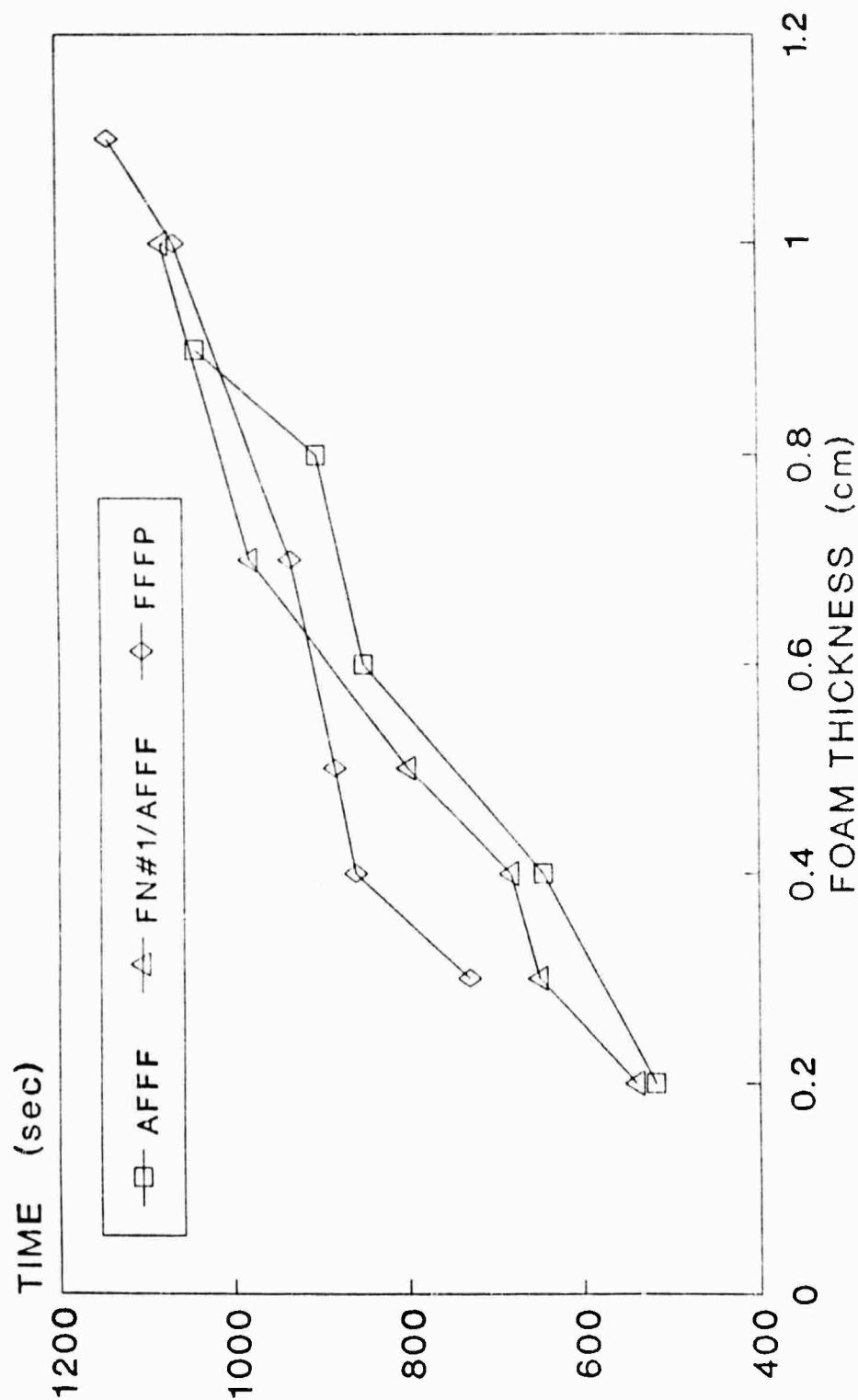


Figure 45. Time to 25% Burn of AF3, F3P and FN1 Foams

TABLE 25. RAW DATA ON BURNING TEST OF AFFF, FFFP AND FN AGENT.

Commercial
AFFF Foam

<u>Foam Thickness</u> (cm)	<u>Burnback</u> (sec)	<u>25% Burn</u> (sec)
0.2	216	525
	198	510
0.4	325	640
	300	650
0.6	427	850
0.8	580	903
0.9	632	1,050
	615	1,032

Commercial
FFFP Foam

0.3	385	738
	360	722
0.4	465	860
0.5	522	877
	510	890
0.7	652	920
	670	915
	650	930
	630	970
1.0	775	1,070
	770	1,060
1.1	870	1,230
	720	1,050

FN Agent

0.2	270	510
	310	570
0.3	330	650
0.4	410	655
	440	710
0.5	510	790
	510	810
0.7	618	990
	614	970
1.0	680	1,080

[PAM] % vs PHASE SEPARATION TIME EMULSION STABILITY

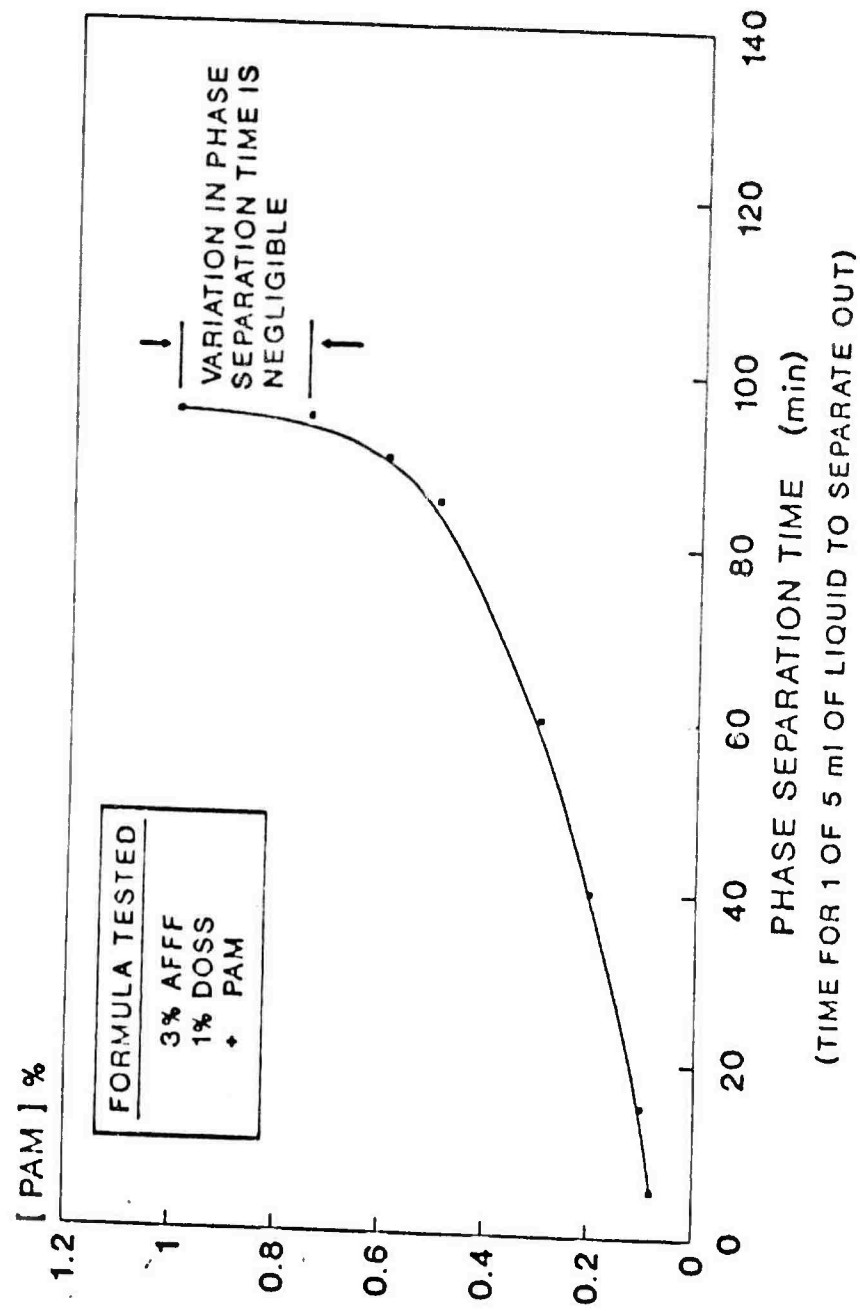


Figure 46. Emulsion Stability of FNI as a Function of PAM Concentration

PERCENT [PAM] VS IGNITION TIME

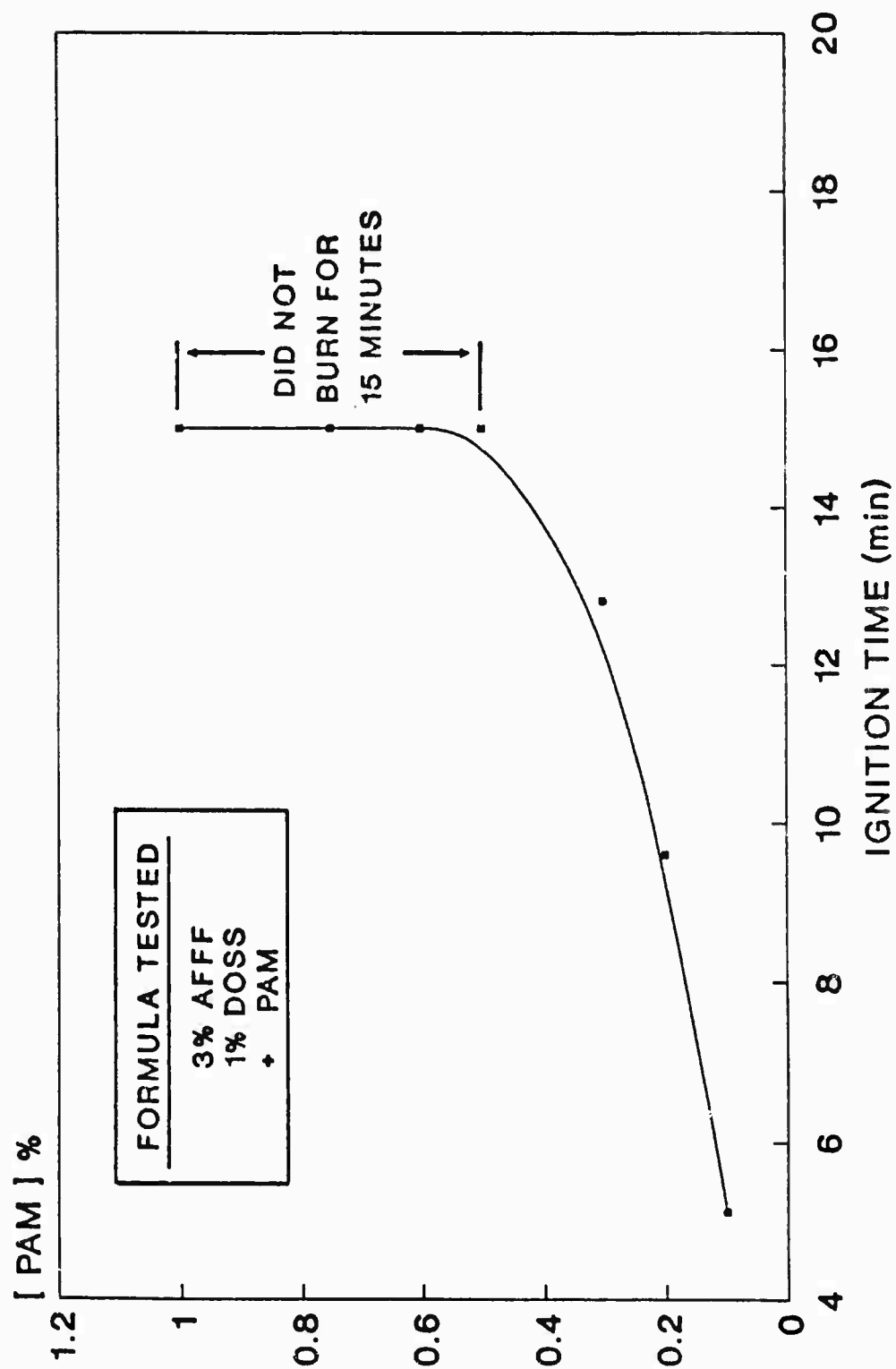


Figure 47. Burnback Resistance as a Function of PAM Concentration

(3) Foam Expansion Ratio:

A Foam Collector was constructed according to the NFPA 11A-1983 edition, Figure A-6-1.1.2, and we include a reduced copy of the blueprint in Appendix A of this report.

We also measured the expansion ratio using graduated cylinders to collect 100 ml of foam, shot in by siphon, and then measured the volume of liquid resulting after the foam broke up. Results typical of these tests and corresponding to particular burnback times observed in a series of mixtures of AF³ and FM are given in Table 26.

These burnback times were obtained by spraying the foam onto a backboard and letting it slide onto the JP-4 surface, as we were studying the effect of the water polymer on making the foam tougher and the emulsifier on draining into the fuel with water.

Throughout our tests we consistently achieved the best results by forming low-expansion (2-3) foams, dense like shaving creams.

During the laboratory development of high-performance emulsifier mixtures, AFFF and FFFP foam was used as a basis of performance comparison. The laboratory work consistently showed the AFFF agent to be a superior emulsifier to the FFFP agent.

TABLE 26. FOAM EXPANSION RATIO OF AF³/FM MIXTURES WITH ADDITIVES.

<u>Mixture</u>	<u>Pressure</u>	<u>Liquid</u>	<u>Est. Expansion Ratio</u>	<u>Burnback Test</u>
AF ³ /FM/PVP-PG/ DOSS 3% /1%/.25-1.25%/1%	60 psi	47 ml	2.13	4'20"/5'00"
AF ³ /FM/DOSS 3%/1%/ 1%	60 psi	42 ml	2.38	6'40"/7'40"
AF ³ /FM/DOSS 3%/.5%/ 1%	60 psi	40 ml	2.50	6'00"/7'50"
AF ³ /FM/DOSS/PAM 3%/1%/ 1% /.3%	110 psi	27 ml	3.70	5'20"/6'50"
AF ³ /FM/DOSS/PAM 3%/.5%/ 1% /.3%	110 psi	30 ml	3.33	5'10"/6'00"

Unpublished tests conducted at the FFFP manufacturer's laboratory and reported to Beltran, Inc., showed similar trends. In these tests, a known amount of foam was injected onto fuel. The foam was collected and frozen in liquid nitrogen at selected times after injection. Following thawing, a three-phase mixture exists: foam, fuel, and a fuel/foam emulsion. In this manner the rate of absorption of fuel into a foam is estimated. FFFP was found to be consistently less effective as an emulsifier than AFFF. The reduced fuel absorption by FFFP as compared to AFFF is reported by the manufacturer as a major factor in the improved burnback suppression times associated with FFFP. Of course, in this program which sought emulsification, these data indicated that the agent mix of AFFF was more suitable for the objectives.

Considering the variables inherent in application of the emulsifier/foam, we compared burnback times obtained in the 16-inch pan by three application methods; spraying into fuel ("sf"), spraying onto a backboard ("sb") and mixing fuel ("m") and formula with a magnetic stirrer. Both the cocktail siphon ("S") and fire extinguisher ("E") were charged at 110 psi. The results are shown in Table 27.

It is a well-known fact that fire extinguishing foams must stay on top of the fuel to be effective. Therefore, the task of formulating an effective neutralizing agent may therefore be achieved with some latitude for non-burning spills, but is immensely difficult to approach as an additive to an agent being used to extinguish flame.

g. Field Tests

A series of field tests was conducted using the "best" two formulations. These mixtures are denoted as FN#1 and FN#2, with compositions as follows:

FN-1: FC100/FC135 (2/1, 0.3% total), SW (0.5%) added to AFFF (3%), and

FN-2: FC100/FC135 (2/1, 0.3% total), SW (0.5%), DOSS (1.25%)

This first mixture was demonstrated in the laboratory to be significantly superior to AFFF at extinguishing and burnback suppression. The second mixture was found to be superior to the first at burnback suppression with no significant change in extinguishment properties. The FN-1 mixture is used in conjunction with AFFF. The FN-2 mixture is used as a stand-alone agent for the fuel spill situation.

The field tests were developed and performed by Applied Research Associates, Inc., at Tyndall AFB. The tests were divided into two series, the first series consisting of fuel neutralization tests performed on a quiescent fuel layer designed to simulate a fuel spill. The second test series was performed along the lines of Mil. Spec. 24385D, with minor

TABLE 27. EFFECT OF APPLICATION METHOD ON BURNBACK, 16-INCH DIAMETER.

Run	V _{fuel}	V _{emu}	Apparatus	Press.	Method	Results: (x/y): x = time for reignition start y = time until 25% surface is burning.)
#1	1l	FAD-1l	Siphon (S)	110 psi	Shot to fuel dir.	Very foamy. Result foam thickness is around 10 cm. Some bubbles have diameter ~1/2 in. When put burning basket into pan flame. Keep on flushing over the surface. Bubbles burned out <== (disappeared) in 1 min. ==>. Do have some "emulsion" observed. 3'10"/5'30" ==> is not very stable.
#2	1l	AD-1l	Premix	--	M	No burnback in 22 min (thickness ~ 6 cm).
#3	1l	AD-1l	S	110 psi	SB	Very foamy but not as foam as #1. Max. diameter of bubbles is ~ 1 cm. The foam did not burn after put the burn basket into pan (i.e., no flame flushed over surface). But the foam seemed not as strong as either AF ³ foam. F ³ p foam or summer formula (AF ³ /F ³ p/SW mix). 5'03"/7'20". After bubbles disappeared (broke by themselves), no emulsion can be observed (i.e., see clear liquid). When burnback starts, spreads very fast. Very hard to put out by AF ³ (AF ³ drained into the bottom).
#4	1l	FSD 1l	S	110 psi	SF	Foamy, but the dia. of bubbles considerably small (< 1 cm). Others are similar to Run #1 3'20"/5'00"
#5	1l	ISD-1l	S	110 psi	SB	Bubble dia. are about same as #4, but the foam weaker than #3 3'40"/5'10". Easier to put out by AF ³ .
#6	1l	FAD-1l AF ³ -0.2l	S & (E) exting.	S=110 psi E=100 psi	FAD = SB AF ³ = SF	First apply FAD--> foam looks similar to #3. Then shot AF ³ --> result foams like #1. Burning test = 4'00"/5'50", also very similar to #1.
#7	1l	FAD-1l AF ³ -0.2l	S & E	S=110 psi E=100 psi	AF ³ = SF FAD = SF (i.e. not "shot")	Apply AF ³ by E first then FAD. Most FAD stays on top of AF ³ (remember, AF ³ looks denser) 6'40"/8'50"
#8	1l	FAD-1l AF ³ -0.2l	S & E	S=110 psi E=100 psi	AF ³ = shot FAD = shot	FAD seems to destroy the AF ³ foam --> bring fuel vapor into bubbles --> results similar to #1 3'00"/5'20"

FAD = AF³ (3%) - PAM (0.3%) - DOSS (1%)
FSD = F³p (1%) - SW (0.5%) - DOSS (1%)
SF = Sprayed into fuel
SB = Sprayed against backboard
M = Magnetically stirred

modifications. The complete test plan is included as Appendix B. The tests were performed September 12-14, 1989.

Data from the test series are summarized in Tables 28 (Fuel Spill Neutralization) and 29 (Extinguishment and Burnback). For fuel spills, the FN-1 in conjunction with AFFF provided ignition suppression for more than 1 hour. The FN-2 Table 28 emulsion mixture provided ignition suppression for 5-10 minutes, much less than seen in the laboratory. The mixture appeared to break, liberating fuel that would freely ignite. The FN-2 was applied with vigorous mixing through a specially developed 1 gpm nozzle. The FN-2 was also applied in a more gentle rain method using the four in-place nozzles.

The results for extinguishment and burnback (Table 29) showed a significant improvement in extinguishment time for both FN mixtures in conjunction with AFFF as compared with AFFF alone. The improvement was about a factor of 2-3. In burnback, both FN mixtures did not equal the measured burnback times of AFFF alone. In a repeat of the AFFF baseline extinguishment test, the extinguishment time for neat AFFF dropped, inexplicably, to about 75 seconds.

The results achieved in the field in the 6-foot pan did not compare with those achieved in the laboratory at the 16-inch scale. The comparison is presented in Table 30. Fuel neutralization time for a nonburning spill was a factor of 10 less in the field tests than was seen in the laboratory. Post-extinguishment burnback times were decreased by a factor of 2 in the field trials as compared with the laboratory data. The reasons for this difference will be reviewed in a later section.

4. Conclusions & Recommendations

In both approaches used to cool the reaction zone, we succeeded in identifying either additives to improve the speed or durability of the AF^3 film or formulae of emulsifiers blended with fluorosurfactants which could fully intermix water with JP-4 at 1:1 volume ratios, with virtually no mixing energy. Description of these formulas is given for particular experimental observations and is summarized in a preliminary patent disclosure in Appendix D.

We recommend a series of experiments in which simple combinations are made up of each of "water thickener," at a few different concentrations, with 3 percent AF^3 . Each should be delivered as a foam (from a charged siphon) onto JP-4 in bench scale extinguishant and burnback tests. The best of those reagents should then, each on its own, be combined, at a few different concentrations, with a starch grafted copolymer (0.02-0.05 percent) and AF^3 and also delivered and tested as a foam.

TABLE 28. TEST RESULTS - NONBURNING SPILL

<u>FN#1 ÷ AFFF</u>	<u>TIME TO IGNITION</u>
TEST 1	>1 HR
TEST 2	>1 HR
TEST 3	>1 HR
<u>FN#2</u>	
TEST 1	10 MIN
TEST 2	5 MIN
TEST 3	10 MIN

TABLE 29. TEST RESULTS - FIRE SUPPRESSION AND BURNBACK

<u>AGENT</u>	<u>TIME TO EXTINGUISH</u>	<u>25% BURNBACK TIME</u>
AFFF BASELINE	127	596
FN#1 + AFFF (50/50)	40	568
FN#2 + AFFF (70/30)	70	378
AFFF->FN#2 SEQUENTIAL	67	244

NOTE: TIME IN SECONDS

TABLE 30. DATA COMPARISON - IGNITION TIMES

<u>6' TEST PAN</u>		<u>16" LABORATORY</u>
<u>NON-BURNING SPILL</u>		
	<u>Time to Ignition (min)</u>	<u>Time to Ignition (min)</u>
FN#1	>60	>60
FN#2	7-8	55
<u>FIRE SUPPRESSION & BURNBACK</u>		
	<u>Time to 25% Burnback</u>	<u>Time to 25% Burnback</u>
FN#1	596	1080
FN#2	378	>1800 (no ignition)

a. Laboratory Scale Tests

(1) Additives to AF³:

Two distinct effects, from two different chemical types of additives to AF³, were observed. One group permitted the AF³ to reseal the fuel surface after 5-10 minutes. This group included the Clindrols, Neodol-25, and Atlox 3404F. The other group caused a dramatic enhancement of initial sealing efficacy and speed. Some, such as Siponic E-10, formed films which did not last very long. However, the vapor cap did last long when water structuring agents, such as the starch copolymers, were combined with fluorosurfactants at concentration levels of 0.017 and 1 percent w/v respectively and added to AFFF.

(2) Emulsions:

As previously mentioned, two formulas were selected for use in the large-scale bench tests based on their overall performance in the small-scale experiments. Both mixtures were found to be self-mixing and nonburning. The large-scale bench tests focused on extinguishment and burnback properties.

For fire extinguishment, the application of the best FN agent in conjunction with AFFF and water results in the same extinguishment time as AFFF alone (Table 25). However, for hot surface burnback prevention, the film and foam formed by this combination improves the burnback suppression ability. The FN agent foam composition was FM 1 percent/DOSS 1 percent and SW (.05) (II). The FN agent showed a 20-30 percent delay in flashback reignition over AFFF. The time required for this fire to spread over the foam was also shown to increase marginally (1-10 percent).

b. Field Tests

The most dramatic success achieved in the field tests was the reduction of time to extinguish using FN-1 as an additive to AFFF. However, an improvement in burnback resistance was not observed.

The FN-2 forms an emulsion, cloudy pea soup, simply upon being mixed into JP-4 by pouring or directing the nozzle stream into the fuel. It did not, however, perform to delay or prevent burnback as effectively in the 6-foot field tests as in the 16-inch laboratory tests.

c. Factors Influencing Experimental Results

The reasons for the disagreement between results from the bench tests to the field tests must lie in the differences between the tests themselves, which are as follows:

- (1) Emulsion Geometry, constant vs. variable depth
- (2) Water, pH, ions concentration
- (3) Ignition by spark, not flame
- (4) Source of AF³ (Ansul field vs. 3M - lab)
- (5) Mechanical Delivery - Application Techniques

Each of these is discussed briefly below.

(1) Emulsion Geometry. The laboratory scale experiments were performed such that the fuel was at a constant depth throughout the pan. However, the apparatus of an improved design in Mil. Spec. D, to test the efficacy of the aqueous film-forming chemicals in putting and keeping out fires, has walls which contain the fuel at variable depth. To the film-forming mechanism of extinguishment and burnback prevention, the depth of fuel is not a factor, while the surface area of fuel is. To the emulsion-forming mechanism of burnback retardation, however, the depth of the fuel is a primary factor affecting efficacy.

(2) Water. Samples of the water used in Florida and in Brooklyn were sent for analysis to determine and compare pH, conductivity and hardness. Each of these properties has the potential to influence the stability of the emulsion. The analyses of the two water source are shown in Table 31 and explanatory notes.

(3) Ignition by spark vs. flame. Our tests in the laboratory were conducted with either a direct flame ignition sources or a hot surface ignition source generated by a flame. Direct flame impingement on a foam layer with a water-in-fuel emulsion underneath will always ignite the mixture if held long enough. The flame will provide a continuous supply of heat to the mixture. The foam will evaporate exposing the emulsion at the fuel surface. With continued application of heat the water in the emulsion at the fuel surface will eventually evaporate, liberating neat fuel to the flame region. There is some reason to believe that the steam will even crack the fuel into lighter fractions as in steam distillation; thereby increasing ease of ignition. In most of our laboratory work, if the emulsion was tough enough, the flame generated at the fuel surface would self-extinguish as the ignition source (burner flame) was removed from the flame region.

A spark ignition source is a more localized higher temperature source than a flame. The spark source, if placed sufficiently high relative to the fuel surface, basically provides a measure of ease of ignition of the fuel vapor and air mixture above the fuel/water emulsion layer. If too close to the fuel surface, it provides a more intense thermal source to break the emulsion. In the field test series, the spark was placed 1-2 inches above the fuel or foam surface and did not appear visually to disturb the foam or fuel surface through excessive heat transfer.

The substitution of a spark in the field tests for the flame source used in the laboratory test series was not a great contributing factor to the difference in results achieved in the two test series.

TABLE 31. ANALYSIS OF LAB VS FIELD WATER.

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RESULTS OF ANALYSIS

<u>Sample Location</u>	<u>Brooklyn, New York</u>	<u>Florida</u>
<u>Parameter</u>		
pH	6.74	7.9
Conductivity, umhos	60	350
Hardness, ppm CaCO_3	188	360

The parameters tested for were pH, conductivity and hardness. Samples for each analyte were collected at the areas designated on the "Results" form.

Measurements of pH is an important test in water chemistry, pH is a measure of the acid content of water. A value of 7 is neutral. Natural water usually have pH values in the range of 4 to 9.

The conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions and their total concentrations. This measurement will determine the degree of mineralization. The conductivity of drinking water has a range from 50 to 1500 umhos.

Hardness is defined as the sum of the calcium and magnesium concentrations and is expressed as calcium carbonate in milligrams per liter (ppm). Water hardness is a measure of scale forming salts and salts that will precipitate soap. It is also an indicator of overall mineral content.

October 16, 1989

(signed)
Laboratory Manager

dms 6095-89

(4) Source of AF³. A different commercial product was used in the laboratory from that used in the field. It is therefore recommended that laboratory tests be repeated using 3M as a control for Ansul.

(5) Mechanical Delivery - Application Technique. As previously discussed in sections of this report related to the development of the water/fuel emulsion, several different methods were used to assess the ability of candidate emulsifiers to achieve "good" emulsions. The mixing techniques ranged from a simple inversion, to shaking, to stirring with a mechanical mixer. The screening procedures then provided formulations that would have the lowest energy requirement for mixing with the fuel with tradeoffs made for the stability of the resulting mixture.

Following successful screening the most promising formulations were screened again in simulations closer to a field application situation. The mixture was applied to a fuel layer using several techniques. The techniques included:

- (a) unaspirated directly upon the fuel with a small jet nozzle.
- (b) aspirated directly upon the fuel, with expansion ratio varied
- (c) unaspirated and indirectly applied to the fuel off a backboard
- (d) aspirated and indirectly applied to the fuel off a backboard.

The mixing techniques used in the screening procedures are semi-qualitative at best. The mixing techniques used to simulate in the laboratory the field application are very scale dependent. It is very difficult to extrapolate from these screening procedures to the field environment, where the means of mixing is supplied solely by the mechanical energy. Even after jet penetration, mixing is really accomplished through flow patterns developed in the fuel and mixing/diffusion of the emulsifier mixture through the fuel.

In the 6-foot field tests, the candidate FN agents were applied directly upon the fuel. Basically two approaches were used. The first approach was vigorous application around the entire pan with an unaspirated jet that penetrated completely through the fuel layer. The second approach was a low velocity raining of the agent directly upon the fuel surface. The test results showed that there was little difference in fuel neutralizing times using each of these approaches. The mixing approaches used in the field, likely bracket the unit mixing energy of the mixing approaches simulated in the laboratory.

It must be concluded, although not with complete confidence, that the means of mixing used in the field tests did not contribute to the differences between the field and laboratory results.

d. Recommendations

We recommend that the blends identified as most effective emulsifiers and flame retardants be tested in a series of large scale bench tests which more closely simulate the field conditions in everyone of the five aspects discussed above.

We also recommend design of field tests which more closely approximate a spill. The following discussion of neutralization of spilled fuels is offered toward devising a test which more accurately permits estimation of efficacy of different formulae which neutralize by emulsifying water into the fuel.

The fire hazard presented by a ramp, runway, or post-crash fuel spill depends on several factors: 1) spill depth; 2) thermal inertial of the surface upon which the spill occurs; 3) fire point of the fuel; 4) thermal energy available to heat the fuel to the fire point; and 5) the availability of an ignition source to ignite the spill after reaching the fire point. The factors are obvious to most personnel involved in fire control. The approach of developing a fuel-in-water emulsion was to provide hazard mitigation in all the above areas.

Successful emulsification would provide benefits in all areas listed above. The important factor is achieving complete emulsification and stable emulsification. These factors are controlled by the mixing processes occurring between the emulsification agent and the fuel. More mixing energy is required to emulsify a thick fuel layer than a thin one.

It must be known how to achieve good emulsification with fuel spills reasonably expected to occur in aircraft operations and accident situations. Specifically, factors such as thickness of the spill and running velocity of the spill are important in achieving emulsification. Actually, little real analysis has been done in this area.

The existing information indicates that for unconfined fuel spills the fuel depth is approximately 0.22 mm for Number 2 fuel oil. For comparison purposes, the depth of 0.75 mm was measured for an unconfined spill of Pennzoil 30-HD. No common material similar to aircraft fuel shows a measured fuel spill depth greater than 1.0 mm.

Of course, with spills over non-level surfaces the fuel would pool to the low areas with less fuel available to spread over a large surface area. In regions of ramps and runways, it appears that emulsification can be achieved on the relatively thin fuel layers that would be expected. Partial emulsification would be achieved on thick fuel layers that might form in low spots.

C. CHEMICAL INHIBITION

As described in Section II A.3., any chemical which can inhibit the combination of carbon and/or hydrogen with oxygen will quench the oxidation of the hydrocarbon and stop the fire. The National Institute of Standards and Technology (NIST, formerly NBS) has been doing considerable research on

fire extinguishants over many years. For the purposes of discussion in connection with fuel neutralization, these fall into two categories, additives to hydrocarbon fuels and chemicals applied postcrash to non-burning fuel.

1. Fuel Additives

These are chemicals which, in small concentrations, as necessary for an additive to fuel, may modify the oxidation reaction, which is fire, to such an extent as to promote nonflammability or self-extinguishment. These are sometimes known as "superkinetic modifiers" and in some tests by the NIST have shown to be an order magnitude better flame retardants than the halon materials.

During the early stages of our planning experiments we discussed with Air Force technical advisors, a maximized effort to provide formulae compatible with existing equipment and practices. We therefore did not design apparatus or experiments to study and compare the efficacy of various potential additives to JP-4.

The following summary of those species is provided as a potentially useful background for a future study.

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

Egerton and Gates (Reference 43) showed that 2.5 g/liter of lead tetraethyl raised the spontaneous ignition temperature of benzene by 18°C, cyclohexane by 27°C, heptane by 83°C, and petrol by 82°C. Using a concentration of 2 g/liter, Weerman (Reference 44) showed that it raised the spontaneous ignition temperature of petrol by about 100°C, although Ormandy and Craven (Reference 45) had reported a decrease of 14°C in the spontaneous ignition temperature of heptane when using the same additive in similar concentrations.

Weerman (Reference 44) 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 46) 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 47) 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 ml/Imp. gal increased the limit to 5.9 psia.

Work at the Boeing Company (Reference 48) 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 49). 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 50) and of diethyl ether/oxygen (Reference 51) 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 52). Salooja (Reference 53) 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 ease with which this reaction occurs and also to differences in stability of the amino radical so produced.

2. Halogen Systems

Although many chemical compounds have good extinguishing efficiency (see Table 1), most of the best are either very toxic (the cyanides and lead-containing compounds) or not readily available.

Halogen systems, therefore, become the most widely used commercial reagents for fire prevention and extinguishment. For example, CCl_4 was used in early portable fire extinguishers. Currently, Freons such as CF_3Br are used as extinguishants, particularly in connection with fuel fires associated with aircraft mishaps, and also for the protection of electronic equipment. Phosphorus-halogen or antimony halogen (among others) are incorporated in formulations to impart flame retardance to materials.

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 polyvinylchloride, or as phosphorus chlorides or oxychlorides formed during decomposition of a polymer substrate, or as antimony halides from polymer substrates.

For this reason, although we looked into and provided background information on the halon extinguishants, we only carried out simple tests on the 1,2-dibromotetrafluoroethane "2402," with the idea of possibly using it as an additive to enhance fire retardance of successful emulsifying formulae. The physical properties of the halon extinguishants, and their nomenclature, are summarized in Table 32 (Reference 54). The halon 2402 was chosen as a potential additive by combining the fact that it is a liquid at room temperature (bpt. 117°F) and it is less poisonous than either the 1011 or 1202 (Table 33) (Reference 55). The 1301, the least toxic halon, is a gas at room temperature and therefore unsuitable for consideration as a formula component.

In a preliminary screen we combined aqueous solutions of increasing concentrations of 2402 with neat JP-4, from 4 percent up. No reduction in the ignitability characteristics of the JP-4 was observed for up to 16 percent halon by volume. This is equivalent to approximately 32 percent w/v as the specific gravity of 2402 is about 2 g/cc (Table 33).

As the presence of water, even in small quantities, is known to accelerate the degradation of some halons, another experiment was performed in which the 2402 was added directly to the JP-4. The result was the same. A self-extinguishing flame developed only at 16 percent 2402 by volume, and above.

We therefore chose to not pursue further study of the halons, even as additives to emulsifying formulae, as the quantity required seemed too great. This decision was also made in the context of increasing pressure to find substitutes for halons due to environmental considerations.

TABLE 32. NOMENCLATURE AND PHYSICAL PROPERTIES OF SELECTED HALONS.
(Reference 4)

<u>Agent</u>	<u>Formula</u>	<u>Halon*</u> <u>No.</u>	<u>Boiling</u> <u>Point</u> <u>°F</u>	<u>Melting</u> <u>Point</u> <u>°F</u>	<u>Specific</u> <u>Gravity</u> <u>of Liquid</u> <u>at 68°F</u>
Bromochloromethane	CH ₂ BrCl	1011	151	-124	1.93
Dibromodifluoromethane	CBr ₂ F ₂	1202	76	-223	2.28
1, 2-dibromotetra- fluoroethane	CBrF ₂	2402	117	-167	2.17
Bromotrifluoromethane	CBrF ₃	1301	-72	-270	1.57
Dichlorodifluoromethane	CCl ₂ F ₂	1220	-22	-252	1.31
Bromochlorodifluoro- methane	CBrClF ₂	1211	25	-257	1.83
1, 2-dichlorotetra- fluoroethane	CClF ₂	2420	39	-137	1.44

*Halon No. indicates the numbers of: carbon, fluorine, chlorine and bromine atoms in this order in the chemical formula.

TABLE 33. TOXIC PROPERTIES OF SELECTED HALONS.
(Reference 5)

<u>Halon No.</u>	<u>UL Toxicity Grouping*</u>	<u>Approximate Lethal Concentration (ppm) for 15-Minute Exposure of Rats</u>	
		<u>Natural Vapor</u>	<u>Decomposed Vapor</u>
1011	3	65,000	4,000
1202	4	54,000	1,850
2402	5	126,000	1,600
1301	6	832,000	14,000
1220	6	-	-
1211	5	324,000	7,650
2420	6	-	-

*UL toxicity groupings are based on a numbering system where 1 is highest in toxicity and 6 is lowest.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

Several approaches for "neutralizing" fuel following a fuel spill incident or following extinguishment of an aircraft fire were investigated. The approaches included separation of fuel and oxidizer, cooling of reaction zone, and chemical inhibition.

Most emphases in this study were placed on developing formulations to achieve a fuel-in-water emulsion that would reduce combustibility of the fuel. The key was developing low mixing energy emulsion formulations that would form a stable emulsion. The emulsion would have to form using solely the energy that would be available during application of the agent to the fuel spill. The investigators knew that good fuel-in-water emulsions could be achieved with high energy inputs due to their previous work in emulsified crash-safe fuels.

The benefits of emulsification in hazard reduction would be large as the entire fuel mass is neutralized. This is an improvement over the current technique of providing a foam blanket over the fuel. This blanket eventually fails through fuel absorption, breaking of the seal, and fuel running out from under the blanket.

Toward this end, an extensive set of laboratory screening measurements was performed. These measurements included mixing ability, fuel vapor sealing ability, mobility of the mixture over the fuel, extinguishability, resistance to ignition by a direct flame, and resistance to ignition by a hot surface. An optimized mixture meeting all of these tests could be expected to provide vastly improved protection in the aircraft fuel spill and crash environment. Such mixtures were developed from the laboratory screening tests. Two mixtures were tested in larger scale field simulation. The results achieved in the laboratory were not achieved in the field simulations. The scale-up in area of the fuel treated was a factor of 20. Efforts were made to scale application rates and mixing techniques during the scale-up to the larger area. The reasons for the failure in the scale-up remain unknown.

Specific results and conclusions are therefore summarized below in each category of effort.

RAPID FLOWING TOUGH FILM/FOAM

Addition of a starch grafted copolymer to a mixture of aqueous film-forming and protein-containing fluorosurfactant foams produced a film with both enhanced spread speed and durability. Small field tests of these blends are recommended (See Figure 8 and Table 4).

B. FUEL GELLING

A commercially available polymer with outstanding fuel gelling capability at concentration levels of 0.2 percent, weight/volume, was identified and tested. The speed of solubility of the polymer must be increased, however,

to make it eligible for field applications. This may be accomplished by chemically modifying the polymer either intrinsically or in a coating. It is recommended that this be proposed as an Air Force contract research task in an SBIR solicitation as a "Request For Proposal" to industry.

C. COOLING OF REACTION TONE

Studies were made of the effect of emulsifiers on the sealing characteristics of AF³ films. Forty-nine commercially available chemicals, representing nine substantively different emulsifier chemical families (see Table 5) were selected for testing from the food, cosmetic, paint and drug industries. If successful, any one of these already had acceptable handling and environmental toxicity characteristics required to position the experimental formula for application in the field. The results are summarized in Figures 19-33.

Levels of emulsifier concentration which were not damaging to the AF³ initial percent sealing were generally .05 to .5 percent (w/v). At a 1 percent level, the initial sealing by AF³ was reduced to 10-20 percent from 80-95 percent. Several emulsifiers permitted AF³ to reseal, forming a vapor cap after 5-10 minutes, during which the low-boiling-point (highly volatile) components of the JP-4 had been vaporized. Clindrol 101 CG, Corexit 9550 and Neodol 25 (Figures 24, 25 and 26) were three such species. These deserve further study as additives to AF³, in small-scale burn tests designed to detect improved burnback resistance after 5-10 minutes.

We then focused on a search for chemicals which could emulsify a maximum amount of water into the JP-4 in a minimum time and with minimum mixing energy. Water, with its great heat capacity, could cool the reaction zone if intermixed with fuel. The minimum water:fuel ratio was 1:2 to permit maximum water incorporation independent of emulsifier concentration within a range of 0.5-5.0 percent w/v. From the studies of efficacy of AF³ on emulsified fuel (Table 6), it will be remembered that AF³ efficacy is profoundly affected above 1 percent emulsifier concentration, even for those emulsifiers which permit resealing and vapor cap on the higher boiling point volatiles, i.e., after 5-10 minutes.

A benchtop burn test was designed in which a torch flame was directly applied to emulsified "pea soup" mixtures of JP-4 and water. Hundreds of combinations were screened and found to vary in ease and stability of emulsification and ignitability. Many formulations easily formed good JP-4/water emulsions but burned easily. These are summarized in Tables 16 and 17. Others did not form emulsions easily, but once shaken hard, did resist ignition by flame contact for over 10 minutes. Dioctylsulfo-succinates performed best in both emulsification and burn trials and were blended with fluorosurfactants and water structuring polymers in subsequent screens to search for a self-mixing, nonburning formulation. Two formulae were chosen as best (Table 24), and developed for larger-scale benchtests. scaled down to 16 inches from full-scale MIL-F-24385 test specifications. These revealed to us the suitability of these emulsion-forming formulae for nonburning as opposed to burning spills (Table 27). Any additive to an agent being used to extinguish flame must permit effective separation of fuel and oxidizer.

In the field tests, Fuel Neutralizing Formula 1 (FN-1) dramatically reduced the time to extinguish a burning fire, compared with AFFF alone and also prevented ignition of a nonburning spill, by periodically applied spark, for over one hour, as also observed in the 16-inch laboratory tests. FN-2, which formed a cloudy "pea soup" emulsion immediately upon mixing with JP-4, did not delay or prevent burnback as effectively in the 6-foot field tests as in the 16-inch laboratory tests (Table 30). Factors which could have caused this disparity included pan geometry, water properties, ignition source, and chemical sources were reviewed.

In exploring chemical inhibition of fire by additives to AF³, the only experiments we carried out were simple tests using the liquid Halon 2402. All other additives would have required, if successful, modification of existing delivery equipment and practices in the field. A minimum of 16 percent by volume was required to extinguish the flame of burning JP-4 in laboratory tests. This was impractical and abandoned for further development.

D. RECOMMENDATIONS

On flaming fuel extinguished by AFFF, four types of chemicals, to be used with or subsequent to AFFF, were observed to significantly improve extinguishment time or burnback prevention. FN-1, which succeeded in both aspects, in large-scale laboratory tests, should be modifiable to succeed in 6-foot and then 100-foot tests. The key discovery is that a water-structuring polymer in conjunction with a biological, polar polymer and fluorosurfactant as found in AFFF, all at correct concentration levels, can both enhance knockdown speed and seal vapors to inhibit fuel reignition.

We recommend this be used as the basis for developing an improved performance AFFF formulation. Three other approaches showed significant potential to improve AFFF performance if delivered after the flame knockdown.

In one, a category of emulsifiers, at the correct concentration levels, was observed to permit AFFF to reestablish a vapor cap on the spilled fuel. In another, a different category of emulsifiers, if delivered subsequent to extinguishment by AFFF, could instantly intermix the water into the fuel, forming a cloudy "pea soup" emulsion, which offered the most promising tactic against burnback, with minimum alteration of current field equipment and practice.

Finally, one fuel gelling additive, which also could be delivered subsequent to flame knockdown by AFFF, showed sufficient efficacy at low enough concentrations to warrant recommending a study which modifies it to increase the speed of its solubility to permit meaningful practical trials with it.

Areas of fruitful investigation remain and it is felt that these would be worthwhile as the potential safety increases are large. The major area of investigation would include modification of the formulations so that additional promising formulations could be tested at the larger field scale.

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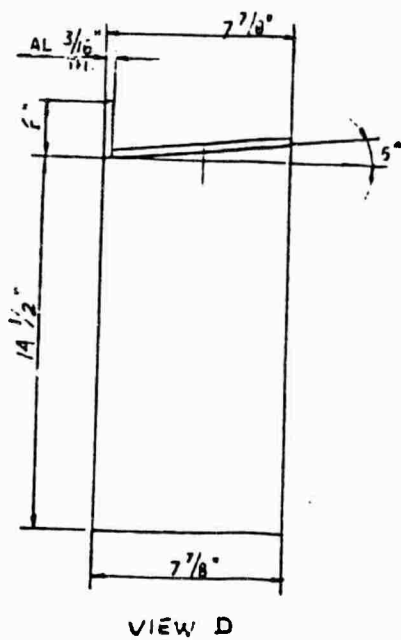
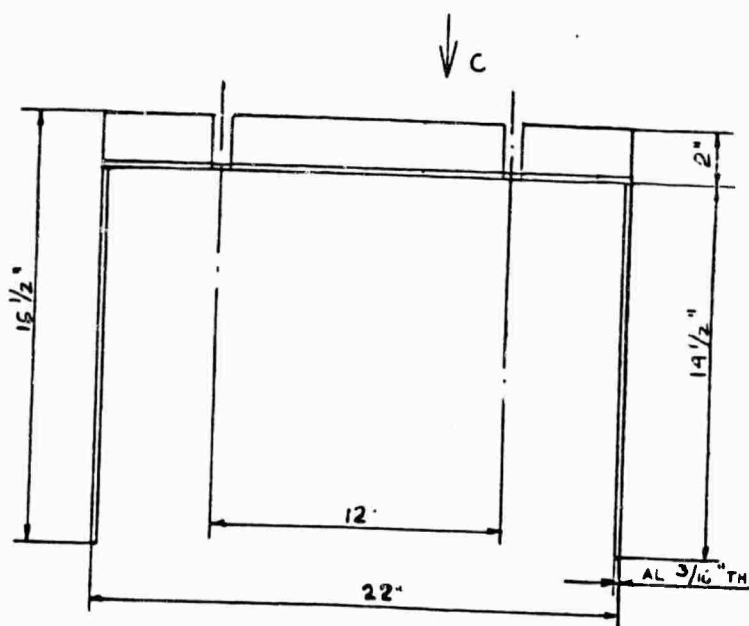
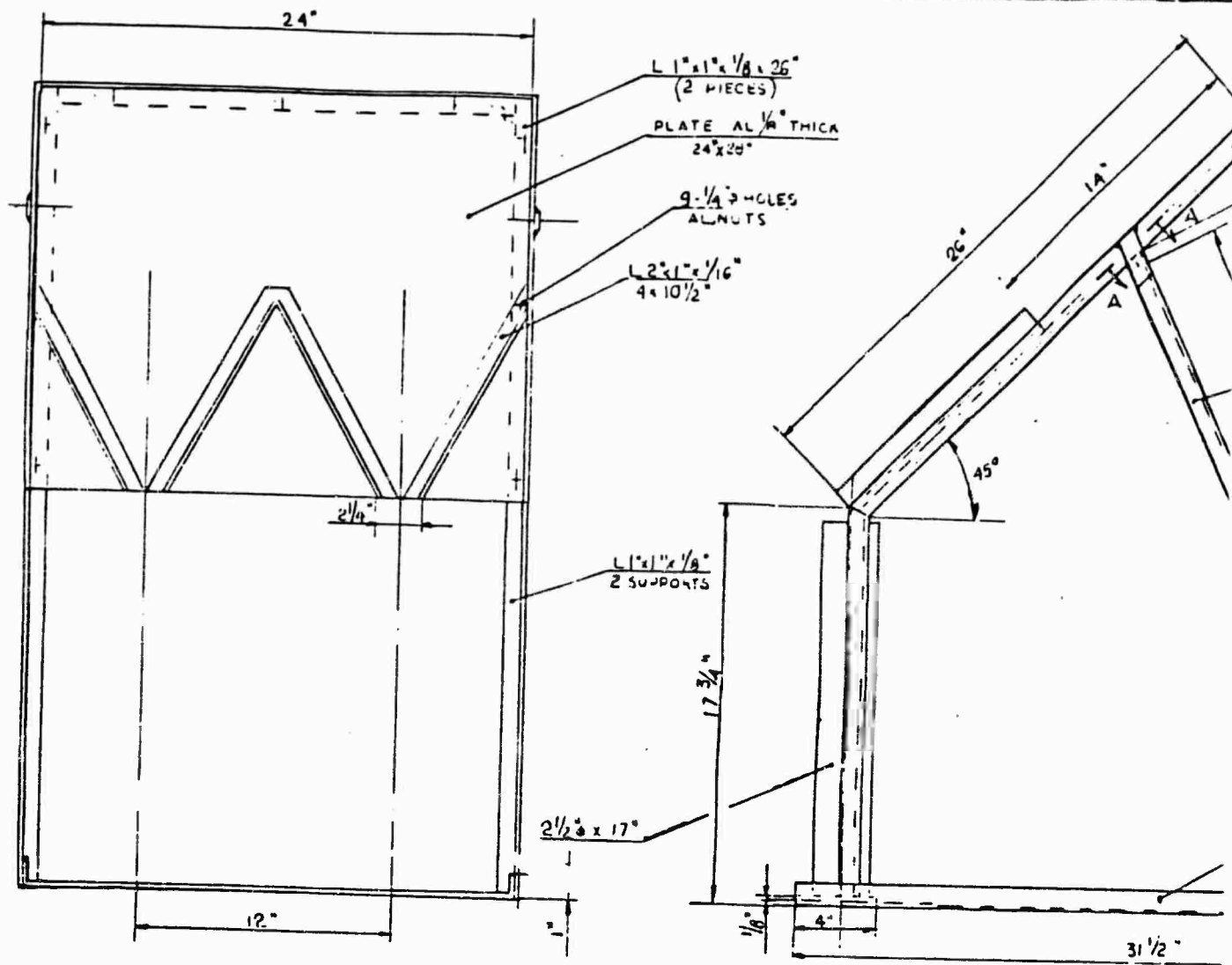
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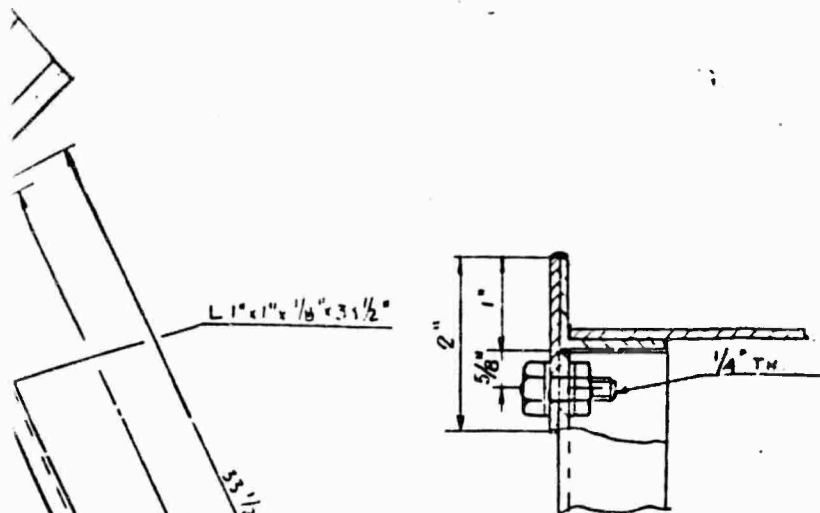
APPENDIX A

BLUEPRINT OF FOAM COLLECTOR

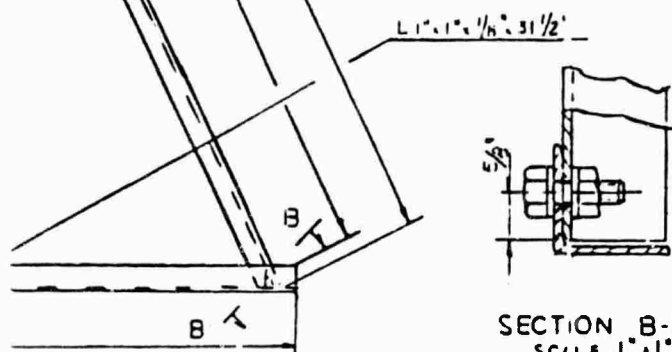
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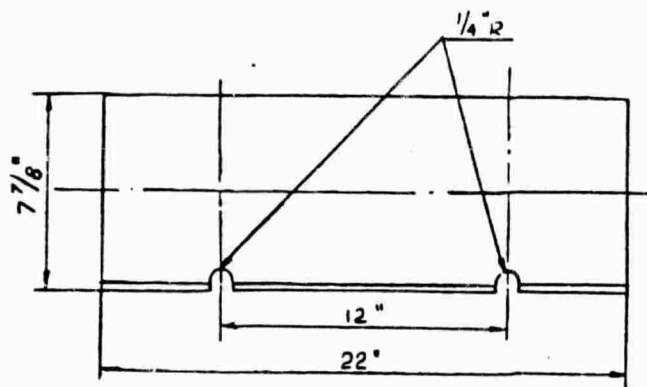
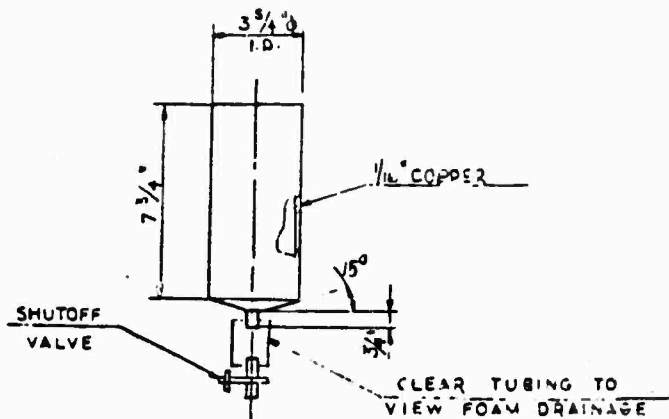
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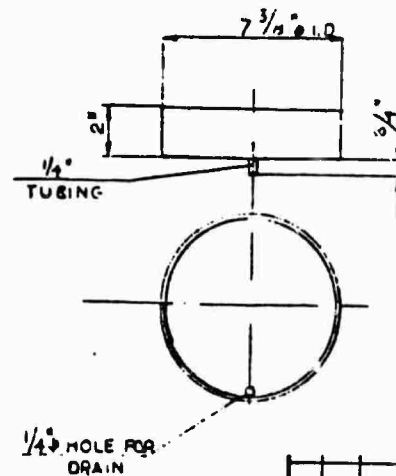
SECTION A-A
SCALE 1"=1'



SECTION B-B
SCALE 1"=1'



VIEW C



FOAM SAMPLE
CONTAINER
(2 PIECES)
(1/16' COPPER)

NOTE:

MATERIAL: ALUMINUM 1/8'
EXCEPT AS NOTED

QTY.	ITEM	PART NO.	DESCRIPTION
THIS DRAWING IS THE CONFIDENTIAL PROPERTY OF BELTRAN ASSOCIATES, INC. AND SHALL NOT BE DUPLICATED WITHOUT PERMISSION. IT IS LOANED THIS OCCASION AND IS RETURNABLE UPON DEMAND.			
FOAM SAMPLE COLLECTOR			
SCALE 1"=1/4'		UNLESS OTHERWISE SPECIFIED	
DATE 6-28-88		FRONT DEC. ANNUAL	
BELTRAN ASSOCIATES, INC.		DRAWN BY: C. H.	
		CHECKED BY: J. H.	
		DATE	
		DRAWING NUMBER	
		D-1260	

APPENDIX B
FUEL NEUTRALIZATION TEST PLAN, AFESC 8/89
SUBTASK 3.05.1

The documents contained in this appendix were published according to their own internal style, which deviates from ESL format. They have, therefore, been published without editing.

AIR FORCE ENGINEERING AND SERVICES CENTER
Tyndall Air Force Base, Florida 32403

FUEL NEUTRALIZATION

AUGUST 1989

TEST PLAN

This test plan has been reviewed and approved by:


RICHARD N. VICKERS
Test Director


ALVAH R. PARSONS
USAFADWC/SEG (GROUND SAFETY)


JOSEPH L. WALKER
Chief, Engineering Research Division

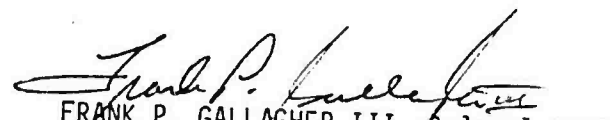

FRANK P. GALLAGHER III, Colonel USAF
Director, Engineering and Services
Laboratory

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SECTION I

INTRODUCTION

A. SCOPE

This project will Evaluate two fuel neutralization (FN) agents (hereafter referred to as FN #1 and FN #2) for their ability to neutralize spilled JP-4 fuel to prevent ignition and for their ability to extend the burnback suppression capability of Aqueous Film Forming Foam (AFFF) when used to extinguish JP-4 pool fires. Six-foot pan fires will be used for the initial evaluation with 50-foot fuel neutralization tests and 100-foot pool fires for the final demonstration.

B. BACKGROUND

Jet fuel spills on the flight line, POL storage area, or other locations have historically posed a significant threat to high-value weapon systems, equipment, and personnel. Aircraft crashes frequently produce associated fuel pool fires that are not only difficult to extinguish but are easily rekindled by contact with the hot metals of the burned aircraft. It is highly desirable to be able to rapidly neutralize the spilled or residual fuel to prevent ignition or reignition, thereby providing a safe environment for the rescue and cleanup operations and preventing further losses. Beltran, Inc. of Brooklyn, New York has been developing and testing candidate fuel neutralization agents under an SBIR contract with AFESC/RDCF. After extensive laboratory testing at their facility, two promising candidate FN agents will be tested in full-scale tests at the Air Force's Tyndall AFB, Florida Fire Test Facility.

C. AUTHORITY

HQ USAF Program Management Directive (PMD) Number 63723F (2104), dated March 1985, provides the authority for this test. This test program will be conducted as directed in the PMD and AFR 80-14.

D. PURPOSE

The purpose of this test series is to demonstrate the fuel neutralization and burnback suppression capabilities of two candidate FN agents that have been previously demonstrated in laboratory tests.

SECTION II

TEST OBJECTIVES AND TESTING MEASURES OF MERIT

A. TEST OBJECTIVES

1. Demonstrate that fuel neutralization agents will neutralize spilled JP-4 fuel and prevent ignition when exposed to open flames.
2. Demonstrate that fuel neutralization agents added to standard 3 percent AFFF and water mixtures will extend the burnback times after extinguishing JP-4 pool fires containing hot metal ignition sources.

B. MEASURES OF MERIT

1. The FN agent, when applied to a JP-4 fuel spill, should prevent ignition by direct flame application of a period of at least 1 hour.
2. The burnback suppression agent, when applied either with or directly after a 3% mixture of AFFF and water, should increase the burnback time, as compared to using only the AFFF mixture, by 100% or more. If no ignition occurs after 15 minutes, the test will be concluded and the FN will be considered as passing the test.

SECTION III
MANAGEMENT AND ORGANIZATIONAL RESPONSIBILITIES

A. MANAGEMENT

Overall test responsibility rests with the AFESC/RDCF Test Director. The Test Director will delegate authority, as necessary. Specific responsibilities for safety, instrumentation, photography, and engineering support are listed in the following paragraphs.

B. ORGANIZATIONAL RESPONSIBILITIES

1. HQ AFESC

The Air Force Engineering and Services Center is responsible for overall test management.

2. AFESC/RDCF (and SETA Contractor)

RDCF will:

- a. Develop, coordinate, and publish a test plan.
- b. Provide the test director.
- c. Prepare a test report describing the method of test and test results.

3. Beltran, Inc.

Beltran, Inc. will:

- a. Provide on-site engineering coordination throughout the test period.
- b. Provide all Fuel Neutralization agents required for the test.
- c. Provide the fuel neutralization application nozzle for the 6-foot fire suppression tests requiring separate FN application.

SECTION IV

TEST EXECUTION

A. INTRODUCTION

This test program will be conducted in two phases. Phase I will consist of the 6-foot pan fuel neutralization and fire suppression and burnback tests. Two fuel neutralization agents (FN #1 and FN #2) will be evaluated. Phase II will consist of full-scale demonstrations of the Fuel Neutralization capability in a 50-foot concrete test pit and the Fire Suppression and Burnback demonstrations in the 100-foot fire pit. Phase I testing, data reduction and analysis will be completed before the initiation of Phase II. Phase II test parameters may be modified after analysis of Phase I test data, by mutual agreement of the development contractor's on-site engineer and the AFESC Test Director.

B. PHASE I TESTS (Small-scale).

1. Fuel Neutralization Tests (6-foot pan). These small-scale tests will consist of a small simulated fuel spill in a 6-foot burn pan. One gallon (3.8 liters) of JP-4 will be placed in a level stainless steel burn pan. The fuel neutralization agent will be applied to the JP-4 at a rate of 3 liters/minute for 1.25 minutes (3.8 liters (1 gal.) Total). If the amount of fuel used in each test is modified, the ratio of fuel spilled to FN agent used will be maintained at 1:1. Ignition will be attempted by direct application of a propane torch for not more than 15 seconds per attempt at a height of one inch above the fuel level; immediately after the fuel neutralization agent application, 10 minutes later, and at 10-minute intervals up to one hour. No sustained ignition of the fuel/agent mixture shall take place. Spurious flashes of flame are not considered as sustained ignition. This test will be repeated three times for each fuel neutralization agent. This 6-foot pan test is a preliminary evaluation of the agent performance before proceeding with the larger pool spill test at the Tyndall AFB, Florida fire department facility on the north side of the main runway.

2. Fire Suppression and Burnback Tests (6-foot pan). This series will evaluate the effectiveness of the FN agents, when mixed with standard 3 percent AFFF, in suppressing burnback in JP-4 fuel fires with fuel in contact with hot metals (the edge of the pan in this test case). The burnback suppression times of the two AFFF/FN mixtures and straight AFFF/water will be compared. This series of tests will be conducted in the same manner as the 28 ft² pan fires used to certify AFFF performance in accordance with MIL-24385C. The following tests will be repeated three times to insure an adequate data sample:

<u>TEST</u>	<u>AGENT MIXTURE</u>	(each test repeated 3 times)
1	AFFF 3% mixed with water	
2	(AFFF/FN#1 50/50%) mixed at 3% with water	
3	(AFFF/FN#2 70/30%) mixed at 3% with water	
4	AFFF 3% and water, followed by FN#2 3% and water	

Test procedures are as follows: Ten gallons of JP-4 will be floated over water, sufficient to cover the bottom of the level stainless steel burn pan. The fuel will be ignited using an electrical igniter or torch and allowed to burn for 30 seconds. The fire will be attacked and extinguished using standard 3 percent AFFF and mixtures of AFFF and each of the two candidate FNs using the standard AFFF Test 2 GPM nozzle. Foam application will continue for 90 seconds. For test 4, FN#2 will be applied immediately after the completion of the AFFF 90-second application. After the AFFF/FN mixture or FN alone application is completed, the 1-foot diameter burnback pan with burning gasoline will be placed in the center of the larger pan. If the fuel in the test pan is reignited the 1 foot diameter pan is removed. The time to burnback to 25% of pan area will be measured and recorded. If no reignition occurs within 15 minutes the burnback suppression agent test will be considered passed. Detailed test procedures are contained in Annex 4, Fire Performance Tests, 28 ft². These 6-foot pan tests are a preliminary evaluation of the agent performance before proceeding with the 100 foot diameter fire test at Fire Test Pit #1, Tyndall AFB, Florida.

C. PHASE II TESTS (Large-scale).

Phase II testing will begin only after a thorough evaluation and review of Phase I data. Phase II test parameters may be modified pending the results of Phase I testing with the concurrence of the development contractor on-site engineer and the AFESC Test Director.

1. Fuel Neutralization Tests (50-foot concrete burn pit). This test series will consist of two 50 foot diameter pool fuel spills which more accurately represent an actual fuel spill on an aircraft ramp. Large-scale fuel spill neutralization testing will be conducted at the base fire department's concrete dish facility, located on the north side of the runway at Tyndall AFB, Florida. One hundred gallons of JP-4 fuel will be placed in the concrete dish. A like amount of each fuel neutralization agent will be applied to the JP-4 in separate tests. Ignition will be attempted by direct application of a long-handle torch by personnel in fire protection clothing; immediately after the fuel neutralization agent application, 10 minutes later, and at 10 minute intervals for one hour. No sustained ignition of the fuel/agent mixture shall take place. A fully serviced firefighting vehicle (P-4 or P-19) will be at the test site to rapidly extinguish the fire should one occur. This test will be completed once for each fuel neutralization agent.

2. Fire Suppression and Burnback Tests (100-foot Burn Pit). This series will evaluate the effectiveness of the FN agents, when mixed with standard 3 percent AFFF, in suppressing burnback in JP-4 fuel fires with fuel in contact with hot metals. Large pieces of steel will be placed into the pit prior to the fires to provide the hot ignition surface and simulate a burning aircraft. Two large-scale fires will be conducted, one with standard 3% AFFF and water and a second with the FN agent, selected from Phase I test results. The burnback suppression times of the selected AFFF/FN mixture and straight AFFF/water will be compared. These large-scale fire tests will be conducted at Fire Test Pit #1, Tyndall AFB, Florida. One thousand gallons of JP-4 fuel will be placed in the pit and floated over a sufficient quantity of water to cover the aggregate. The fuel will be ignited using the installed electrical ignition system and allowed to burn for 30 seconds. The fire will then be attacked and extinguished using a P-19 firefighting vehicle and standard 3

percent AFFF or a mixture of AFFF and the selected FN. At the discretion of the Test Director and the recommendation of the development contractor on-site engineer, the selected FN will be applied by a separate fire truck immediately after the fire has been extinguished by the P-19 using only AFFF and water. A P-4 with 3 percent AFFF will be readily available and manned as a backup fire-fighting vehicle. Time to extinguish the fire will be recorded. Immediately after the fire has been extinguished the 1-foot diameter burnback pan with burning gasoline will be placed in the pit. This task will be accomplished by appropriately protected fire fighting personnel only. The time to burnback to 25% of the pit area will be measured and recorded. The fire will be permitted to burn out completely to remove any residual fuel. If no reignition occurs, the burnback pan will remain in the pit for 15 minutes and the Fire Suppression and Burnback test will be considered passed. Details of large-scale fire testing and the operation of the fire test pit are contained in Annex 5, Large-scale Fire Test Pit Operational Procedures.

SECTION V

SAFETY

A. GENERAL

Safety is an integral part of the test. The test director is responsible for accident prevention. Personnel and equipment safety will take precedence over test execution at all times. Special emphasis will be placed on providing thorough supervision and guidance throughout all test phases. Pretest briefings will be conducted daily by the test director detailing the test procedures for the day and emphasizing safety in all test phases.

The AFESC Test Director will function as the safety officer and will monitor all test phases. He will suspend the test any time a safety hazard is observed. Identification of a potential safety hazard will result in test suspension until the hazard can be evaluated and corrected to the satisfaction of all responsible agencies.

B. IDENTIFIED HAZARD

A JP-4 open pit fire, by its very nature, is hazardous. The largest fire planned for this test series will be 100 feet in diameter and will burn for approximately 2 minutes. The approved test pit has been thoroughly examined for safety distance from surrounding objects and found to be well within safe distance limits. A P-19 test fire fighting vehicle and a backup P-4 fire fighting vehicle will be on hand at the test site during all large-scale fires.

C. SAFETY REPORTING

Accidents, incidents, and serious hazards will be reported in accordance with AFR 127-4 through AFESC/SEG and HQ USAFADWC/SEG. The appointed on-site safety officer is responsible for accident/incident reporting.

The Test Director will ensure that all appropriate safety procedures are followed throughout all testing. Testing will be suspended if an event occurs contrary to this checklist. During the large-scale fire testing, personnel will be located a minimum of 500 feet west of the edge of the fire pit.

Additional safety procedures are contained in Annex 3.

SECTION VI
ENVIRONMENTAL IMPACT

In accordance with AFR 19-2, Air Force Form 813 has been completed and approved. The determination has been made that this test series qualifies for a Categorical Exclusion 2y. As stated in the Form 813, it is anticipated that all evidence of visible smoke will be dispersed within two hours. Using the Air Quality Assessment Model (AQAM), initial calculations were made for the levels of particulate matter, hydrocarbons, carbon monoxide, and oxides of nitrogen for the 500 gallon fires, planned for this series. The results are contained in Table 4.

Table 4. AIR EMISSION ESTIMATES FOR LARGE HYDROCARBON FIRES

FIRE SIZE		AIR POLLUTANTS*				
GALLONS JP-4	POUNDS JP-4	POUNDS PM	POUNDS CO	POUNDS HC	POUNDS NOx	TOTAL
500	3,275	420	1,834	1,048	14	3,315

APPROXIMATE TOTAL FOR TEST SERIES

1,000	6.550	840	3.668	2,096	28	6,630
-------	-------	-----	-------	-------	----	-------

- * PM - Particulate Matter
- CO - Carbon Monoxide
- HC - Hydrocarbons
- NOx - Oxides of Nitrogen

Reference: A Generalized Air Quality Assessment Model for Air Force Operations, AFWL-TR-74-304, February 1975.

Any major fuel spills or other unplanned event that may affect the environment will immediately be reported to the AFESC and Tyndall AFB environmental offices.

ANNEX 1
TEST SCHEDULE

<u>ACTIVITY</u>	<u>DATE</u>
Conduct 6-foot pan fire demonstrations	AUG 89
Conduct 6-foot fuel spill tests	AUG 89
Conduct 50-foot fuel spill tests	AUG 89
Conduct 100-foot fire tests	AUG 89
Prepare Test Report	SEP-OCT 89

ANNEX 2

LOGISTICS SUPPORT

A. FACILITY REQUIREMENTS

The test facility for this test is the Sky X Fire Test Facility and the 100-foot Fire Test #1, located approximately 7 miles southeast of the main gate and the 50-foot concrete fire test pit located on the north side of the runway at Tyndall AFB, Florida. Phase I will be conducted at the Sky X facility with Phase II testing to be completed at the 50-foot test pit and the 100-foot test pit.

B. PERSONNEL REQUIREMENTS

Personnel to support this test will be provided by the AFESC SETA support contractor, Applied Research Associates, Inc. with engineering assistance provided by an on-site representative from the development contractor, Beltran, Inc. Following is a listing of the associated agencies and organizations and the personnel requirements of each:

<u>Agency/Organization</u>	<u>Personnel Required</u>
AFESC/RDCF (SETA contractor)	Test Director Fire Pit Operator (2 ea) Data collector (3 ea) Video Operator (2 ea)
Beltran, Inc.	Engineer

C. MATERIAL REQUIREMENTS

Material requirements are as follows:

ITEM	QUANTITY	SOURCE
JP-4	1,000 gal.	HQ AFESC/RDCF
Gasoline (MIL-G-5572)	50 gal.	HQ AFESC/RDCF
AFPP 3%	65 gal.	HQ AFESC/RDCF
Video tape	24 cassettes	AFESC/RDCF

D. EQUIPMENT REQUIREMENTS

ITEM	QUANTITY	
P-4 Fire Fighting Vehicle	1	
P-19 Fire Fighting Vehicle	1	
Portable Fire Extinguishers	4	
Protective Clothing (sets)	3	
First Aid Kit	1	
Hand Held Radios	2	
12" Burn Back Pan w/Two Handles	1	
Electric Ignition System	1	
35mm Still Frame Cameras	2	
VHS 1/2" Video Cameras	2	
Temperature Reading Devices	2	
3 gallon buckets	4	
Various Size Fire Hoses		
Stopwatches	2	
Wind Direction Sock	1	
Hydrant or Tanker if needed	1	
Test Nozzle, 2 GPM	1	
Burn Pan, 6-foot stainless steel	1	
Foam Tank	1	
Foam Stand	1	
Assorted Beakers	1	

HQ AFESC/RDCF

ANNEX 3

SAFETY

A. PURPOSE

This Safety Plan establishes the safety areas for the large- and small-scale fuel neutralization fire test program. Fire tests will be conducted at the Sky X Fire Test Facility and the 100-foot Fire Test #1, located approximately 7 miles southeast of the main gate and the 50-foot concrete fire test pit located on the north side of the runway at Tyndall AFB, Florida. This plan identifies the agency responsible for the test area. This document contains detailed Safety Rules which govern the conduct of the Test Series. The senior on site representative will act as Supervisor of Fire Test (SOFT) and will insure adherence of all safety policies. Before conducting any live fire tests at the Fire Research Facility, the Base Fire Department Communications Center will be notified. The following documents are applicable to this test:

- AFOSH 127-40 & 42, Emergency Eye Wash
- AFOSH 127-11 & 50, First Aid Kits
- AFOSH 127-31, Personal Protective Clothing and Equipment
- AFR 92-1, Paragraph 4-14, Safety Equipment for Fire Fighters
- AFR 127-4, Accident Reporting

B. OVERALL SAFETY RESPONSIBILITY

HQ AFESC/RDCF, as Test Director, is responsible for enforcing the overall safety program for the test. The Test Director or his designated representative will act as the Safety Officer during all tests and all other events at the test sites. The Test Director will maintain close coordination with the AFESC Safety Officer and the Air Defense Weapons Center Ground Safety Officer on all safety matters.

C. GENERAL SAFETY

1. Safety Briefing. The Test Director will brief all test personnel on known safety hazards in associated with this test and test site. Supervisors will, in turn, brief their personnel on these hazards.

2. Visitors. Visitors will be permitted at the test site only with the approval of the Test Director. Visitors will be instructed on applicable safety regulations.

3. Individual Safety Responsibility. Careful attention to potential hazards associated with fire testing must be stressed at all levels of responsibility. The purpose of the safety rules outlined herein is to present the most important elements in experimenting with controlled fires. These rules do not cover all the possible hazards which may occur at the site. As new problems arise, new safety measures must be established. This Safety Plan must be strictly adhered to by all personnel and enforced by all supervisors. The procedures outlined in the plan shall be accepted as minimum safe conduct. Only the Test Director, with the concurrence of the AFESC Safety Officer, may authorize a deviation from this plan.

4. Vehicles. For vehicles other than fire-fighting vehicles conducting actual fire-fighting operations, speeds shall not exceed 20 mph when driving on unpaved roads. Seat belts will be used at all times while vehicles are in motion. When a vehicle is parked, the hand brake will be set and the transmission put in park or reverse.

5. First Aid. An adequate supply of first-aid items will be maintained at the site. These items will be properly stored and periodically inspected. All personnel will be briefed upon the locations of first aid kit/supplies.

6. Hazardous Materials Precautions. All personnel will wear protective equipment, to include face shields and gloves while handling hazardous materials.

7. Accident Reporting (Emergency).

a. Scope. The purpose of this procedure is to ensure expedient handling and care of personnel injured in an accident or disaster. All post-emergency reporting and investigation of an accident will be performed in accordance with applicable Air Force Regulations.

b. Responsibility. Each person involved in this program must be familiar with the emergency reporting procedures established by this plan and immediately implement these procedures in the event of an accident. The Test director will insure that all supervisors and subordinates are familiar with this procedure.

c. Emergency Reporting Procedures. In the event of an accident at the test site, the following procedures will be followed:

(1) The SOFT will direct appropriate first aid. Caution will be exercised to prevent aggravation of an accident-related injury.

(2) Tyndall Air Force Base Hospital Ambulance Service will be notified by calling extension 911. The nature of the accident, including apparent condition of injured personnel and the location of the test site, will be reported to the medical personnel. The Test Director or, in his absence, the SOFT will decide whether to transfer the injured directly to a hospital or to request emergency ambulance support.

(3) The Test Director or, in his absence, the SOFT will determine the seriousness of the accident. If the accident is not serious enough to require emergency hospitalization or ambulance service, the injured person will be taken to a doctor or hospital by normal means of transportation.

(4) All accidents requiring emergency treatment or first aid must be reported to the Safety Officer or the Safety NCO.

D. FIRE PREVENTION, REPORTING, AND EMERGENCY PROCEDURES

This paragraph defines the responsibility for fire prevention and reporting procedures related to the test.

1. Responsibility. The Test Director will be responsible for the implementation of the procedures established by this plan. All on-site personnel must be completely familiar with these procedures to ensure proper response to an emergency.

2. Fire Prevention Procedures. The procedures listed below are to be followed in an effort to reduce chances of an uncontrolled fire. Three portable fire extinguishers will be at the test site, and all personnel participating in the fire test will be briefed on the locations and proper use of the extinguishers.

E. TEST SITE LOCATIONS

Fire tests will be conducted at the Sky X Fire Test Facility and the 100-foot Fire Test #1, located approximately 7 miles southeast of the main gate and the 50-foot concrete fire test pit located on the north side of the runway at Tyndall AFB, Florida. These tests be conducted in accordance with AFESC Office Instruction dated 7 April 1988, titled "Live Fire Demonstration/Tests."

F. NOTIFICATION

Before conducting a fire test, notify the Fire Department Communications Center at Extension 3-2884.

1. The Communications Center will be requested to notify the following:

- a. Command Post - 3-2155
- b. Air Traffic Control Tower - 3-4553
- c. Base Hospital - 3-7514
- d. Security Police - 3-2028
- e. Division of Forestry - 3-2641
- f. Base Weather - 3-2856

2. The Fire Department Communications Center will need an estimate of the duration of the live fire tests.

CHECK LIST
TO BE USED BEFORE CONDUCTING FIRE TESTS AT
FIRE RESEARCH FACILITIES NO. 1

DATE: _____ TIME: _____

VERIFIED

PROCEDURES

- Brief all personnel on proper safety procedures.
- All personnel at the test site are required for the test or are an approved visitor?
- Brief all personnel on accident and fire reporting procedures.
- Radio or telephone communications available?
- Post telephone numbers for the ambulance and fire department by the telephone or radio.
- Ensure that adequate first aid kit is available.
- Ensure that an emergency eye wash station is available.
- Ensure that all fuel valves are closed and that there are not fuel leaks prior to fuel ignition.

CHECK LIST
SUPPRESSION ACTIVITIES

DATE: _____ TIME: _____

VERIFIED

PROCEDURES

_____ Determine if adequate personnel protective equipment is being worn.

_____ Notify the Fire Department Communications Center.

_____ The Supervisor of Fire Test (SOFT) will conduct a radio check with Building 9706.

_____ Brief all personnel of the locations of fire extinguishers and first aid kits.

ANNEX 4

SMALL-SCALE (28 FT²) FIRE PERFORMANCE TESTS

A. GENERAL

The small-scale will be conducted to evaluate the performance of two different fuel neutralization agents in neutralizing a fuel spill and in increasing the burnback resistance of a recently extinguished JP-4 fuel fire with hot metal ignition surfaces. A general description of these tests follows. A one-half inch layer of water will be placed in the burn pan to protect the bottom of the pan and to ensure an even surface upon which to burn the fuel. The prescribed amount of JP-4 will be placed on the water in the burn pan. The fuel will be ignited and given a short preburn. After the preburn period, the fire shall be attacked as expeditiously as possible and the fire extinguishing. The extinguishing time will be recorded. Foam application shall continue for a total of 90 seconds. Foam is applied at a rate of 2 gallons per minute, for a total of 3 gallons for each size of pan.

Within 60 seconds of the completion of the foam application, a burning pan (1-foot in diameter) shall be placed in the center of burn pan and a timer started. When it appears that the fire has spread outside the pan so that the burning will continued after the pan removal, the pan shall be removed. The burnback time is that time at which it is estimated that 25 percent of the total area is engulfed in flames.

B. TEST PROCEDURE

1. Prepare the test fire extinguisher and foam concentrate mixture as follows:

- a. Clean the test fire extinguisher and rinse with fresh water.
- b. Place the appropriate portions of AFFF concentrate, FN agent, and water into the container. The water will be mixed at 23 degrees celsius + 5.0 degrees. Mix the solution thoroughly.
- c. Screw the fill cap on and close the discharge valve. Connect the high pressure hose from the nitrogen cylinder to the extinguisher. Make sure the regulator valve on the nitrogen tank is all the way out before opening the main valve. Slowly open valve on nitrogen tank. Slowly turn in regulator valve to 100 psi. Care should be taken not to over pressurize, or to pressurize the extinguisher too fast. The extinguisher shall be connected to the nitrogen tank throughout the test to ensure a constant 100 psi extinguisher pressure.

2. Prepare the burn pan as follows:

- a. Close drain valve on bottom of burn pan. Cover the bottom of the pan with 1/2 inch of water.
- b. After all personnel have donned protective clothing and are ready to proceed, the fuel shall be dumped into the fire pan within a 30 second period.

3. Ignited the fuel with a long-handle torch within 30 seconds of fueling and allow it to burn freely for 10 seconds. A halon 1211 extinguisher will be manned during this procedure.

4. Proceed with foam application as follows:

After the preburn period, the fire shall be attacked and extinguished as expeditiously as possible. Time from the start of foam application to the cessation of all flame will be recorded. Foam application shall continue for a total of 90 seconds. A total of 3 gallons of premix shall be applied at a rate of 2 gallons per minute.

5. Within 60 seconds (90 seconds if the dry chemical test is being accomplished) of the completion of the foam application, a burning pan (1-foot in diameter with 2-inch side) shall be placed in the center of the larger burn pan and a timer started. When the fire has spread outside the pan remove the pan. The burnback time is that time at which it is estimated that 25 percent of the total area is involved in flames.

6. After reignition all pan fires shall be allowed to burn back to 100 percent of the area. This burnback time shall be recorded. The fuel shall then be allowed to burn off completely. The water shall be drained and the pan cooled down before the next test.

C. DATA COLLECTION

Record all data on the data collection sheet contained in this annex. Video and 35mm slides will be recorded of selected fire tests. Transfer all hand-recorded data to a microcomputer for future data reduction and reporting.

PRETEST CHECKLIST
AND DATA ACQUISITION FORM
28 FT² FIRE PERFORMANCE TESTS

TEST NUMBER: _____ DATE: _____ TIME: _____

TEST LOCATION: AFESC Fire Research Facility Sky X - Tyndall AFB, FL

TEST PARTICIPANTS: 1.

2.

3.

4.

VERIFIED

PROCEDURES

Pretest Briefing
Fire Department o.k.
Test Equipment Checked
Suppression Equipment Checked
Unprotected Personnel cleared from Burn Area

AFFF mixture ratio: 3 % Concentrate 97% water

Concentrate composed of AFFF _____ % FN#1 _____ % FN#2 _____ %

Water Temperature/deg F: _____

Ignition time: _____ Foam Application - Start: _____ End: _____

Extinguishing time: _____

Place 1 ft burnback Pan time: _____ Time to Reignition: _____

1 ft Pan pan removed time: _____ Time to 25% Burnback Area: _____

Time to 100% burnback: _____ Time to burnout: _____

NOTES:

PRETEST CHECKLIST
AND DATA ACQUISITION FORM
28 FT² FUEL NEUTRALIZATION TESTS

TEST NUMBER: _____ DATE: _____ TIME: _____

TEST LOCATION: AFESC Fire Research Facility Sky X - Tyndall AFB, FL

TEST PARTICIPANTS: 1.

2.

3.

4.

VERIFIED

PROCEDURES

Pretest Briefing
Test Equipment Checked
Suppression Equipment Checked
Unprotected Personnel cleared from Burn Area

Amount of fuel (JP-4): _____

Fuel Neutralization Agent (Gallons): FN#1 _____ FN#2 _____

	IGNITION	
	YES	NO
Ignition attempts: Initial:	_____	_____
10 min:	_____	_____
20 min:	_____	_____
30 min:	_____	_____
40 min:	_____	_____
50 min:	_____	_____
60 min:	_____	_____

Comments:

POST TEST PROCEDURES:

After the fire has been extinguished, proceed with the following steps:

1. At the ELECTRICAL SERVICES SHELTER, turn "OFF" the IGNITER LOCKOUT SWITCH and ALL IGNITER TOGGLE SWITCHES.

2. Slowly "OPEN" the PIT WASHOUT DRAIN VALVE at the oil separator. TWO TURNS to begin draining the burn area.

3. Turn "ON" separator outlet pumps P6B and P6C and verify flow to the effluent holding pond.

4. Turn "ON" PIT WASHDOWN PUMP P4 and allow to run until it automatically turns off. The pump is controlled by a preset timer and will turn off after 9 minutes.

5. As the effluent flows to the separator, adjust the flow using the PIT WASHOUT DRAIN VALVE until the unburned fuel skims into the reburn skimmer barrel.

6. Allow Pumps P6B and P6C to run to the low level cutoff. The water level in the first stage of the oil/water separator should be at the bottom edge of the oil separator concrete inlet slab in the first stage when the low level cutoff occurs.

7. "RECORD" the number of gallons of fuel used from the resettable counter and the fixed counter fuel meter reading on the OPERATIONS CHECK SHEET. These readings are on the fuel meter at the JP-4 fuel storage pit.

8. Turn "ON" SEPARATOR TO STORAGE PUMP P2 and pump the unburned fuel from the skimmer drum to the storage tank at the oil separator. Turn "OFF" Pump P2 when the top of the foot valve just becomes visible. DO NOT attempt to pump all the fuel from the barrel. Further pumping will result in the loss of the prime for the P2 PUMP. To prime, see the note below.

NOTE: SHOULD THE PRIME IN THE SEPARATOR TO STORAGE PUMP P2 BE LOST, (1) TURN OFF PUMP, (2) REMOVE THE PIPE PLUG FROM THE PIPE TEE IN THE SUCTION LINE, (3) FILL PIPE WITH WATER THRU THE TEE, (4) THEN REINSTALL THE PIPE PLUG.

9. "RESET" the fuel meter counter to zero.

10. "COMPLETE" the OPERATIONS CHECK SHEET recording the fuel used and the other required operations information.

11. Replenish fuel tank for next test. See Pre-Test Instructions.

12. Drain P-19 foam tank; measure volume of concentrate remaining.

13. Measure and record water level in P-19 tank.

14. Collect and measure agent in sampling pans.

15. Proceed with preparations for the next test.

After the last test for the day, complete the following action:

FACILITY SHUTDOWN:

NOTE: COMPLETE THIS SECTION OF THE PROCEDURES WHEN ALL FIRE HAS BEEN EXTINGUISHED AND ALL FIRE TESTS HAVE BEEN TERMINATED.

1. "CLOSE" the FUEL PUMP ISOLATION VALVE between the fuel pump and fuel tank.
2. Turn "OFF" all DISCONNECT SWITCHES at the ELECTRICAL SERVICES SHELTER.
3. Turn "OFF" the MAIN DISCONNECT SWITCH at the ELECTRICAL SERVICES SHELTER.
4. Notify the fire department that testing has been completed.
5. Secure and lock the gates and facility switches as required.

LARGE-SCALE FIRE TEST
TEST CONDUCT AND DATA COLLECTION CHECKLIST

TEST NO. _____ DATE: _____ TIME: _____

P-19 FIRE-FIGHTING VEHICLE DATA:

FOAM MANUFACTURER: _____ LOT #: _____ MIXTURE RATIO: _____

FUEL NEUTRALIZATION AGENT: FN#1 _____ FN#2 _____ (gal.)

INITIAL QUANTITY: _____ gal.

TANK LEVEL - INITIAL: _____ inches FINAL: _____ inches

WATER TANK LEVEL - INITIAL: _____ inches FINAL: _____ inches

CALCULATED MIXTURE RATIO: _____ AGENT FLOW RATE: _____ gpm

APPLICATION DENSITY: _____ GAL/FT²

METEOROLOGICAL DATA:

TEMPERATURE: _____ PRESSURE: _____ WIND: _____

TEST READINESS:

_____ Weather within limits	_____ Communications check
_____ Fire trucks operational	_____ Ignition system ready
_____ Video cameras ready	_____ Fuel in pit
_____ Emer. Medical notified	_____ Access gate secured

CLEARANCE FOR IGNITION:

_____ Safety Officer	_____ Tyndall Tower
_____ Fire Department	_____ Forestry Division

IGNITION TIME: _____

FOAM APPLICATION: START: _____ END: _____

EXTINGUISHING TIME: _____ PLACED BURNBACK PAN: _____

25% BURNBACK TIME: _____ 100% BURNBACK TIME: _____

BURN OUT TIME: _____

COMMENTS:

**PRETEST CHECKLIST
AND DATA ACQUISITION FORM
50 FT FUEL NEUTRALIZATION TESTS**

TEST NUMBER: _____ DATE: _____ TIME: _____

TEST LOCATION: 50-FOOT BURN PIT - Tyndall AFB, FL

TEST PARTICIPANTS: 1.

2.

3.

4.

VERIFIED

PROCEDURES

Pretest Briefing
Test Equipment Checked
Suppression Equipment Checked
Unprotected Personnel cleared from Burn Area
Safety Firefighting vehicle in place

Amount of fuel (JP-4): _____

Fuel Neutralization Agent (Gallons): FN#1 _____ FN#2 _____

IGNITION

YES

NO

Ignition attempts:	Initial:	_____	_____
	10 min:	_____	_____
	20 min:	_____	_____
	30 min:	_____	_____
	40 min:	_____	_____
	50 min:	_____	_____
	60 min:	_____	_____

Comments:

APPENDIX C

SPECIFICATIONS 3m NOZZLE: 1 GALLON/MINUTE

APPENDIX C

Specifications 3M Nozzle (1 gal/min)

BILL OF MATERIAL		
ITEM	DWG. NO.	PART NAME
1	12-1442-5091-2	BODY
2	12-1442-5092-0	JET ADAPTER
3	12-1442-5093-8	RECEIVER
4	12-1442-5094-6	AIR INLET
5	12-1442-5095-3	DISPERSAL CONE
6	12-1442-5096-1	ADAPTER
7	12-1442-5098-7	REDUCER
8	COMM. PART	NIPPLE
9	12-1442-5097-9	JET WRENCH

USED ON

M/F No.	311					
© 3M COPYRIGHT 1984 This document is the copyrighted property of the 3M Company and may not be reproduced without 3M written permission or used for other than 3M authorized purposes.						
TOLERANCE AND SURFACE ROUGHNESS UNLESS NOTED						
OPERATION	PLACES IN DIMENSION					
	0	00	.000			
MACHINING	±.1	±.02	±.005	✓		
CUT-OFF (SAW, BUHN, SHEAR)	±.1	±.04	///			
	±	±	±			
WELDING	±.1	±.08	DR.	G. HARVIEUX		
ANGULAR DIM.	±	CH.				
SCALE	1/1	APP.				

A DEC 09, 84

ISSUE

ISSUE DATE AND CHANGE RECORD

REV

CH

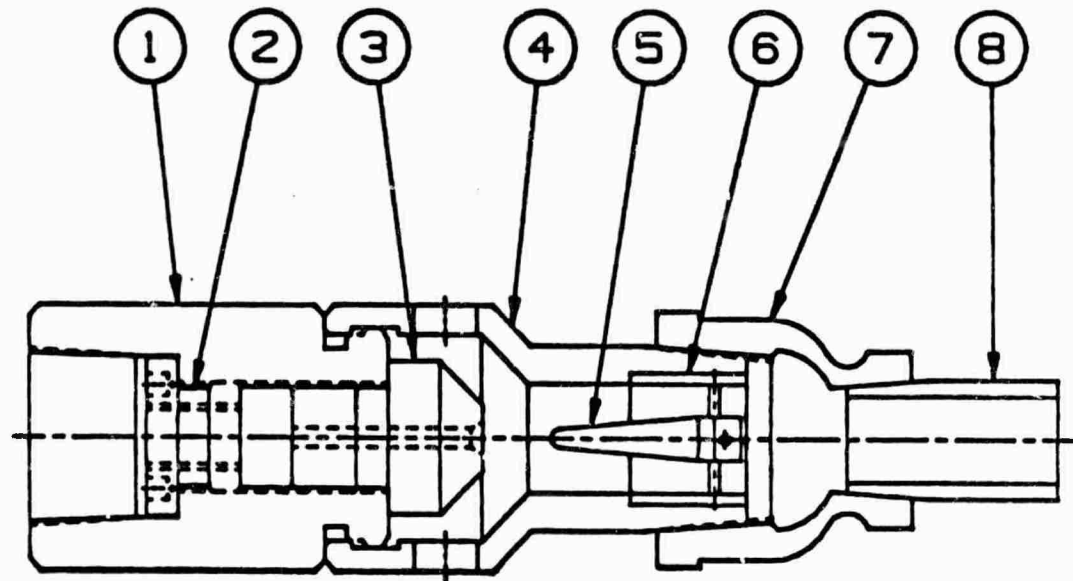
TITLE

ASSY. - NOZZLE

B

PART NO.

12-1442-5090-4



NOTE:

1) ITEM 9, JET WRENCH, NOT SHOWN.

APPENDIX D

INVENTION DESCRIPTION: FUEL NEUTRALIZATION

INVENTION DESCRIPTION

FUEL NEUTRALIZER

An invention of chemical formulations to prevent or delay the ignition or reignition of hydrocarbon fuels spilled in a crash or other accident. Some formulae, Type I, can be applied simultaneously with AFFF foam, being used to knockdown flames from a burning spill and other formulae, Type II, can be used on their own, to prevent ignition or delay/prevent reignition of a non-burning fuel spill. The concentration ranges (all in w/v percent) and species are similar in both formulae types, with combinations differing. Ingredients include:

1. 1.0-4.0% Emulsifier with non polar terminus, composed of 1-3 alkyl chains of average lengths to match average alkyl chain lengths of the predominating species in the hydrocarbon fuel being neutralized. The polar terminus should be anionic in an oxyl group such as a sulfate or a phenol, stabilized as a salt or ester. One alone or two species may be used in combined concentration to not exceed 4%.
2. 0.02-0.1% amphoteric fluoroalkyl
3. 0.1-0.5% pasteurized denatured protein, eg. collagen or synthetic gel-promoting polymer eg., polyvinyl pyrrolidone (PVP), polyacrylamide (PAM) or carboxymethylcellulose (CMC).
4. 0.015-0.05% starch polyacrylonitrile graft copolymer

Examples of Formula I include:

- | | | |
|----|--------|----|
| A. | 0.06% | #2 |
| | 0.3% | #3 |
| | 0.027% | #4 |
| B. | 0.03% | #2 |
| | 0.03% | #2 |
| | 0.3% | #3 |
| | 0.02% | #4 |

Examples of Formula II include:

- | | | |
|----|-------|----|
| A. | 1.50% | #1 |
| | 1.50% | #1 |
| | 0.06% | #2 |
| | 0.2% | #3 |
| | 0.05% | #4 |

B.	3%	#1
	0.03%	#2
	0.03%	#2
	0.3%	#3
	0.5%	#3

Summary:

Invention; Chemical formulae to promote instant intermixing of water into a hydrocarbon fuel spill to prevent or reduce the ignition or "burnback" reignition. Formulae combine an emulsifier (1.-4% w/v) with amphoteric fluoroalkyl (0.02-0.1%) and gel promoting polymers of protein, PVP, PAM or CMC (0.1-0.5%) and starch copolymers (0.015-0.05%). The emulsifier is omitted if application is simultaneous with Aqueous Film Forming Foam (AFFF).