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16. Abstract

Information was obtained by conducting laboratory experiments and large-scale fire tests which were of value in estimating the fire extinguishing effectiveness of eight Aqueous-Film-Forming-Foams (AFFF), 11 fluoroprotein foams (FPF), and three protein foam (PF) agents.

Large-scale fire tests were performed under fixed fire conditions employing air-aspirating and non-air-aspirating nozzles on 82.4-, 101-, and 143-foot diameter Jet A fuel fires. Experiments were performed with only one foam agent which was considered representative of each class.

Experiments tend to validate the continuation of allowing a 30-percent reduction in the water requirement at certificated U.S. airports when AFFF is substituted for protein foam (Federal Aviation Regulation (FAR) Part 139.49) and to maintain a 1:1 equivalency ratio when fluoroprotein foam is substituted for protein foam. The data also tend to substantiate the validity of allowing an equivalent reduction in water requirements at airports when the 3-percent AFFF, FPF, and PF agents are substituted for the 6-percent agents within each class.

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INTRODUCTION

PURPOSE.

The project objective was to study and test all currently available firefighting foam agents and to rank these agents in accordance with the method developed at the National Aviation Facilities Experimental Center (NAFEC) (appendix A) according to their potential value where applicable in the control and extinguishment of aircraft fuel ground fires.

BACKGROUND.

The development of larger commercial aircraft and the enormous increase in general aviation aircraft activities has emphasized the need for the most effective firefighting capabilities at certificated and general aviation airports. This goal can be achieved both efficiently and economically by employing the most effective firefighting agents and equipment combinations.

The principal fire extinguishing agents employed in aircraft fire protection are aqueous foams. The development and effective utilization of these agents involve many of the fundamental principles of chemistry and the surface and interfacial tension of liquid systems. As a consequence of the recent rapid advance made in firefighting technology, a periodic assessment of the impact of these new developments on aircraft fire protection is indicated.

DISCUSSION

COMPOSITION AND TYPES OF FIREFIGHTING FOAM AGENTS

PROTEIN FOAM AGENTS. There are two protein foam (PF) agents in general use in the United States, based primarily upon the differences in their use concentration. The 6-percent type and 3-percent type are recommended for proportioning with water to produce 6-percent and 3-percent solutions by volume.

The 6-percent agent is used by the Federal Government and procured under Federal Specification 0-F-555C (reference 1). At present there is no Federal or military specification for procuring the 3-percent agent. However, it is recognized by the National Fire Protection Association (NFPA) and listed for commercial use by the Underwriters' Laboratories, Inc. (reference 2). Most of the 3-percent PF foam liquid is consumed by industry in the protection of hydrocarbon fuel storage tanks and related applications.

The definitive 3-percent and 6-percent PF liquid concentrates employed in the United States (U.S.) are not in common use on a world-wide basis.

AQUEOUS-FILM-FORMING FOAM. The recorded firefighting accomplishments of PF agents are long and impressive. However, the chemical advances in fluorine technology made significant improvements in mechanical foam technology a reality. It had long been the goal of foam research chemists to develop new and improved products which would materially reduce the fire control and extinguishing times for complex class B fires.

This goal was finally achieved at the Naval Research Laboratory under the direction of Dr. R. L. Tuve. A very significant technical document appeared in March 1964, entitled " A New Vapor Securing Agent for Flammable Liquid Fire Extinguishment" authored by Tuve, Peterson, Jablonski, and Neil (reference 3). This document provided detailed information on the chemical and physical properties of a new class of mechanical firefighting foams based on proprietary products developed by the 3M Company.

The fluorochemicals provided by the 3M Company during these early efforts were derivatives of perfluorooctanoic acid produced by an electrolytic process in the Simons cell (reference 4). An important paper authored by R. A. Guenthner and M. L. Vietor entitled "Surface Active Materials from Perfluorocarboxylic and Perfluorosulfonic Acids" appeared in 1962 (reference 5).

The aqueous-film-forming foam (AFFF) agents are currently available in both the 3-percent and 6-percent concentrations. The 6-percent type is procured by the Federal Government under a military specification, MIL-F-24385, Navy (reference 6).

The original composition of the AFFF firefighting foam liquid concentrates developed by the Naval Research Laboratory (NRL) comprised a combination of one or more highly fluorinated surface-active agents in combination with foam stabilizers and pour point depressants or other additives (reference 7). In an effort to reduce the cost as well as to improve the fire extinguishing characteristics of AFFF agents certain modifications to this basic composition were developed by Arthur F. Ratzer in a paper presented at a technical meeting of concerned government agencies and manufacturers convened on Campabello Island, N. B. during August 11 through 13th, 1964, under the aegis of The Mearl Corporation. This new composition comprised a combination of hydrocarbon foaming agents and highly fluorinated surfactants which could be readily formulated to meet the optimum surface and interfacial tension requirements of the aqueous film to achieve the most rapid spread rate and stability on a liquid hydrocarbon surface. Previous studies conducted by Bernette and Zisman (reference 8) at the NRL demonstrated the synergistic surface tension-reducing effects produced upon water from mixtures of fluorinated alcohols with conventional hydrocarbon surfactants. These fundamental principles were subsequently incorporated in a U.S. Patent (reference 9) which discloses a fire extinguishing composition comprising a fluoroaliphatic surfactant and a fluorine-free surfactant. Presently, firefighting foam liquid concentrates incorporating these basic concepts are being produced on a world-wide basis.

FLUOROPROTEIN FOAMS. A logical offspring of the development of AFFF was a combination of PF and the fluorocarbon surface-active agents.

This combination is called "fluoroprotein" foam (FPF), and the variable physical properties which can be achieved by different proportions of a protein hydrolyzate and fluorinated surfactants are indicated in figure 1.

In this diagram, the FPF agents are indicated as lying in a variable position between PF on the left and AFFF on the right. If a small quantity of a suitable fluorocarbon is added to protein foam, the resulting product may produce foam with excellent stability toward Purple-K powder (PKP) without the formation of an aqueous film on the surface of the hydrocarbon fuel. However, when increased quantities of suitable fluorocarbon surfactants are added to a protein hydrolyzate, the surface tension of the solution draining from the foam decreases until it reaches a point where it may spread across the surface of a liquid hydrocarbon. Under these conditions the generic term "fluoroprotein" foam would still apply, but the physical characteristics of the foam would approach and perhaps equal those of a true AFFF.

The FPF liquid concentrates were developed by the Naval Applied Science Laboratory (NASL) and industry specifically to achieve an acceptable degree of compatibility between PF and Purple-K powder from candidate formulations submitted principally by the National Foam System, Inc. This effort therefore recognized the basic incompatibility between the current 6-percent PF and Purple-K powder.

As a result of this work, a protein-type agent was developed which demonstrated a greatly improved compatibility with Purple-K powder. The FPF agents demonstrate complete conformance with the requirements of the Federal specification for PF, and in addition may display a high order of compatibility with Purple-K powder when evaluated in accordance with tests developed by the NASL (reference 10).

From the standpoint of chemical composition, the only difference between the FPF agents and those approved under the Federal Specification is the presence of a relatively small quantity, generally less than 1 percent by weight, of a perfluoronated surfactant.

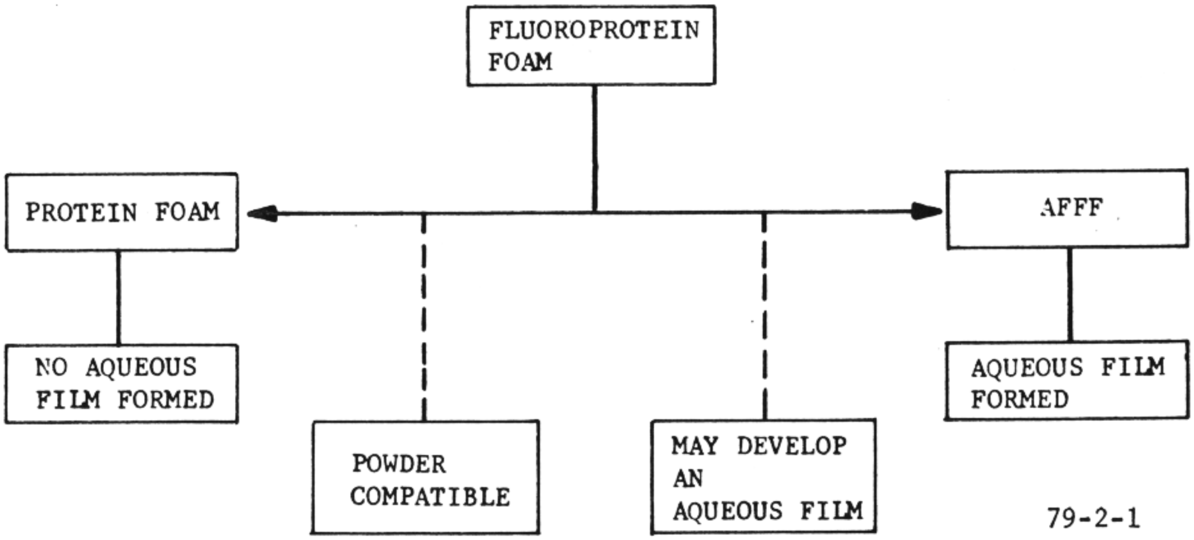

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FIGURE 1. RELATIONSHIP OF FLUOROPROTEIN FOAM WITH PROTEIN FOAM AND AQUEOUS-FILM-FORMING FOAM (AFFF)

These fluorocarbons convey powder compatibility to PF through a physical rather than a chemical property. The fluorocarbon molecule is functionally double ended; that is, one end is hydrophilic, or water loving, and the other is hydrophobic and/or oleophobic; that is, water and oil hating.

The manner in which the fluorocarbon protects the protein foam from destruction by powder may be visualized by considering the way in which a drop of hydrocarbon fuel, such as JP-4 or gasoline, spontaneously spreads when placed on the surface of water. This same spreading phenomenon may be considered to occur when an aqueous protein-base foam is placed on the surface of a hydrocarbon fuel. That is, a very thin film of fuel, probably monomolecular in thickness, "climbs" or spreads up and across the foam surface. This hydrocarbon film in itself is not destructive to the foam. However, when Purple-K powder is present in the system, a synergistic foam-destructive mechanism is established between the powder and the fuel which causes a very rapid and progressive destruction of the foam body. When a fluorocarbon is present in the foamed solution, the surface tension of the aqueous phase is lowered from approximately 45 dynes/centimeter (cm) to approximately 34 dynes/cm in some formulations, and the fluorocarbon molecules are oriented in the foam wall in such a way that the fluorocarbon end is extended outward and forms an oleophobic or oil-repelling barrier at the interface between the foam and fuel. This interpretation of the phenomenon implies that the hydrocarbon film is no longer able to spread over the surface; therefore, the fuel parameter is excluded from the foam-destructive mechanism involving Purple-K, fuel, and foam. This system is dynamic, however, and only a few seconds are required to establish the optimum foam-fuel interfacial equilibrium condition.

LABORATORY EVALUATION OF FOAM AGENTS.

PHYSICAL PROPERTIES OF AQUEOUS FLUOROCARBON FILMS PRODUCED BY THE AFFF AGENTS.

The firefighting effectiveness of the foam produced by the perfluoronated surfactants is greatly enhanced by the aqueous fluorocarbon film which floats on the surface of hydrocarbon fuels as it drains from the foam blanket.

The mechanism whereby the fluorocarbon surfactants function as effective vapor securing agents is based upon their outstanding effect in reducing the surface tension of water and of their controllable oleophobic and hydrophilic properties. These properties provide a means for controlling the physical properties of water enabling it to float and spread across the surface of a hydrocarbon fuel even though it is more dense than the substrate. This unique property led to the term "light water" which appeared in several of the early military specifications defining the properties of this class of agents.

According to classical theory (reference 11) concerning the spreading of insoluble films on liquid surfaces, the following equation maintains:

$$SC = \gamma o - (\gamma w + \gamma i),$$

where: SC = spreading coefficient of the aqueous fluorocarbon solution,

γo = surface tension of the fuel,

γw = surface tension of the aqueous film, and

γi = interfacial tension between fuel and the aqueous film.

If the spreading coefficient has a value greater than zero (i.e., positive), the aqueous phase can spread spontaneously upon or "wet" the fuel. A coefficient below zero (i.e., negative) indicated that it cannot spread spontaneously. When the spreading coefficient is zero, the two liquids are miscible.

Although this equation is applicable to pure liquids, there is wide variation possible when aqueous fluorocarbon films spread on a hydrocarbon fuel because of the variable oleophobic and hydrophobic properties of the fluorocarbon moieties. Therefore, to assess the interrelationship between firefighting effectiveness and the surface activity of the aqueous films produced by the 3- and 6-percent AFFF agents, a study was conducted to determine the film spread rate of each agent as a function of its interfacial tension on Jet A aviation fuel (appendix B). The Jet A fuel employed in these and all subsequent laboratory experiments had a surface tension of 27.0 dynes/cm.

In an effort to obtain better insight into the aqueous film spreading phenomenon on hydrocarbon fuels four separate aliquot liquid fractions were taken of the solution as it drained from the foam body. The spreading coefficients obtained by this procedure using four different 6-percent AFFF solutions on Jet A fuel are summarized in table 1. From these data it is apparent that only one agent (Lorcon 6) showed a negative spreading coefficient indicating that the first aliquot liquid fraction which drained from the foam would not spread spontaneously on Jet A fuel. It is speculated that this behavior resulted from the temporary adsorption of the active fluorocarbon moietie(s) within the body of the foam from which it was slowly released toward the end of the foam drainage cycle. However, this same agent produced relatively high spreading coefficient values for the unfoamed solution and of the third aliquot fraction which drained from the foam.

Similar experiments were performed using the three 3-percent AFFF agents, and the results are presented in table 2. A comparison of the film spreading coefficients obtained for the 3- and 6-percent type AFFF agents shows a strong similarity in pattern between the unfoamed solution and the three aliquot fractions of the drained foam liquid, with the exception of the anomalous performance of Lorcon 6. Based upon these data, it is apparent that all of the AFFF agents produce an aqueous fluorocarbon film capable of spontaneously spreading over the surface of Jet A fuel.

However, a second factor considered of equal significance in determining the firefighting effectiveness of the AFFF agents is the rate at which the aqueous fluorocarbon film spreads over the hydrocarbon fuel surface. To accomplish this objective, the apparatus shown in figure 2 was developed.

The film spread rate experiments were conducted by discharging 4 milliliters (ml) of solution down the inclined trough onto the surface of the Jet A fuel at the uniform rate of 0.10 ml/second and observing the distance traveled by the solution at appropriate time intervals. The film spread rates obtained for the unfoamed solution and each of the three aliquot foam drainage samples are presented in table 1 for the 6-percent agents and in table 2 for the 3-percent agents.

TABLE 1. SURFACE TENSION CHARACTERISTICS AND FILM SPREAD RATE OF THE 6-PERCENT AFFF AGENTS

Agent and Sample	Surface Tension of the Aqueous Film (dynes/cm) γw	Interfacial Tension between Fuel and the Aqueous Film (dynes/cm) γi	Spreading Coefficient of Aqueous Film (dynes/cm) S C	Film Spread Rate (cm/sec)
FC-206				
Not Foamed	15.20	5.20	6.90	1.26
1st Fraction	17.88	4.60	4.82	0.58
2nd Fraction	18.43	4.80	4.07	0.93
3rd Fraction	15.88	5.20	6.22	1.33
AER-O-WATER 6				
Not Foamed	18.68	2.37	5.78	1.17 $= \frac{100 \text{ cm}}{85.13 \text{ sec}}$
1st Fraction	17.95	2.33	6.55	0.10
2nd Fraction	17.95	2.43	6.45	0.28
3rd Fraction	17.05	2.10	7.68	1.22 $= \frac{100 \text{ cm}}{81.83 \text{ sec}}$
ANSUL 6				
Not Foamed	18.0	2.20	6.80	1.00
1st Fraction	21.50	2.80	3.00	0.23
2nd Fraction	20.90	2.55	3.85	0.48
3rd Fraction	19.31	1.95	6.04	1.11
LORCON 6				
Not Foamed	17.50	1.70	7.80	0.54
1st Fraction	25.45	2.67	-1.12	0
2nd Fraction	24.28	2.53	0.19	0
3rd Fraction	18.58	2.27	6.15	0.14

Note: Surface Tension of Jet A Fuel = 27.0 dynes/cm.

TABLE 2. SURFACE TENSION CHARACTERISTICS AND FILM SPREAD RATE OF THE 3-PERCENT AFFF AGENTS

Agent and Sample	Surface Tension of the Aqueous Film (dynes/cm) γw	Interfacial Tension between Fuel and the Aqueous Film (dynes/cm) γi	Spreading Coefficient of Aqueous Film (dynes/cm) S C	Film Spread Rate (cm/sec)
FC-203				
Not Foamed	16.37	4.53	6.10	1.04
1st Fraction	16.37	4.37	6.26	0.52
2nd Fraction	16.30	4.40	6.30	0.81
3rd Fraction	16.37	4.43	6.20	1.13
AER-O-WATER 3				
Not Foamed	19.20	1.77	6.03	1.08
1st Fraction	20.00	2.00	5.00	0.20
2nd Fraction	19.90	1.70	5.40	0.41
3rd Fraction	18.50	1.47	7.03	0.86
AER-O-WATER PLUS 3				
Not Foamed	19.33	1.23	6.44	1.10
1st Fraction	19.67	1.90	5.43	0.20
2nd Fraction	19.97	1.90	5.13	0.38
3rd Fraction	18.37	1.27	7.36	0.58

Note: Surface Tension of Jet A Fuel = 27.0 dynes/cm.

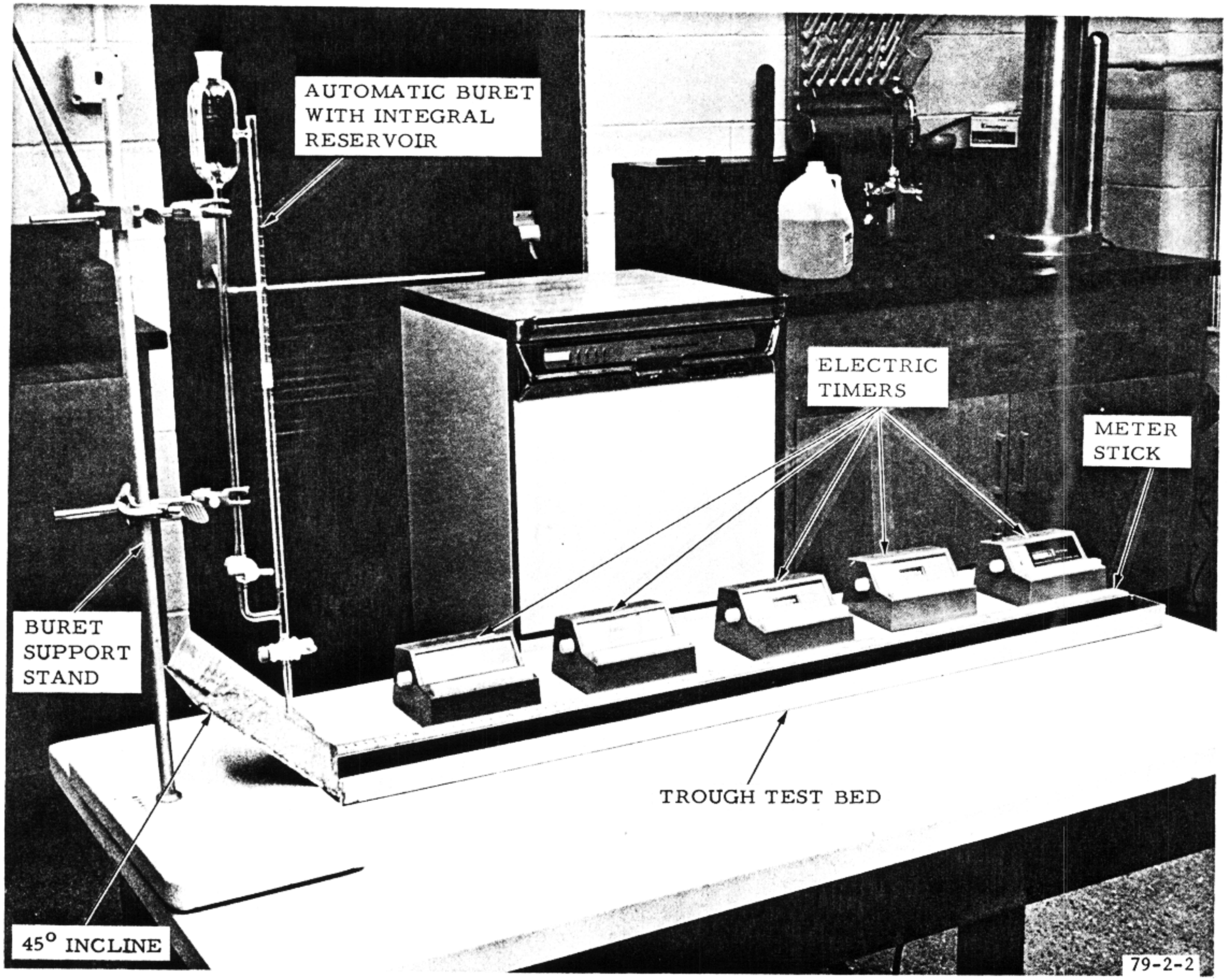

FIGURE 2. APPARATUS USED TO MEASURE FILM SPREAD RATE OF AFFF AGENTS

For comparative purposes, these data are plotted in figures 3 and 4 for the 6-percent and 3-percent AFFF agents, respectively. A comparison of these profiles show similar trends for both the 3-percent (FC-203 and Aer-O-Water 3) and 6-percent (FC-206 and Aer-O-Water 6) agents. However, it is considered noteworthy that the film spread rate obtained with the third aliquot sample drained form FC-206 and Aer-O-Water 6 foams achieved the same film spread rate as the unfoamed solution. Therefore, these data tend to indicate that the foaming of an AFFF solution may retard the rate at which the aqueous film spreads over Jet A fuel. This phenomenon was, in fact, later demonstrated in large-scale fire tests in which the foam solution was discharged through a non-air-aspirating nozzle.

Visual evidence of the rate at which an aqueous fluorocarbon film (Aer-O-Water 6) spreads over Jet A fuel is illustrated by the sequential photographs presented in figure 5.

MUTUAL COMPATIBILITY BETWEEN FOAM LIQUID CONCENTRATES. The probability that firefighting foam agents produced by different manufacturers will be used concurrently in airport firefighting operations is increasing and requires that tests be performed to determine the effects upon the resulting composite liquid system if these agents are inadvertently mixed. Accelerated aging tests were therefore performed in nominal conformance with Federal Specification O-F-555C (reference 1) to determine the degree of compatibility between the different brands within each class of agents employed at the same usage concentration (i.e., either 3- or 6-percent by volume). A summary of the manufacturers and the agents tested for compatibility within each class is presented in table 3.

Appendix C contains the results of the compatibility experiments conducted with binary mixtures at concentrations of 25, 50, and 75 percent by volume of each agent. From these data it is apparent that the four 6-percent AFFF agents demonstrated an acceptable degree of compatibility when evaluated in accordance with the test procedures established in appendix C for all liquid mixtures.

Although the 3-percent AFFF agents are not manufactured in accordance with a military specification, as are the 6-percent agents (reference 6), they also demonstrated excellent mutual compatibility in all of the laboratory experiments.

In contrast with the AFFF agents, the 6-percent FPF liquid concentrates showed a low order of compatibility in the accelerated aging cycle. Of the 10 binary combinations tested, only two showed a sediment of 0.25 percent (maximum allowable) or less in the aging experiments.

Similar results were obtained when combinations of the 3-percent fluoroprotein agents were subjected to the accelerated aging test. A total of six mixtures were tested of which only one combination produced a sediment of 0.25 percent or less by volume.

From these data it is evident that combinations of the fluoroprotein agents should be avoided if they are to be stored for any prolonged period of time. However, it does not necessarily preclude their being mixed when they are required for immediate use.

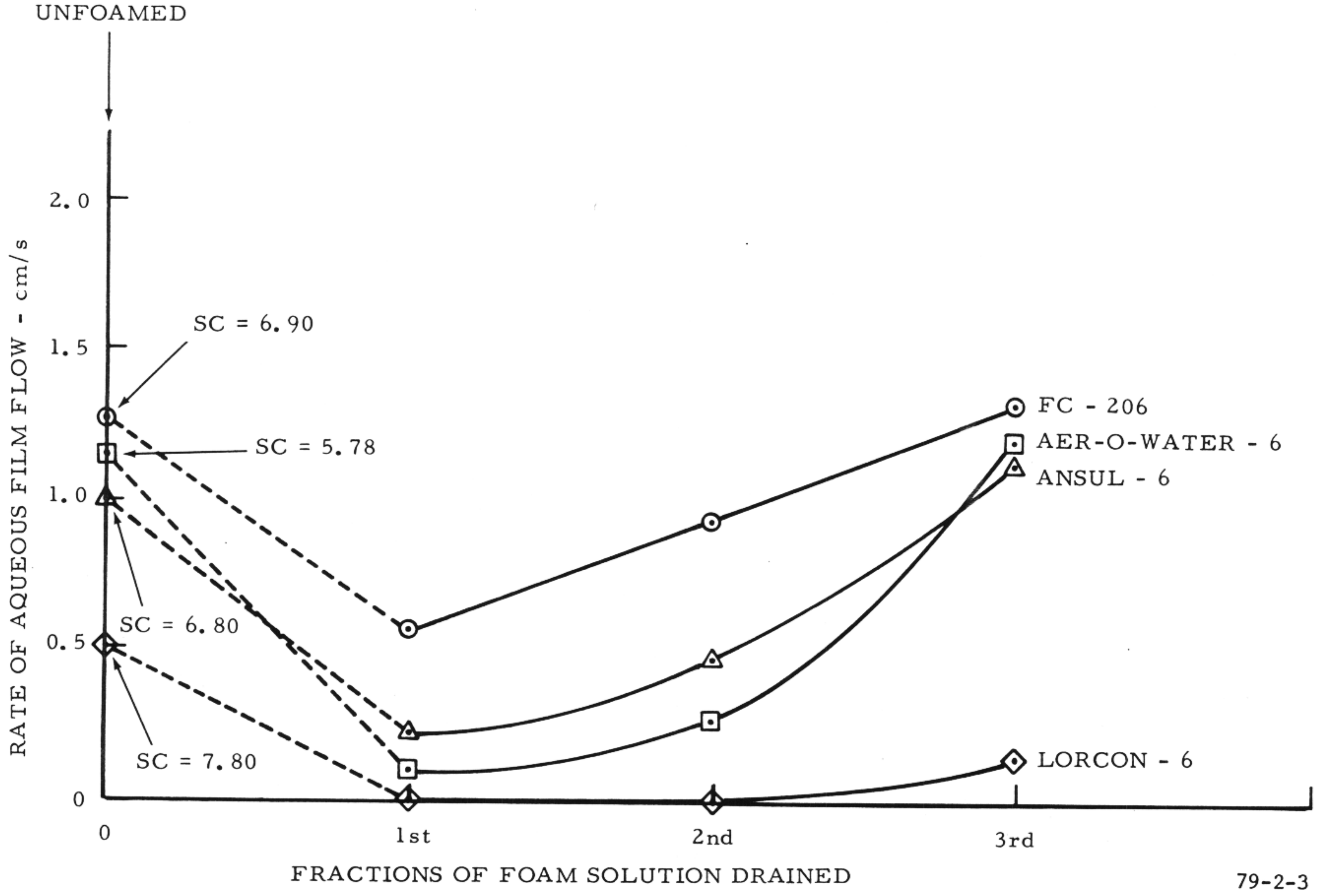

FIGURE 3. AQUEOUS FILM SPREAD RATE ON JET A FUEL FOR UNFOAMED AND FOAMED 6-PERCENT AFFF AGENTS

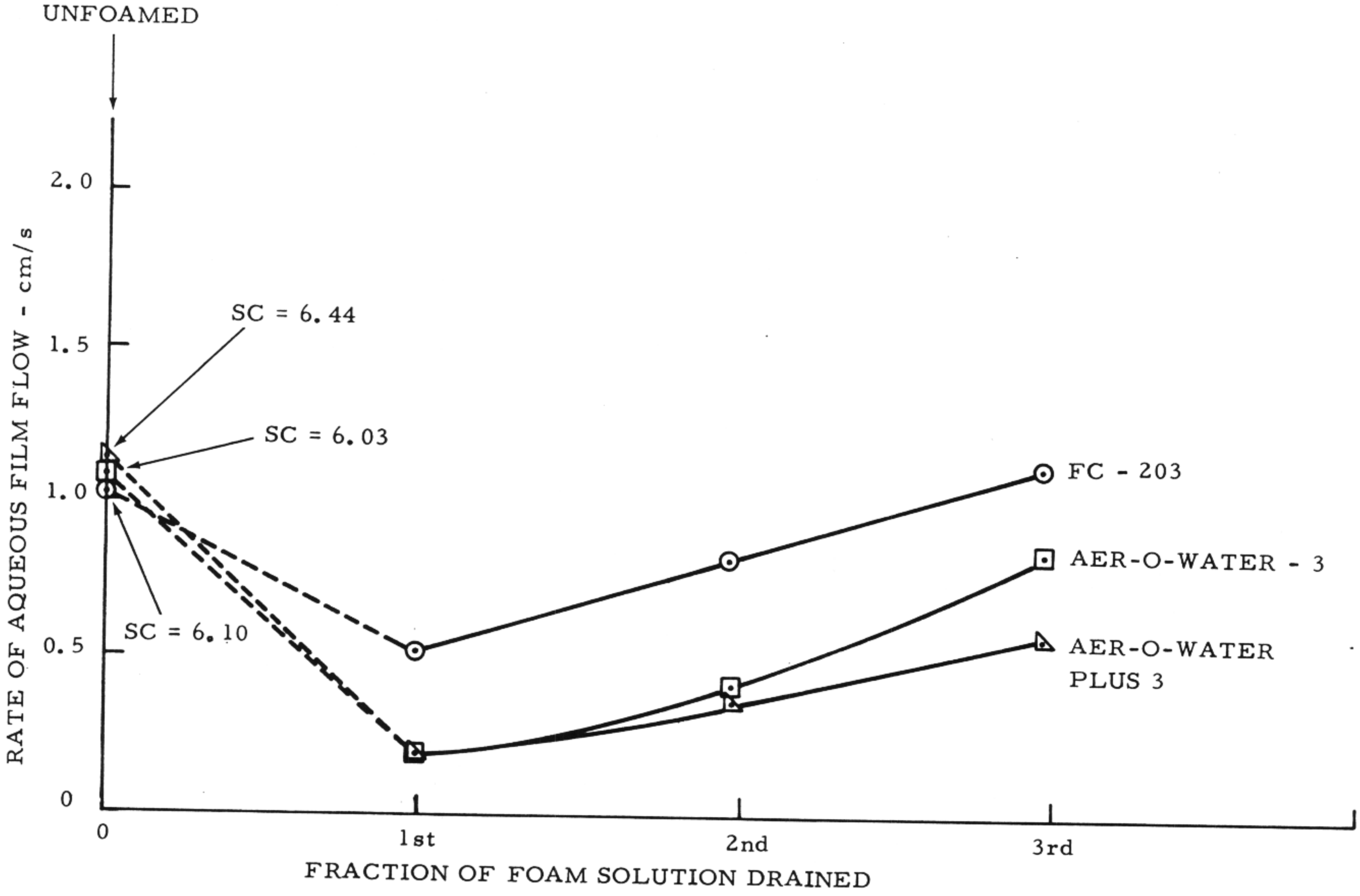

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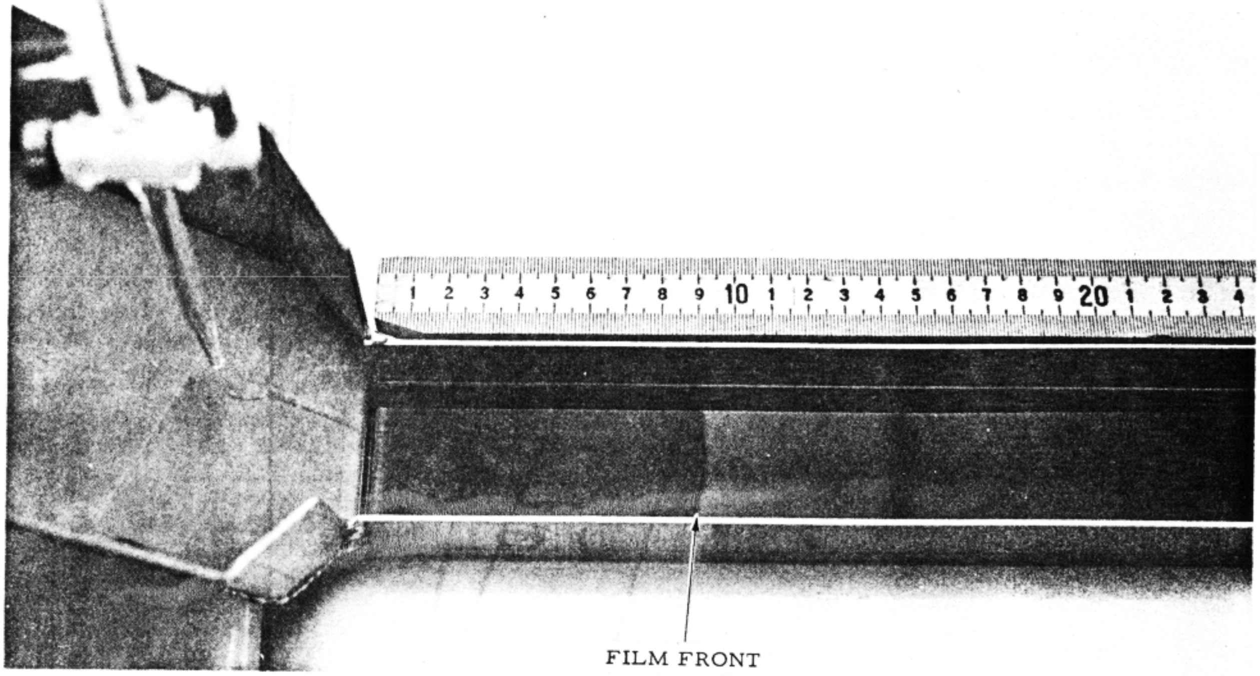
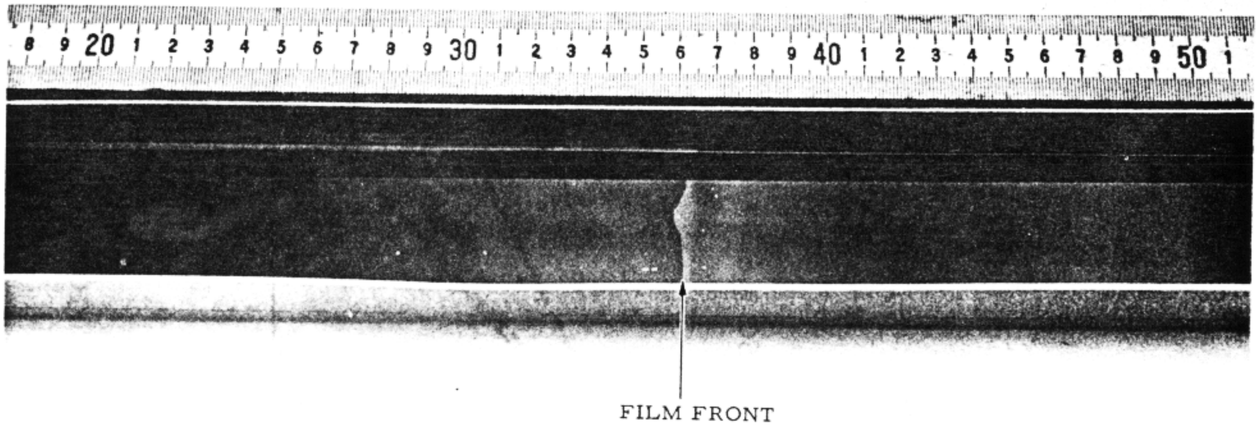
FIGURE 4. AQUEOUS FILM SPREAD RATE ON JET A FUEL FOR UNFOAMED AND FOAMED 3-PERCENT AFFF AGENTS

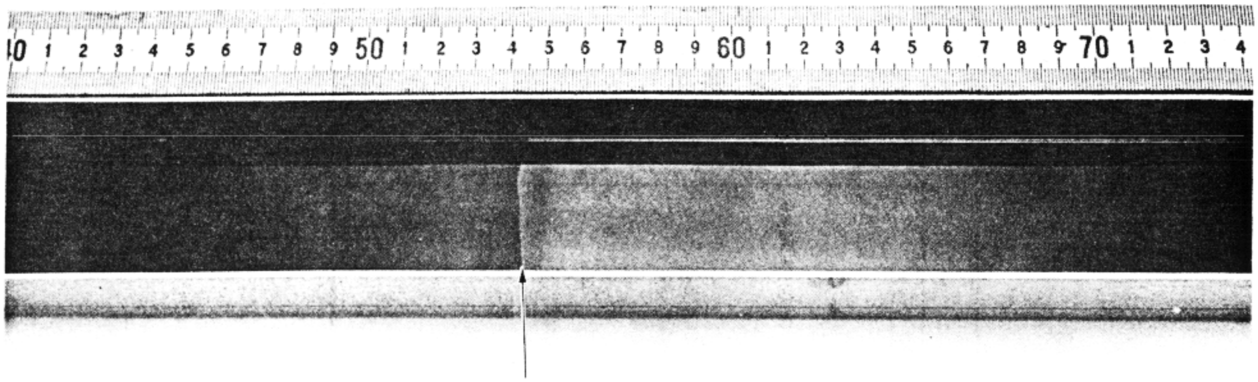


(a) FILM FRONT DISTANCE TRAVELED AT 2.8 SECONDS



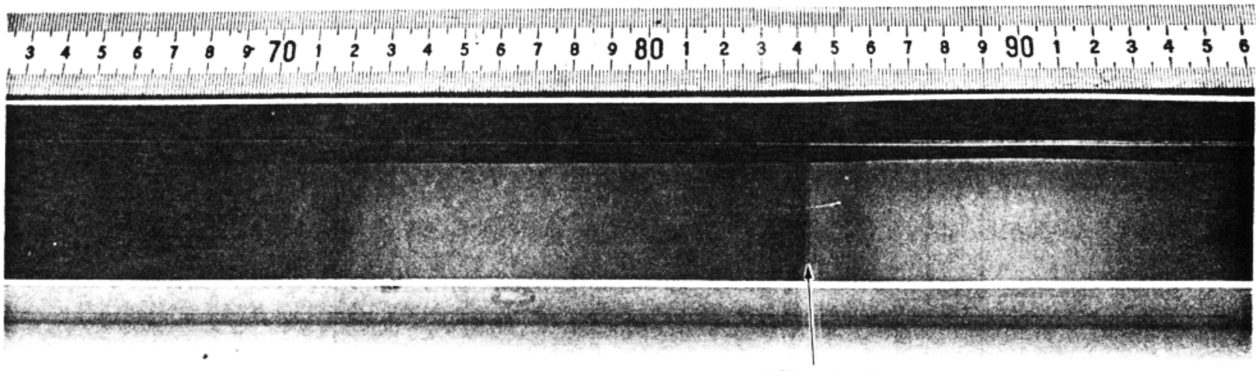
(b) FILM FRONT DISTANCE TRAVELED AT 13.1 SECONDS

FIGURE 5. FILM SPREAD RATE OF AN AQUEOUS FLUOROCARBON FILM (AER-O-WATER 6) ON JET A FUEL (1 OF 2)



FILM FRONT

(c) FILM FRONT DISTANCE TRAVELED AT 25.9 SECONDS



FILM FRONT

(d) FILM FRONT DISTANCE TRAVELED AT 54.6 SECONDS

FIGURE 5. FILM SPREAD RATE OF AN AQUEOUS FLUOROCARBON FILM (AER-O-WATER 6) ON JET A FUEL (2 OF 2)

TABLE 3. CLASSES OF FIREFIGHTING FOAM AGENTS

MANUFACTURER	AFFF AGENTS		FLUOROPROTEIN FOAMS			PROTEIN FOAM	
	3% Type	6% Type	3% Type	Various % Type	6% Type	3% Type	6% Type
3 M COMPANY	FC-203	FC-206					These agents are generally made in conformance with Federal Specification O-F-555C (See reference 1 for details)
NATIONAL FOAM SYSTEM, INC.	AER-O-WATER 3 AER-O-WATER Plus 3	AER-O-WATER 6	AER-O-FOAM XL-3		AER-O-FOAM XL-6	AER-O-FOAM 3	
LAURENTIAN CONCENTRATES Ltd.		LORCON 6	LORCON FP-3		LORCON K LORCON FP		
THE ANSUL CO.		ANSUL 6					
PYRENE Co. Ltd.				PYRENE Plus F 4.5%			
ANGUS FIRE ARMOUR CORPORATION			ANGUS FP-70	ANGUS FP-570 5%			
MEARL CORPORATION			MEARL 3			MEARL 3	
WORMALD INTERNATIONAL Ltd.				PROTECTOFOAM 4%			

It is speculated that the reason for the low order of compatibility between the fluoroprotein agents as a class is the absence of a suitable specification to define pertinent requirements and thereby provide guidance during their manufacture. In this regard, reference 12 specifically emphasizes the fact that the mixing of protein, fluoroprotein, or AFFF liquid concentrates of different types or produced by different manufacturers shall not be permitted unless it has been established that they are mutually compatible under long-term storage conditions and that the mixture will not reduce the firefighting effectiveness of the equipment in which it is used.

Only one experiment was conducted using 3-percent PF liquids (Aer-O-Foam 3 and Mearl 3) in the accelerated aging tests. The results of this experiment showed that an acceptable degree of compatibility maintained between the agents, with sediment not exceeding 0.05 percent by volume after aging.

No compatibility experiments were conducted with the 6-percent PF agents because of the work previously accomplished with these agents (reference 13) and the fact that they are generally produced in conformance with the federal specification (reference 1) which requires mutual compatibility for approval.

COMPATIBILITY OF FIREFIGHTING FOAMS WITH DRY-CHEMICAL POWDERS. The firefighting performance of all dry-chemical powders may be regarded to be of the "go" or "no go" type. That is, the fire is either completely extinguished with the environment cooled below the flash point of the fuel, or the fire will reflash. Therefore, their principal use in combatting complex three-dimensional fuel-spill fires is as auxiliary or complementary agents in conjunction with one or more of the foam-blanketing agents.

The increasing use of dry-chemical powders as auxiliary agents in aircraft accidents requires a knowledge of the compatibility of these agents with different foams. The results of large-scale fire tests performed at NAFEC (reference 14) with incompatible powder-foam combinations resulted in an almost complete cancellation of the firefighting effectiveness of both agents, and fire control was never obtained. To be successful the dry-chemical powders used in either a combined agent attack or as mop-up agents should demonstrate a reasonable degree of compatibility with the foam.

The compatibility between dry-chemical powders and different foams is usually one of degree rather than an absolute value. Therefore, laboratory tests designed to evaluate this property must be correlated with the results obtained using the same agents under actual full-scale crash fire conditions. The laboratory test outlined in appendix D contains the four parameters existent in all aircraft fire situations in which foam and powder are employed; i.e., fuel, heat, foam, and dry-chemical powder. The purpose of employing this test procedure, in which the materials are intimately mixed and exposed to intense thermal radiation, was an attempt to simulate the most severe conditions which might be realized under actual crash firefighting conditions and to avoid the ambiguity sometimes associated with interpreting the results of tests representative of some unknown intermediate degree of fire severity.