AD NUMBER
AD827051
LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; NOV 1967. Other requests shall be referred to U.S. Army Aviation Materiel Laboratories, Fort Eustis, VA 23604. This document contains export-controlled technical data.

AUTHORITY

USAAVLABS notice, 14 May 1969

USAAVLABS TECHNICAL REPORT 67-62

INVESTIGATION AND ANALYSIS OF AIRCRAFT FUEL EMULSIONS

By

James Nixon
Alan Beerbower
Wladimir Philippoff
Patricia A. Lorenz
Thomas J. Wallace

November 1967

U. S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA

D D C
FEB 19 1968
C

This report details the results of an emulsified JP-4 re-
search effort conducted by Esso Research and Engineering
Company, Linden, New Jersey, under the terms of Contract
DA 44-177-AMC-387(T).

The purpose of the program was twofold: (1) to formulate
97 weight percent internal phase (JP-4) emulsions for labora-
tory evaluation of their physical, chemical, and rheological
properties, and (2) to develop a means of demulsifying these
emulsions such that the recovered JP-4 fuel would meet mili-
tary specification requirements.

The program objectives were met, and two promising emulsion
formulations were subjected to extensive laboratory testing.
The nature of these tests and the results obtained therefrom
are presented in narrative, graphic, and tabular form in this
report.

While the fuel emulsions developed under this contract were
first-generation products, data suggest that the use of such
fuels in aircraft systems would prove to be most beneficial
from the standpoint of reducing the fire hazards associated
with aircraft accidents. Consequently, this command has con-
tracted for additional emulsified fuel programs during Fiscal
Year 1968. These programs are designed to optimize the prom-
ising emulsion formulations developed during the past year,
and to further characterize the physical, chemical, rheologi-
cal, and combustion properties of these fuels. Reports
covering these efforts will be available for distribution
during the fall of 1968.

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission, to manufacture, use, or sell any patented invention that may in any way be related thereto.

Disposition Instructions

Destroy this report when no longer needed. Do not return it to originator.

INVESTIGATION AND ANALYSIS OF AIRCRAFT FUEL EMULSIONS

by

James Nixon
Alan Beerbower
Wladimir Philippoff
Patricia A. Lorenz
Thomas J. Wallace

Prepared by

Government Research Laboratories
Esso Research and Engineering Company
Linden, New Jersey

for

U.S. ARMY AVIATION MATERIEL LABORATORIES
FORT EUSTIS, VIRGINIA

SUMMARY

An analysis of statistics from Viet Nam shows that low-flying Army aircraft are vulnerable to small-arms fire. This vulnerability is largely due to the fire hazards associated with JP-4 fuel. These problems can be either minimized or eliminated by thickening the fuel. From a technical and practical standpoint, emulsification appears to be the best approach to this problem.

This report summarizes work aimed at the formulation of JP-4 fuel emulsions which reduce the fire hazards associated with JP-4. Two fuel emulsions were formulated and completely characterized during the course of this program. These were designated WSX-7063 and WSX-7165. Both meet all the stated requirements for a safety fuel. They reduce the rate at which combustible vapors are released; they have yield stresses in excess of what is required to retard flow through a simulated.50-caliber bullet hole (>1000 dynes/cm^2); they are stable over the temperature range of -20°F to 130°F (WSX-7165 is stable over the range of -65°F to 160°F); and they are compatible with elastomers and metals of construction.

Both of the fuel emulsions have been scaled-up to 1000-gallon batch sizes. However, some difficulties were encountered with the scaled-up material. These difficulties involved breakdown of the emulsion from some batches in transit. Bench-scale studies showed that these difficulties were associated with too rapid addition of JP-4 and inadequate mixing in the plant. The area of emulsion scale-up requires further study before the production of much larger quantities of these materials is considered.

Fuel emulsion WSX-7063 was evaluated in a Lycoming T-55 engine fuel control system without any apparent difficulty. The fuel control system response to the emulsion was equivalent to that with the reference liquid fuel. There was no rust, sticking of moving parts, or fungal and bacterial growth observed in this test.

Nozzle studies on these emulsions, which were part of the current program, showed that the emulsions were not viscoelastic; they broke down to varying degrees in the nozzle with as much as 20 percent of the emulsion passing through the nozzle without breakdown, and the particle size of the atomized emulsion was equivalent to that of the unthickened fuel. During the course of this program, plugging of various nozzles by contaminants in the emulsion was a real problem. However, it was possible to overcome this difficulty by filtering the emulsion prior to passing it through the nozzle.

Preliminary pumping studies showed that the fuel emulsions can be pumped using conventional low-speed, high-output pumps. High-speed, low-output pumps cannot be used because they break the emulsion.

Studies were also carried out to develop techniques for determining contamination, drop size, and a simple yield stress method for fuel emulsions. Techniques were developed which appear to allow these determinations to be made. Further work is needed with other emulsions to establish precision and reproducibility.

On the basis of our findings in this program, several recommendations have been made with respect to improving emulsion stability, atomization in nozzles, and yield stress retention. Further work is also needed to define the mechanism of emulsion breakdown in nozzles and the relation between emulsion yield stress and breakdown in nozzles.

FOREWORD

This report summarizes work aimed at the formulation of an emulsified JP-4 fuel. Long-range, it is anticipated that such a fuel will minimize the fire hazards presently associated with JP-4 and decrease the vulnerability of low-flying Army vehicles to small-arms ground fire.

This work was initiated in May 1966 and completed in May 1967. The program was administered by the U.S. Army Aviation Materiel Laboratories, Fort Eustis, Virginia, with Mr. William J. Nolan acting as coordinator. We are grateful to Mr. Nolan for his many timely suggestions.

The fuel control system evaluations of our two most promising candidates were carried out by the Lycoming Division of AVCO Corporation under a subcontract. Mr. George W. Opdyke of the Lycoming Division was responsible for this phase of the program, and we are grateful for his many timely suggestions.

CONTENTS

ILLUSTRATIONS

ix

TABLES

SYMBOLS

HLB   Hydrophile-lipophile balance

δ Solubility parameter

$$\delta = \sqrt{\frac{\Delta E}{V}}$$

ΔE Heat of vaporization

V Molar volume (cc)

E   Energy

γ Interfacial tension

V   Volume of disperse phase (cc)

r   Droplet radius (cm)

M   Throughput (grams/minute)

P   Nozzle pressure (dynes/cm^2)

ρ Density (grams/cc)

A   Area of the nozzle as capillary opening (cm^2)

D   Shear rate (sec^{-1})

Q   Volume flow rate (cc/sec)

R   Radius of capillary (cm)

t_R Shear stress (dynes/cm^2)

L   Length of capillary

Re   Reynolds number

Re cr   Critical Reynolds number

d   Diameter (cm)

INTRODUCTION

In Viet Nam it has been demonstrated time and time again that low-flying Army aircraft are vulnerable to small-arms fire. This vulnerability is largely due to the fire hazards associated with JP-4 fuel. Fire hazards arise with existing fuels whenever fuel lines and/or tanks are punctured either by enemy projectiles or by the force of impact in a crash landing situation. An analysis of these situations shows that, on impact, the fuel forms a mist and comes in contact with ignition sources. The fuel is then ignited and the flames spread very rapidly. The objective of this study was to formulate a candidate safety fuel by emulsification techniques which would either minimize or eliminate the above problems.

1

PREVIOUS APPROACHES TO THE PROBLEM

A number of appro. hes to the safety fuel problem have been considered and explored by various government agencies over the past ten years. The fire hazard which aviation fuels represent in the event of accidents involving spillage develops from uncontrollable ignition sources, the unlimited supply of air, and the presence of flammable vapors. Much can be and has been done to reduce ignition sources, but the rapid release of flammable vapors from liquid fuels is particularly difficult to control. The hazards associated with liquid fuels, past and present, were the subject of a recent symposium (Reference 18). The highlights of this symposium are discussed in detail elsewhere (Reference 18).

Research has been conducted in four broad areas with the objective of minimizing the hazards associated with the use of liquid fuels in aircraft. These are (1) fire inerting systems, (2) breakaway fuel tanks, (3) fuel containment, and (4) modification of the fuel by one of the following techniques:

(a) Use of an inerting chemical in the fuel
(b) Encapsulation of the fuel
(c) Use of high-viscosity fuel
(d) Gelation of the fuel
(e) Emulsification of the fuel

The first three broad areas mentioned above have been quite adequately discussed in a recently issued report (Reference 16). The methods of reducing the hazards associated with liquid fuel through modification of the fuel (area 4 above) are discussed below.

The use of inerting chemicals to make fuels safer has received little attention because it has a number of inherent problems associated with it. This approach was an outgrowth of Navy-supported work carried out at the Aeronautical Engine Laboratcry, Naval Air Engineering Centei, in Philadelphia. In these studies, it was found that by matching the volatility of halocarbon fluids to that of a fuel, one could eliminate the vapor flammability envelope. These results were obtained in small-scale static tests, e.g., in bombs, using about 0.3 to 0.4 percent of the halocarbon. Most investigators agree that, if fuels treated in this manner are ignited in a nozzle, they will burn. In addition, if the fuel is atomized or transformed into a mist on impact, it will also burn quite fiercely. Thus, this approach will protect (inert) the vapor space of a tank but not the liquid fuel. There are also several potential disadvantages associated with the use of halocarbon derivatives; these are (1) toxicity problems, especially in the vicinity of airports, (2) severe corrosion problems in turbine fuel systems, and (3) large performance penalties on the engine because of the poor combustion properties of halocarbons. Therefore, this approach to the problem appears to be impractical

All available evidence on the use of encapsulated fuel, e.g., encapsulation of liquid fuel in urea-formaldehyde resins, suggests that the cost would be prohibitive and the loss in fuel value would be inherently large. Thus, this approach to making liquid fuels safe does not appear to be a feasible solution to the problem.

The use of a high-viscosity hydrocarbon fuel as a "crash-safe" fuel touches on the controversy which still exists concerning the relative safety merits of a gasoline-type fuel versus a kerosene-type fuel in a low-impact crash. Flame spread data on these fuel types reported by the Ministry of the Aviations Working Party in 1962 appear to support the British argument that a kerosene-type fuel is inherently safer with respect to this particular aspect of the fire hazard. Data reported by Kudzakov (Reference 8) on the rate of burning from a free liquid surface indicate that fuels having viscosities higher than kerosene burn at a still slower rate in these circumstances.

All investigators appear to agree that the rate of flame propagation across a free liquid surface is only one aspect of the crash hazard. All liquid fuels, regardless of viscosity, will atomize and form flammable mists if there is sufficient energy in the crash. In this respect, a gelled or emulsified fuel with sufficient cohesive energy to maintain a structure and resist misting and aerosol formation in a crash is bound to be inherently more "crash-safe" than even a high-viscosity liquid.

The use of gelled fuel as a crash-safe fuel is of more recent vintage, and this approach is still receiving limited attention by the Federal Aviation Agency. In 1962, the Army sponsored a program on thickened fuels. In this program, the approach involved having the pilot gel the fuel instantly to a solid if a crash were imminent. The Western Company developed a gelling agent (Jet Gel) which, when injected into aircraft fuel tanks, changed the fuel into a solid instantaneously. It soon became apparent that this approach had several major disadvantages. These are: (1) use of this technique is subject to human error; (2) natural forces, e.g., air turbulence, can initiate the process; (3) once gelation occurs, the aircraft has no readily available source of fuel. In subsequent work sponsored by the Army and the FAA, the Western Company developed a potent gelling agent, N-cocoa-γ-hydroxy-butyramide (CHBA). This material, when used at a level of 1.5 percent in jet fuel forms a firm gel and reduces the flame propagation rate of the fuel by 97 percent (Reference 15). The gelled fuel, which liquifies at 130°F, burned satisfactorily in a J-47 engine. All gels tested to date, however, have several rather serious disadvantages: (1) they are temperature sensitive, especially at low temperatures, where they tend to have a very high viscosity, (2) they are difficult to pump out of tanks, and there tends to be considerable holdup in the tanks, (3) they tend to separate out the fuel phase before they reach the combustion chamber, and (4) they are impossible (except by melting and recovering) to reconstitute once they are broken. Thus, gels do not appear to be an attractive solution to the safety fuel problem.

3

From a technical and practical standpoint, emulsification looks like the best approach to the safety fuel problem. Emulsions have several major advantages: (1) they are temperature insensitive, i.e., there is essentially no change in flow properties over a wide temperature range, (2) they are easy to remove from tanks of low surface energy because they do not wet such surfaces, (3) they appear to be stable when pumped and they break at the nozzle where it is desirable, and (4) they are fairly easy to reconstitute if broken.

As stated above, thickening the fuel appears to be the best approach to the safety fuel problem. Thickened fuel still exhibits the vapor pressure of the original fuel, but it is rendered safer in three distinct ways. First, the rate of vaporization per unit area is reduced under both dynamic and static conditions. Second, the tendency of the fuel to atomize or impact is very much less than with the unthickened fuel. Third, since the fuel is broken up into discrete gobs as opposed to a rather continuous spray under violent impact, rapid flame spread is minimized. Individual gobs may burn fiercely, but a large safety advantage is still gained because the fuel does not cover a large surface area; thus, flames are localized and will not spread rapidly. The basic question that must be answered in this area is what type of thickened fuel should be used.

ARMY-SPONSORED PROGRAM ON EMULSIFIED FUELS

Although the FAA continues its interest in gelled fuels, the Army sought other solutions to the problem. In 1965, the Army Aviation Materiel Laboratories initiated a broad program on emulsified fuels. Originally, three concepts for the use of these fuels were considered. These were:

(1) Logistic hauling of fuel by Army aircraft in active theaters of war. Under this concept, the fuel would be emulsified in a non-combat area, pumped into flexible tanks in the aircraft cargo space, and transported as an emulsion; after arrival at the combat area, it would be de-emulsified and distributed to waiting vehicles.

(2) Another concept envisioned the loading of emulsified fuel aboard an aircraft equipped with a de-emulsification unit. The fuel would be de-emulsified in flight prior to being pumped into the aircraft engine.

(3) The final concept considered envisioned the burning of emulsified JP-4 directly in engines. In this case, the fuel would be maintained in an emulsified state from the time it was pumped into the aircraft fuel cells until it was atomized or vaporized in the engine combustor.

The Army had a number of contracts with engine manufacturers to burn emulsified fuels in various types of engines. While the initial emulsified fuels employed in these studies had a number of deficiencies, the engine tests carried out to date have shown that emulsified fuels can be burned directly in engines (concept 3) (References 10, 11, and 12). Based on these encouraging results, it would appear that the inflight de-emulsification of fuels (concept 2) may be unnecessary. Concept 1 will probably not present any major problems, and it is still of interest to the Army.

PRIOR STATE OF THE ART

As noted above, the emulsified fuels initially employed in the Army's safety fuel program had a number of deficiencies. These are listed below:

- Poor shelf life

- Poor high- and low-temperature stability

- Incompatibility with practical materials of construction (References 10, 11, and 12)

- Lower combustion efficiency in comparison to the unmodified fuel

In the early part of 1966, the Army awarded a contract (DA 44-177-AMC-387(T)) to Esso Research and Engineering Company to formulate and evaluate fuels with more satisfactory physical properties. This report summarizes the work carried out under this contract.

Objective

The objective of this program is as follows:

General

- Prepare a safety fuel emulsion that will substantially reduce the fire hazards associated with JP-4 for two uses:

  (1) Logistical hauling, and
  (2) Burning directly in aircraft engines

Specific

- Formulate a fuel emulsion in which JP-4 is the disperse phase using as low a percentage of continuous phase material and emulsifier as possible, preferably three weight percent or less.

The emulsion must meet the following requirements:

- The rate of flame spread, rate of evaporation, and rate of burning must be substantially reduced.

- The emulsion must retard flow through a hole caused by a .50-caliber bullet measuring 2 inches long and 1/2 inch wide.

- There must be a minimum performance penalty on engines.

6

- The emulsion must be stable at room temperature for a minimum of 30 days.

- It must be stable and pumpable at -20°F to 130°F (desired range: -65°F to 160°F).

- It must be compatible with materials of construction and resistant to bacterial and fungal growth.

RESULTS AND DISCUSSION

An emulsion is a heterogeneous system consisting of at least two immiscible liquids, one of which is dispersed in the other in the form of droplets. Thus, an emulsion consists of three major components:

● A disperse phase (internal or discontinuous phase)

● A continuous phase (external phase)

● An emulsifier (which may be either cationic, anionic, or nonionic)

The phase which is in the form of droplets is the disperse or internal phase, and the phase in which the droplets are dispersed is the continuous or external phase. In our fuel emulsions, JP-4 will be the internal or disperse phase; the continuous phase material is to be defined.

In order to stabilize the emulsion against coalescense of the dispersed droplets, a third component is required: an emulsifier. The emulsifier which will form JP-4 fuel emulsions having the required resistance to flow (yield stress) and stability also has to be defined. In our approach to the problem, we mainly screened nonionic emulsifiers in order to minimize problems such as corrosion and combustion deposits which are frequently observed with members of the other classes of emulsifiers. Thus, the program resolved itself into defining the continuous phase material(s) and emulsifiers(s) which would form a stable, viscous emulsion with JP-4 as the disperse phase and meet the critical requirements previously outlined.

At low concentrations (<74 volume percent) of disperse phase, the droplets are essentially spherical in shape. If the droplets were homogeneous spheres, the emulsion could contain only 74 volume percent of the JP-4 and the droplets would be packed so closely that they would touch one another. (See diagram in Figure 1.)
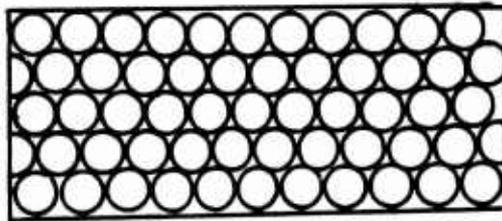
Figure 1. Diagrammatic Representation Of An Emulsion Containing
74 Volume Percent Of Disperse Phase.

The dispersed droplets in our fuel emulsions which contain 97.6 volume percent disperse phase are not spherical. Rather, they are distorted polyhedra; this is shown diagrammatically in Figure 2. This shows the diffi-
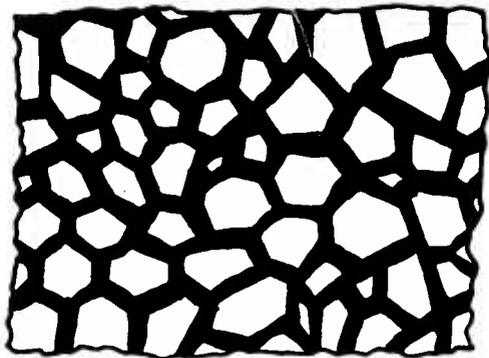
Figure 2. Diagrammatic Representation of Fuel Emulsion Containing
97.6 Volume Percent Disperse Phase.

culty involved with stabilizing such a system. The significance of this is that the interfacial film about the droplets (formed by the emulsifier) is under considerable strain. Thus, for stabilization, an emulsifier which forms a very strong interfacial film is required. Therefore, those emulsifiers capable of forming strong hydrogen bonds are preferred.

It is also obvious from Figure 2 that the more disperse phase present for any given emulsifier system, the more unstable the emulsion. For high-internal-phase emulsions at a fixed internal phase level (97 percent), optimizing the emulsion system resolves itself into minimizing the amount of emulsifier and maximizing the amount of continuous phase. This was, therefore, the strategy followed in this program.

Approach to the Problem

The literature survey carried out in Phase I of this contract (Appendix I) uncovered a number of references which suggested the use of several nonaqueous solvents as possible continuous phases. Our approach involved the screening of continuous phase materials using the following criteria:

- Must be immiscible with JP-4

- Must be a liquid; if not a liquid, must be soluble in a solvent which is immiscible with JP-4

- Must have a solubility parameter ≥ 12 and be capable of hydrogen bonding

The first two criteria are just the basic requirements for emulsification. The last item is based on a literature reference (Reference 17) which indicates that, if the solubility parameter of the continuous phase is less than 12, it is very difficult to form an emulsion. This is due either to the great tendency of such solvents to extract the emulsifier from the interface and/or the ease of solubilizing the disperse phase in the presence of such solvents and an emulsifier.

Continuous phase materials were selected for screening on the above basis, and they are shown in Table 1. Mixtures of these solvents with water were initially investigated as continuous phases; compositions initially corresponded to freezing points of -20°F and -65°F. The pure solvents were not investigated initially as continuous phases because the literature suggested that, for nonaqueous systems, the hydrophile/lipophile balance (HLB) is not applicable (Reference 14). An emulsifier consists of an oil-loving part (lipophile) and a water-loving part (hydrophile); HLB is simply the percent of hydrophile in the emulsifier divided by 5. The HLB system was developed for water-based emulsions and is related to the solubility of emulsifiers in water (Reference 6). Therefore, for non-aqueous solvents mixed with water, the HLB parameter will apply. The advantage to this is that for such systems, only emulsifiers having the required HLB will form stable emulsions; therefore, it will be necessary to try only those emulsifiers having the required HLB. To minimize the number of experiments in search of effective emulsifier-continuous phase combinations, it was highly desirable to have the HLB system apply.

Determination of Required Emulsifier HLB

Using mixtures of water and nonaqueous solvents as the continuous phase, the required emulsifier HLB for emulsification of JP-4 was determined. To do this, we used the standard Atlas HLB Kit in which the emulsifier HLB varied from 2 to 18. The required emulsifier HLB was determined by adding 1 cc of the emulsifier from the HLB Kit to 1 cc of the continuous phase material. To this mixture was added 50 cc of JP-4 with vigorous shaking, after which the mixtures were allowed to stand. The emulsifier blend forming the most stable emulsions represented the required emulsifier HLB for the system. In this way the HLB was determined within ± 1 HLB unit. This was done for all the emulsifier blends in the kit for several systems to establish experimentally that an HLB in excess of 11 was required for the system no matter what the continuous phase (Table 1).

Screening Emulsifiers

After having determined the required emulsifier HLB, we first selected emulsifiers for screening on this basis. This narrowed down the number of emulsifiers considerably but still left a large number for screening. In order for an emulsifier to form a stable emulsion having JP-4 as the disperse phase, the emulsifiers must be most soluble in the continuous phase over the entire workable temperature range of the emulsion (-20°F to 130°F). Thus, the emulsifier must not only have the required

10

TABLE 1

SOME OF THE CONTINUOUS PHASES INVESTIGATED IN THE PROGRAM

Weight Percent

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Ethyl Alcohol	39	72	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ethylene Glycol	-	-	48.5	65	-	-	-	-	-	-	-	-	-	-	-	-
Glycerol	-	-	-	-	55	70	-	-	-	-	-	-	-	-	-	-
Formamide	-	-	-	-	-	-	41	57	100	-	-	-	-	-	-	85
N,N-Dimethyl-formamide	-	-	-	-	-	-	-	-	-	52	68	-	-	-	-	15
Dimethyl Sulfoxide	-	-	-	-	-	-	-	-	-	-	-	54	70	-	-	-
N,N-Dimethyl Acetamide	-	-	-	-	-	-	-	-	-	-	-	-	-	56	72	-
Water	61	28	51.5	35	45	30	59	43	-	48	32	46	30	44	28	-
Freezing Point (°F)	-20	-60	-20	-65	-20	-38	-20	-65	-	-20	-65	-20	-65	-20	-65	-
Required HLB	11.5 ± 1	12 ± 1	13 ± 1	12.5 ± 1	13 ± 1	12 ± 1	12 ± 1	13 ± 2	-	16 ± 1	15 ± 1	15 ± 1	16 ± 1	16 ± 1	13 ± 2	-
Solubility Parameter (Calculated)	18.6	15.2	18.6	17.6	20.1	18.9	21.4	20.5	18.0	17.3	15.6	18.3	16.7	16.2	14.2	17.0

HLB but must be most soluble in the continuous phase rather than the JP-4 from -20°F to 130°F. Therefore, emulsifier solubility in the continuous phase was used as a means of screening emulsifiers. Since hydrogen-bonding represents another means of increasing solubility, continuous phase materials which were thought to have high hydrogen-bonding capabilities were given priority in our screening program.

Screening of emulsifiers with respect to solubility in the continuous phase involved simply mixing one part emulsifier with nine parts of the continuous phase material and observing if a clear solution resulted. If the solution was hazy, a portion of the mixture was titrated with water in an effort to clear it. If it was not possible to clear it, the second portion was titrated with acetone in an attempt to clear it. In this manner, the degree of emulsifier solubility could be estimated and it was possible to assess whether the emulsifier was soluble enough to make it worthwhile for further screening. This approach also allowed us to determine if the solvent plus water (in any combination) would be worth investigating with the given emulsifier system. If the emulsifier-continuous phase mixture was clear or required very little acetone or water to clear it, preparation of an emulsion was attempted with that emulsifier-continuous phase combination.

The data presented in Table 2 basically show the apparent effect of solubility parameter (Reference 3) of the continuous phase on emulsion stability. The data show that for a given emulsifier system, the solubility parameter must be close to that for the continuous phase. With the Span 80 and Tween 80 combination, optimum stability occurs with a continuous phase material having a solubility parameter of roughly 18.0. Because of this trend, we decided to try completely nonaqueous materials such as ethylene glycol, formamide, and dimethyl sulfoxide as continuous phases. The data in Table 2 show that only formamide produced an emulsion, and this emulsion had greatly improved stability over the water formamide system. Formamide apparently works with the Span 80 and Tween 80 combination because there is a reasonable match in solubility parameters and because of strong hydrogen-bonding between formamide and the emulsifier. The latter makes the emulsifiers more soluble in the formamide than in the other solvents. This is further substantiated by the results of our solubility data for the above continuous phase materials with the Span 80 and Tween 80 emulsifiers (see Table 3). Only in the case of formamide is a clear solution formed with this emulsifier combination. Thus, it is necessary to match solubility parameter, HLB, hydrogen-bonding, and polarity of the emulsifier and continuous phase for optimum solubility of the emulsifier in the continuous phase and for the production of an emulsion of maximum stability.

Screening Emulsions

For the purpose of screening emulsions, 500-gram quantities of the emulsion were prepared containing at least 97 weight percent JP-4 using the following procedure:

12

TABLE 2
APPARENT EFFECT OF SOLUBILITY PARAMETER
OF CONTINUOUS PHASE ON EMULSION STABILITY

	Weight Percent								
Ethylene Glycol	100	65.0	48.5	-	-	-	-	-	-
Dimethyl Sulfoxide	-	-	-	-	-	-	54	70	100
Formamide	-	-	-	41.0	57.0	100	-	-	-
Water	-	35.0	51.5	59.0	43.0	-	46	30	-
Solubility Parameter	14.2	16.6	18.6	21.4	20.5	18.0	18.3	16.7	13.4
Stability (Vol % Separation)									
● 30 days @ room temperature	**	-	0.0	0.0	0.0	0.0	-	(90.0)*	**
● Six freeze-thaw cycles	-	65.0	10-15	10.0	5.0	1.5	65.0	-	-

*Broke after 24 hours.
**No emulsion possible.

Composition of the Emulsions

1.5% Emulsifier (Span 80 and Tween 80)
1.5% Continuous Phase
97.0% JP-4

TABLE 3

SOLUBILITY OF SPAN 80 AND TWEEN 80 IN
THE CONTINUOUS PHASE MATERIALS SHOWN

	Weight Percent								
Ethylene Glycol	100	65.0	48.5	-	-	-	-	-	-
Dimethyl Sulfoxide	-	-	-	-	-	-	54	70	100
Formamide	-	-	-	41.0	57.0	100	-	30	-
Water	-	35.0	51.5	59.0	43.0	-	46	-	-
Appearance of Solution with 10% of {19% Span 80, 81% Tween 80}	Hazy	Hazy	Hazy	Hazy	Hazy	Clear	Hazy	Hazy	Hazy
Acetone required to clear haze (ml)	-	1.0	2.0	4.0	2.5	-	2.0	25	>25

All the emulsifier(s) was (were) added to the JP-4 and thoroughly mixed. About 100 cc of this mixture was added in 5 to 10 cc increments to a bottle containing the continuous phase with intermittent shaking. After about 100 cc of the emulsion was prepared, the seed emulsion was charged to a small stirred Hobart mixer. The addition of the JP-4 emulsifier mixture was then continued at such a rate so as to prevent the accumulation of free fuel. All the JP-4 was added in about 35-40 minutes.

The emulsions were evaluated with respect to yield stress and freeze-thaw stability between -20°F and 130°F. The sample had to survive at least six of the freeze-thaw cycles and have a yield stress of at least 1000 dynes/cm² before the emulsion was considered for further characterization and evaluation.

Laboratory Scale-Up of Emulsions

Emulsions passing the screening tests were scaled-up in the laboratory for more complete characterization. Laboratory scale-up involved the preparation of 2500-gram batches of the most promising fuel emulsions. The processes involved in the preparation of 2500-gram batches of WSX-7165 and WSX-7063 will now be described in detail.

For both WSX-7063 and WSX-7165, the emulsifiers are added to the total volume of JP-4 to be emulsified. The continuous phase material (urea-formamide in the case of WSX-7165 and formamide in the case of WSX-7063) is added to a quart bottle fitted with a screw cap. The JP-4-emulsifier blend is then added to the continuous phase in about 10 cc increments with intermittent vigorous shaking. After an amount of the JP-4-emulsifier blend equal to the amount of continuous phase has been added, the JP-4-emulsifier blend is added in 50 cc increments with intermittent shaking. This is continued until about 500 grams of the seed emulsion is prepared. The seed emulsion is then transferred to the Hobart mixer equipped with a 7-inch-wide paddle and a 10-quart-capacity bowl. The Hobart is operated on the number 2 speed range until all the JP-4 has been emulsified. The remainder of the JP-4-emulsifier blend is added at the rate of 45 cc per minute. Sixty to seventy minutes are required to complete the addition.

In the laboratory process, a quart bottle is used to start the emulsion because the small amount of continuous phase is not mixed well by the Hobart. Only after the volume reaches about 600 cc is the Hobart able to do a good job of mixing in the 10-quart capacity bowl.

Screening Tests

Yield stress was measured by the modified ASTM Penetration method which involves the use of a 30-gram plunger-cone assembly used in the ASTM D-217. In this test, the sample is placed in the sample cup and the surface smoothed over. The point of the cone is adjusted so that it just touches the sample for 5 seconds. The yield stress is related to the penetration in a manner shown in Figure 3.

15
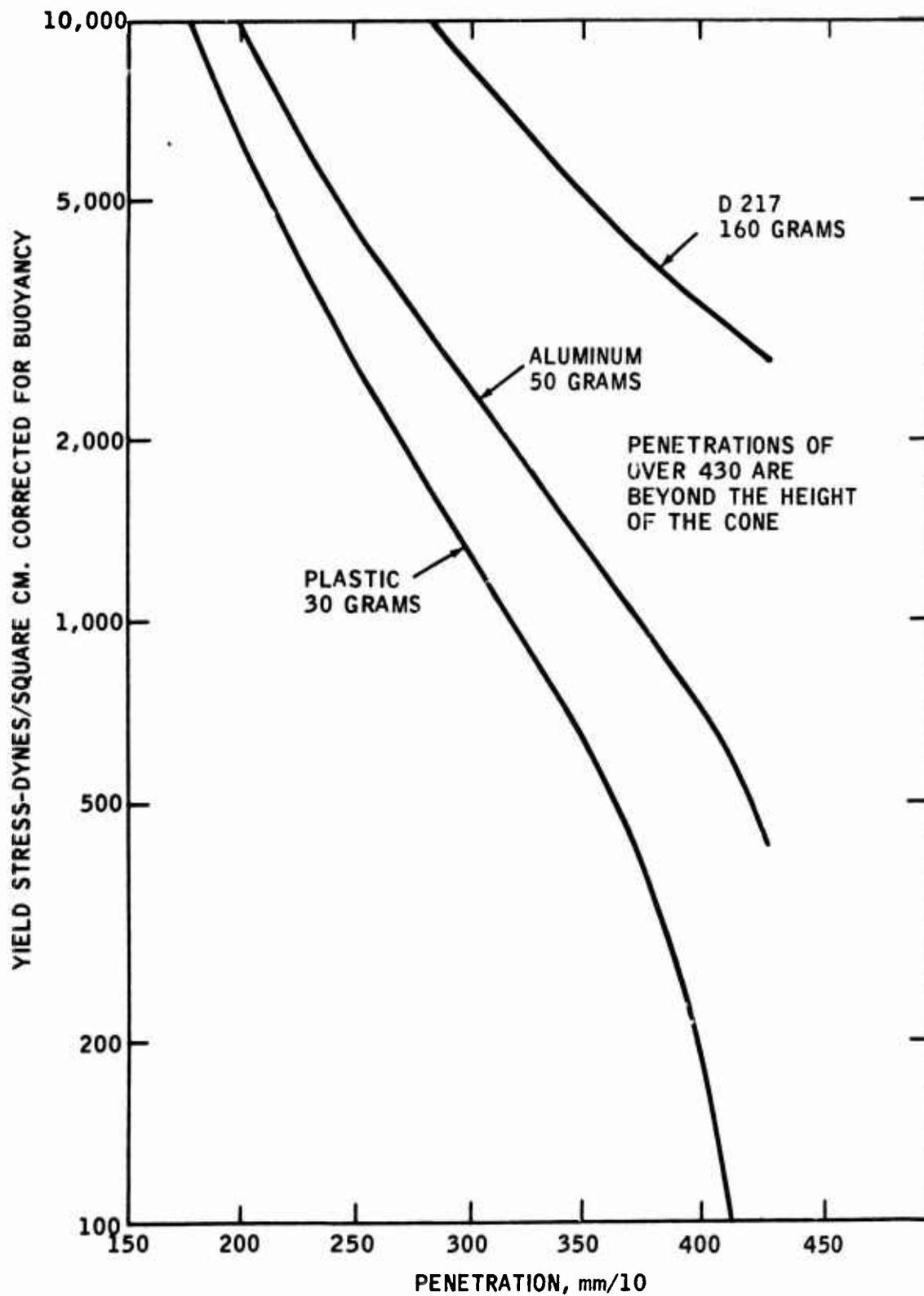
Figure 3. YIELD STRESS FROM LIGHTWEIGHT PENETROMETER ASSEMBLIES

16

The freeze-thaw test was run by first filling a 100 ml graduated conical centrifuge tube with the emulsion. The sample was then stored in the oven at 130°F for six hours. The percent separation was measured every hour. At the end of six hours, the sample was allowed to cool to room temperature. It was subsequently placed in a cold box at -20°F. The sample was maintained at -20°F (or a lower temperature) for 16 hours; it was then removed and allowed to warm up to room temperature, after which the volume percent separation (if any) was measured. The freeze-thaw cycling was continued if the emulsion did not break completely prior to the completion of six freeze-thaw cycles.

Emulsions Formulated and Fully Characterized
Under the Present Contract

Using the above approach, two fuel emulsions were formulated and completely characterized during the course of this program. Several other highly promising emulsion systems were also investigated, but they require further characterization. The two emulsions which were formulated and completely characterized have been designated WSX-7063 and WSX-7165. The latter (WSX-7165) was designed to improve stability and reduce the cost relative to that of the former (WSX-7063). The compositions of these two emulsions are shown in Table 4.

TABLE 4 COMPOSITIONS OF WSX-7063 AND WSX-7165 FUEL EMULSIONS		
	Weight Percent	
	WSX-7063	WSX-7165
Formamide	1.50	1.60
Urea	-	0.40
Span 80	0.42	-
Tween 80	1.08	-
ENJ-5716	-	0.25
Atlas IL-851	-	0.75
JP-4 (MIL-T-5624G)*	97.0	97.0
*Contains both anti-icer and corrosion inhibitor		

17

Table 5 shows the typical properties of both WSX-7063 and WSX-7165. (Other engineering properties for these emulsions are shown in Table 6.) Data for JP-4 are shown for the purpose of comparison. These emulsions are compatible with essentially the same elastomers and materials of construction as JP-4. Slight corrosion of bronze and copper was observed with these emulsions; however, this can be eliminated by use of small quantities of commercially available copper inhibitors (if necessary) (Table 7). However, the level of corrosion of copper and bronze with these emulsions probably does not warrant this. At room temperature for a period of 30 days, the corrosion of copper and bronze with both WSX-7063 and WSX-7165 is almost insignificant as shown by the data in Table 8. These data show that the bronze and copper corrosion with both WSX-7063 and WSX-7165 is indeed very slight. The data indicate that WSX-7166 is slightly more compatible with copper and bronze than WSX-7063.

Evaluation of Emulsions With Respect
to Release of Combustible Vapors

WSX-7063 and WSX-7165 were investigated with respect to evaporation rate over the temperature range of -20°F to 160°F under both dynamic and static conditions. These tests were run to ascertain the extent to which emulsification of JP-4 inhibits the generation of combustible vapors by the fuel (Figures 4 through 9). These data show that both WSX-7063 and WSX-7165 reduce the evaporation rate of the fuel by a significant extent even at 160°F. The release of combustible vapors was inhibited by a significant amount under all conditions with both emulsions. At -20°F, the rate of evaporation was reduced about 95 percent with WSX-7063 and about 99+ percent with WSX-7165 (Figure 4); at 77°F, the reduction was about 97 percent with WSX-7165 and some 90 percent for WSX-7063 (Fig. re 5); at 160°F, the reduction was about 86 percent with WSX-7063 and about 95 percent with WSX-7165 (Figure 7). Figure 9 shows the evaporation rate data plotted for WSX-7063 and WSX-7165 on the same graph at different temperatures. These data show that the evaporation rate of WSX-7165 at 160°F is about 29 percent less than that observed with WSX-7063 at 130°F. Thus, WSX-7165 has a significantly higher degree of thermal stability in comparison to WSX-7063.

Flow Properties of WSX-7063 and WSX-7165

WSX-7063 and WSX-7165 fuel emulsions have yield stresses of 2000 dynes/cm² and 2700 dynes/cm², respectively. The flow curves which demonstrate the non-Newtonian behavior for these emulsions are shown in Figure 10 along with similar data for JP-4. The viscosities of these emulsions are 100,000 to 150,000 times greater than that of JP-4 at very low shear rates. The high apparent viscosity and high yield stress of these emulsions means that they will retard flow from a hole caused by a .50-caliber bullet. It has been estimated that when a bullet of this size enters a tank sideways, it will create a hole with dimensions of 2 inches by 1/2 inch. Thus, the effect of yield stress on the tendency of fuel emulsions to flow through such a hole was investigated. These studies were carried out in a cylindrical can 5-1/2 inches high and 3-7/8 inches in diameter with one end removed. The results are summarized in Table 9.

TABLE 5			
SOME TYPICAL PROPERTIES OF WSX-7063 AND WSX-7165 FUEL EMULSIONS			

Property	WSX-7063	WSX-7165	JP-4
Yield Stress, dynes/cm^2	2000	2700	0.0
Stability (Vol % Separation)			
• 30 Days at Room Temperature	0.0	0.0	-
• Six 6-Hr Cycles at 130°F	2.0	trace-0.50	-
• After Centrifugation for 1 Hr at 500 g (RCF)	0.0	0.0	-
• Six 16-Hr Cycles at -65°F	75.0	0.0	-
Vibration Stability After 8 Hrs at 6 Cycles/Sec and 2 g	No Change	No Change	-
Gross Heat of Combustion, BTU/lb	19,170	19,184	20,345
Four-Ball Wear (mm)	0.55	0.75	0.45
Ash Content, Wt%	$<$0.005	$<$0.005	$<$0.005
Sulfur Content	$<$200 ppm	$<$200 ppm	$<$200 ppm
Reid Vapor Pressure	1.9	2.0	2.3
Compatibility - Corrosion (One Week at 130°F) of:			
Aluminum	0.0 mg/in^2	+0.2 mg/in^2	0.0
Magnesium	$<$0.5 mg/in^2	-	0.1
Bronze	8.5 mg/in^2	5.0 mg/in^2	0.3
Copper	10.0 mg/in^2	∿5.0 mg/in^2	0.2
304 Stainless	0.0 mg/in^2	0.1 mg/in^2	+0.4
Titanium Alloy	0.0 mg/in^2	0.2 mg/in^2	+0.4
Mild Steel	0.1 mg/in^2	0.5 mg/in^2	0.3
Swelling Of (% Increase)			
Neoprene	19	37	26
Butyl Rubber	148	146	143
Buna N (MS-902)	22	18.5	11
Buna N (MS-29513)	43	42	34
Silicone	87	85	86
Viton	5.0	3.4	3.0
Resistance To Organism			
Aerobacter Aerogenes at 86°F	$>$30 days	$>$30 days	$>$30 days
Pseudomonas Aeruginosa at 86°F	$>$30 days	$>$30 days	$>$30 days
Cladosporium Resinae at 77°F	$>$30 days	$>$30 days	$>$30 days
Flame Propagation Rate Relative to JP-4	2.0%	1.0%	100%
Burning Rate/Unit Volume Relative to JP-4	∿20%	$<$10%	100%

TABLE 6 OTHER ENGINEERING PROPERTIES OF WSX-7063 AND WSX-7165 FUEL EMULSIONS		
Property	WSX-7063	WSX-7165
Specific Gravity at 60°F	0.782*	0.782
Evaporation Rate (Relative to JP-4)		
After 1% Loss at -20°F	11%	0%
After 10% Loss at 25°F	7%	2%
After 20% Loss at 130°F	8%	4%
After 20% Loss at 160°F	8%	4%
Specific Heat (BTU/lb °F)*		
At 0°F	0.44	0.44
At 50°F	0.47	0.47
At 100°F	0.40	0.40
Thermal Conductivity* (BTU/sq Ft-Hr-°F)		
At 0°F	0.0815	0.0815
At 50°F	0.0802	0.0802
At 100°F	0.0790	0.0790
Electrical Conductivity Specific, Mhos/cm at 77°F	3.5×10^{-6}	2.8×10^{-6}
Damage To The Following at 77°F		
Methacrylate Plastic	Surface Damage in 8 hrs	Surface Damage in 8 hrs
Teflon	No Damage in 8 hrs	No Damage in 8 hrs
Polyethylene	No Damage in 8 hrs	No Damage in 8 hrs
Paints (alkyd.)	Damage in 8 hrs	Damage in 8 hrs
*Calculated Values		

TABLE 7
EFFECT OF COMMERCIAL INHIBITORS
ON COMPATIBILITY OF WSX-7063 WITH COPPER

Material	Copper Strip Corrosion Test (ASTM D 130)
JP-4	J-4
WSX-7063 without inhibitor	J-9
WSX-7063 with Amoco 150 (0.25%)	J-4
WSX-7063 with UOP Cu Deactivator (0.25%)	J-3
WSX-7063 with NaSul EDS (0.25%)	J-3
WSX-7063 Varilube 601 (0.25%)	J-3
WSX-7063 with Mercaptobenzothiazole (0.25%)	J-3

TABLE 8
COMPATIBILITY OF WSX-7063 AND WSX-7165 WITH MATERIALS
OF CONSTRUCTION AT ROOM TEMPERATURE AFTER 30 DAYS

Metals	Appearance		Wt Loss (Mg/in^2)	
	WSX-7063	WSX-7165	WSX-7063	WSX-7165
Copper	slight discoloration	slight discoloration	2.1	1.3
Bronze	very slight discoloration	very slight discoloration	2.1	0.73
316 Stainless Steel	no change	no change	0.0	0.0
Mild Steel	one very small rust spot	no change	0.0	0.0
Aluminum	no change	no change	0.0	0.0
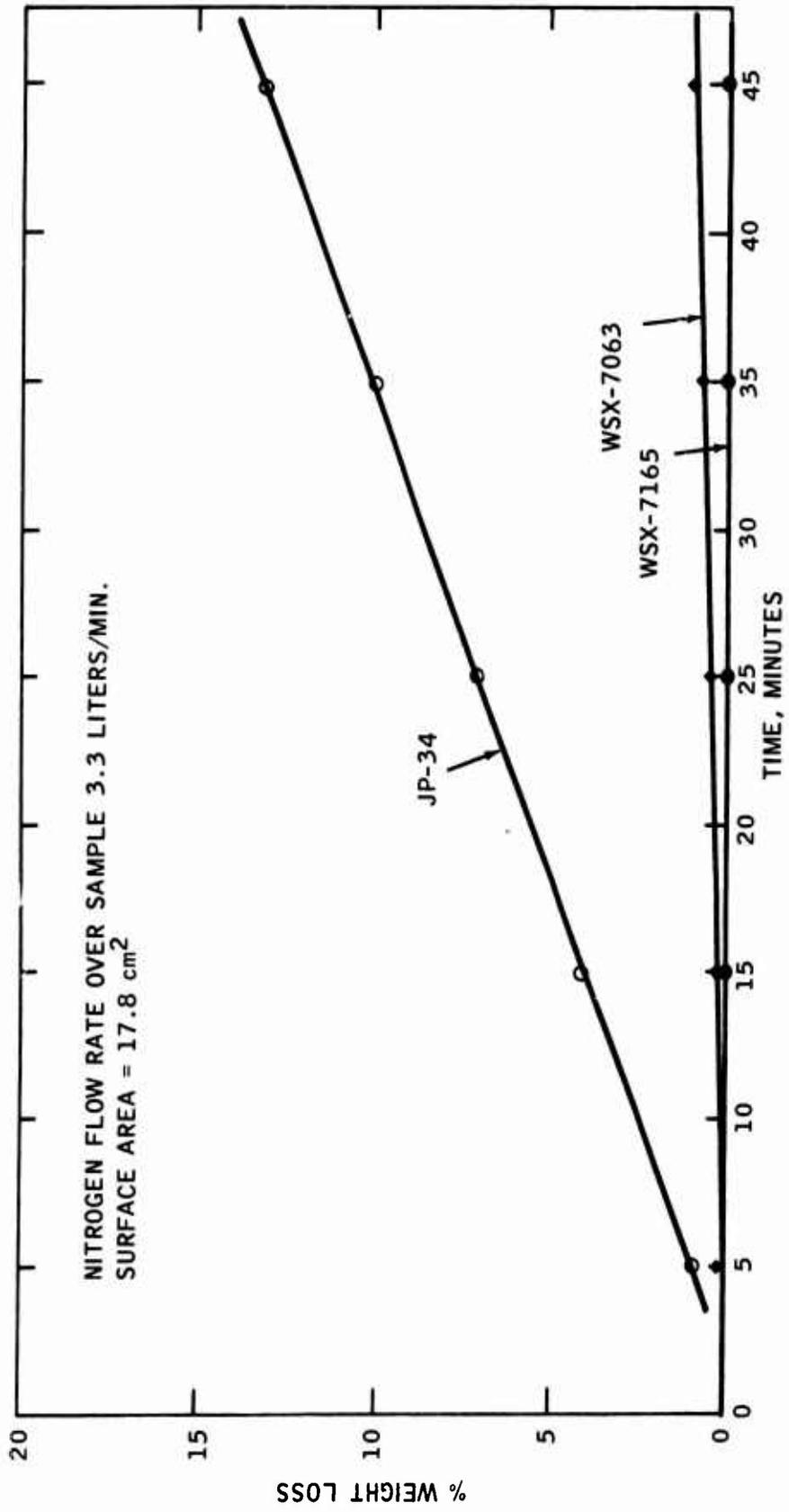
Figure 4. EVAPORATION RATES FOR JP-4 AND FUEL EMULSIONS AT -20°F
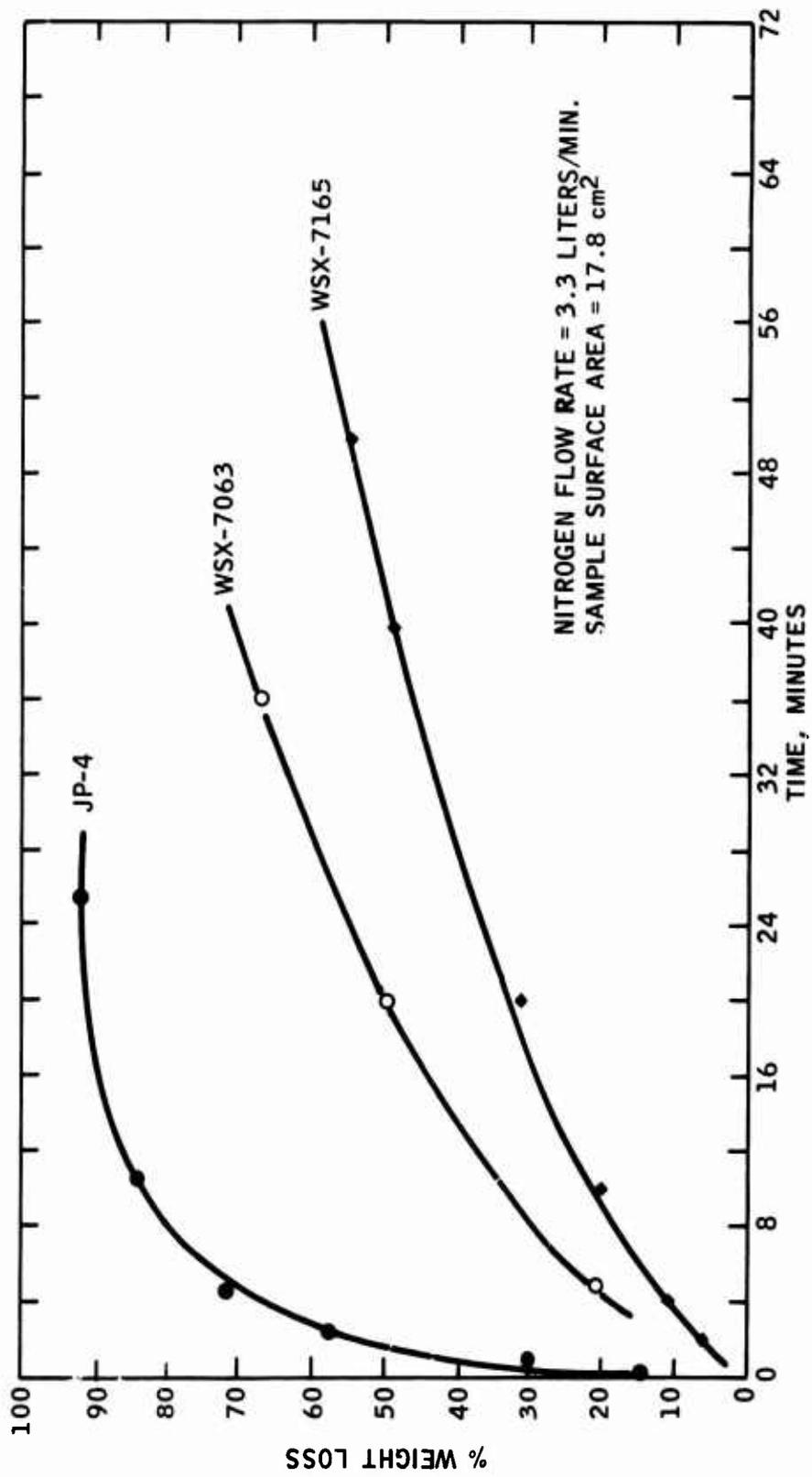
Figure 5. EVAPORATION RATES FOR JP-4 AND FUEL EMULSIONS AT 77°F.

NITROGEN FLOW RATE = 3.3 LITERS/MIN.
SAMPLE SURFACE AREA = 17.8 cm^2

23
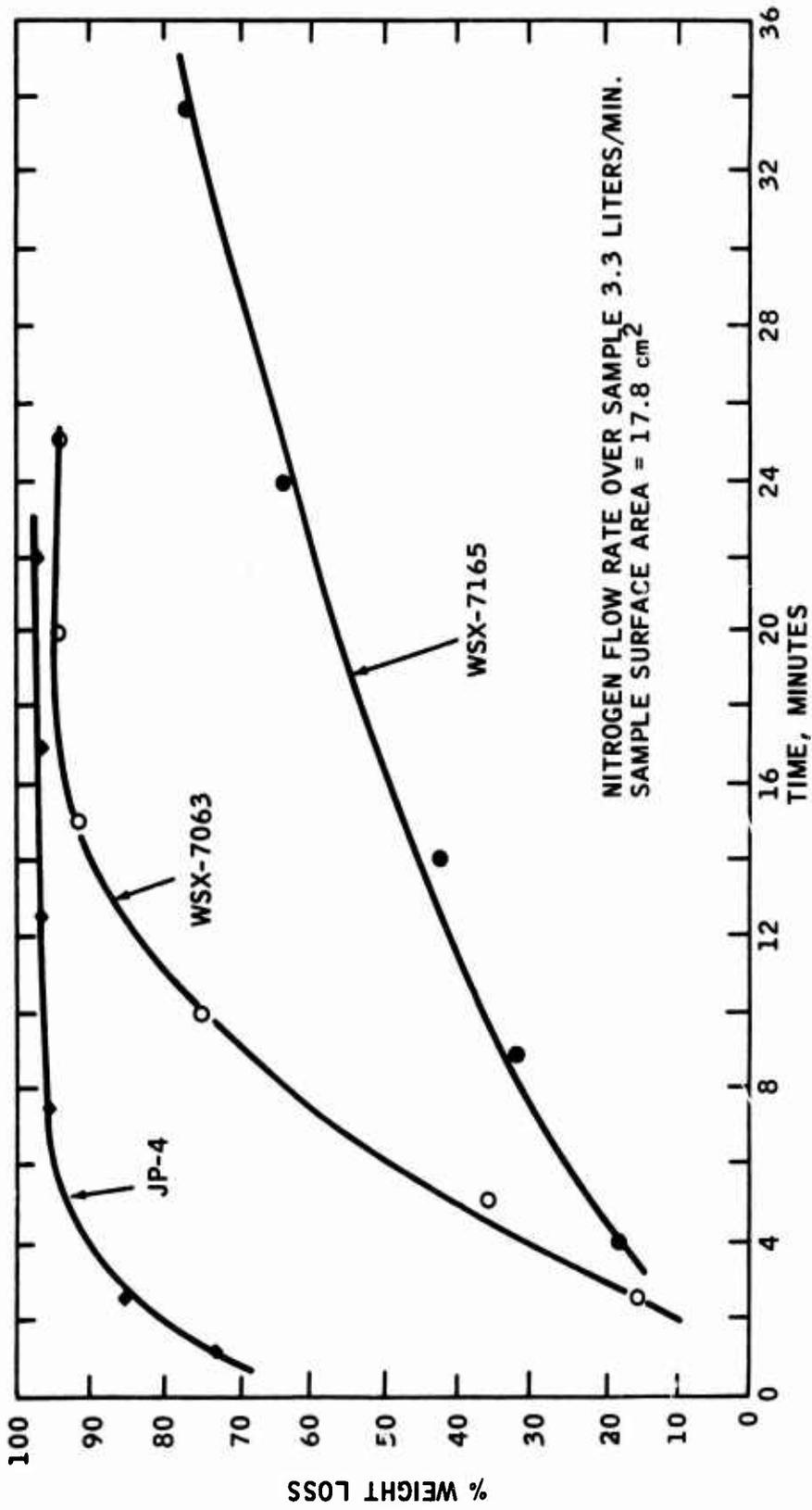
Figure 6. EVAPORATION RATES FOR JP-4 AND FUEL EMULSIONS AT 130°F.
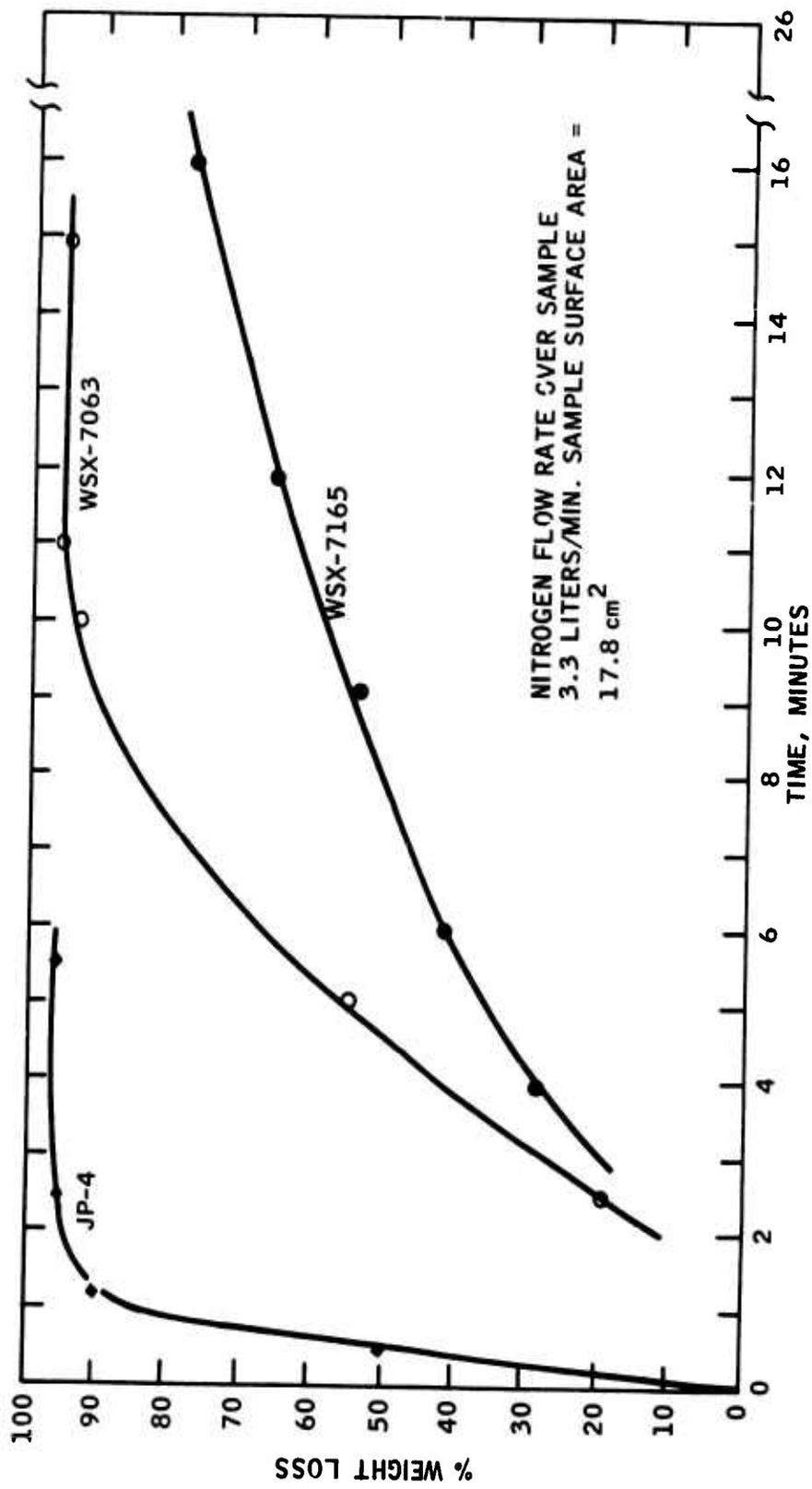
Figure 7. EVAPORATION RATES FOR JP-4 AND FUEL EMULSIONS AT 160°F.
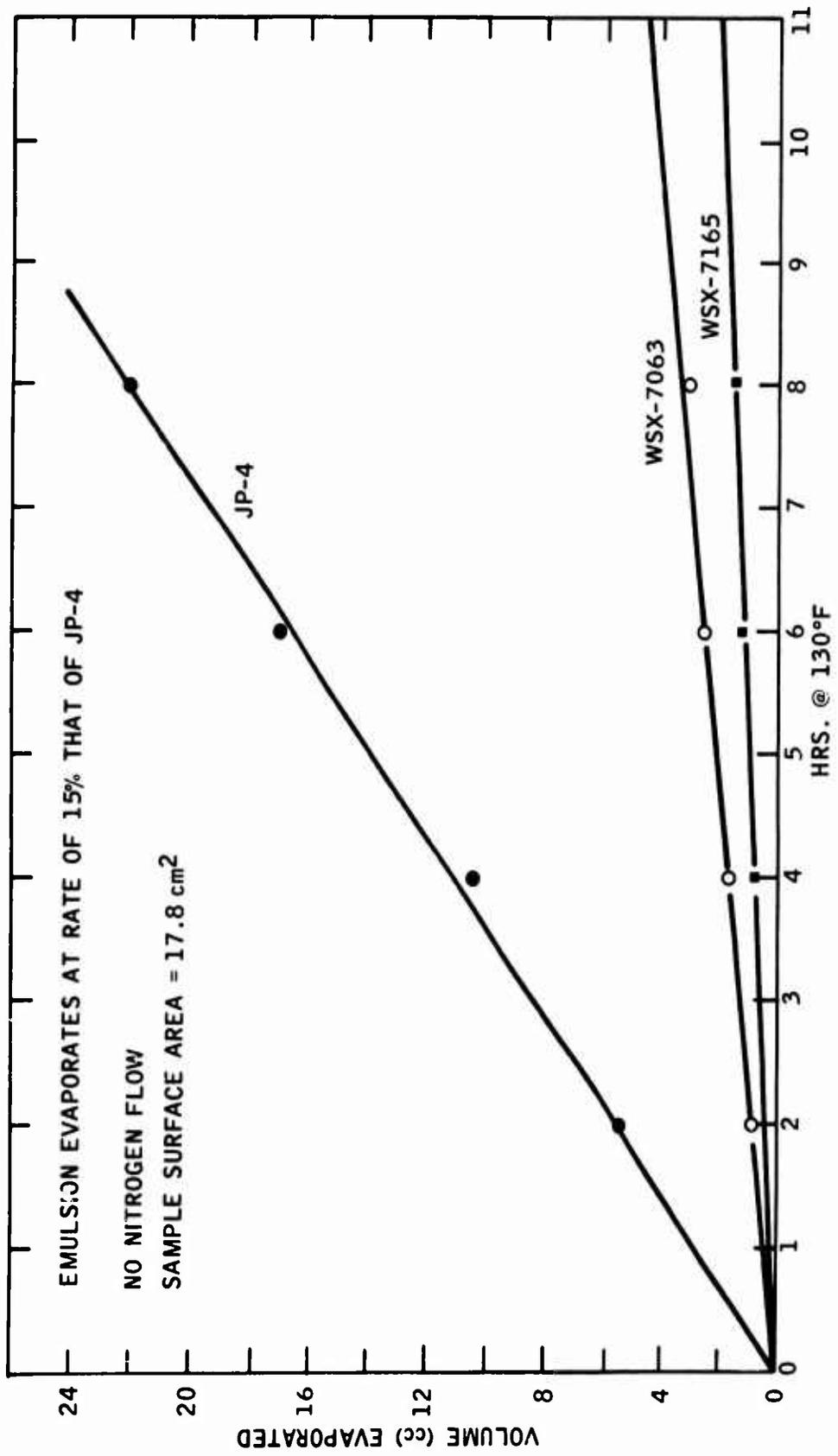
Figure 8. STATIC EVAPORATION RATES FOR JP-4 AND FUEL EMULSIONS AT 130°F.

26
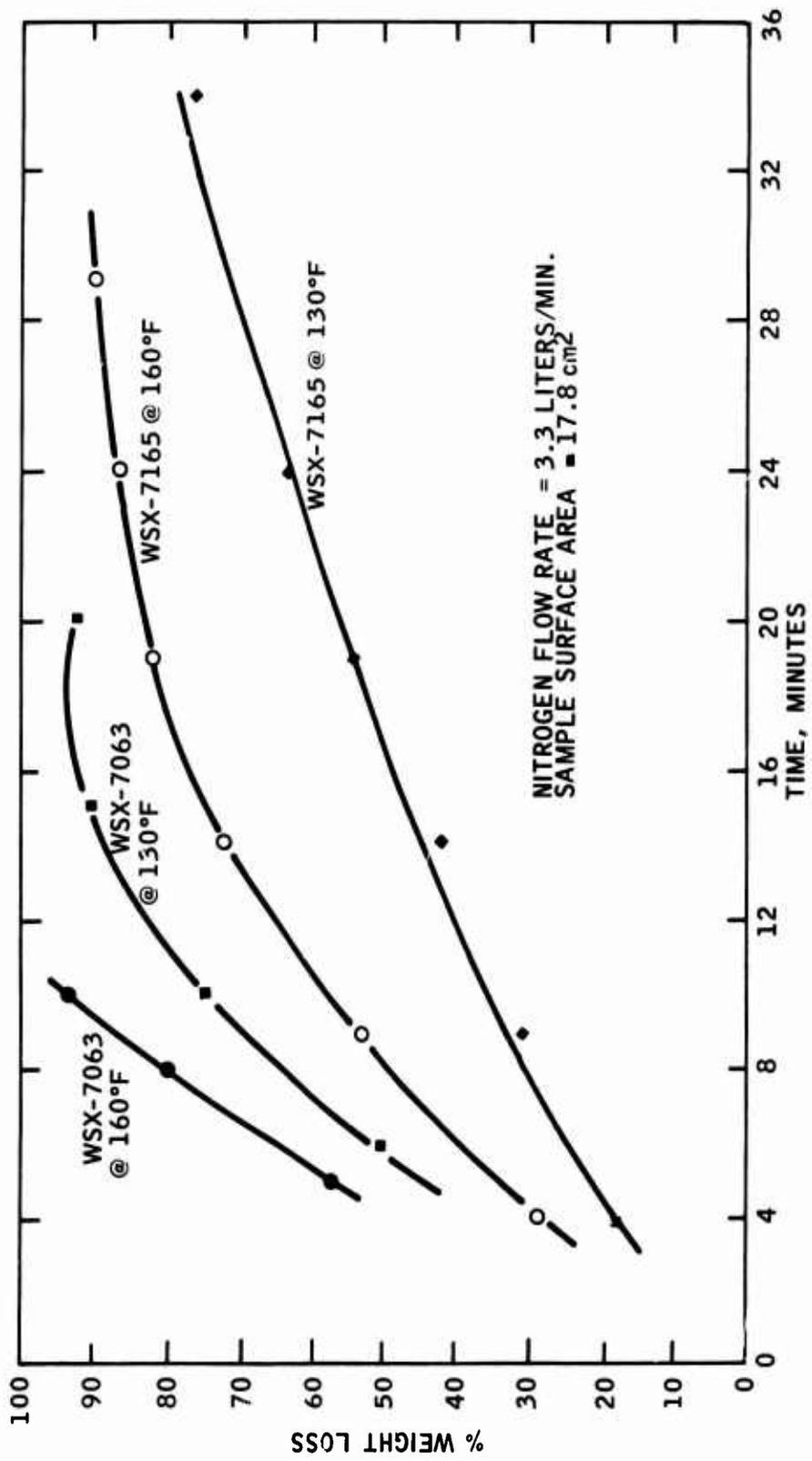
Figure 9. EVAPORATION RATES OF WSX-7165 AND WSX-7063 AT 130°F AND 160°F

27
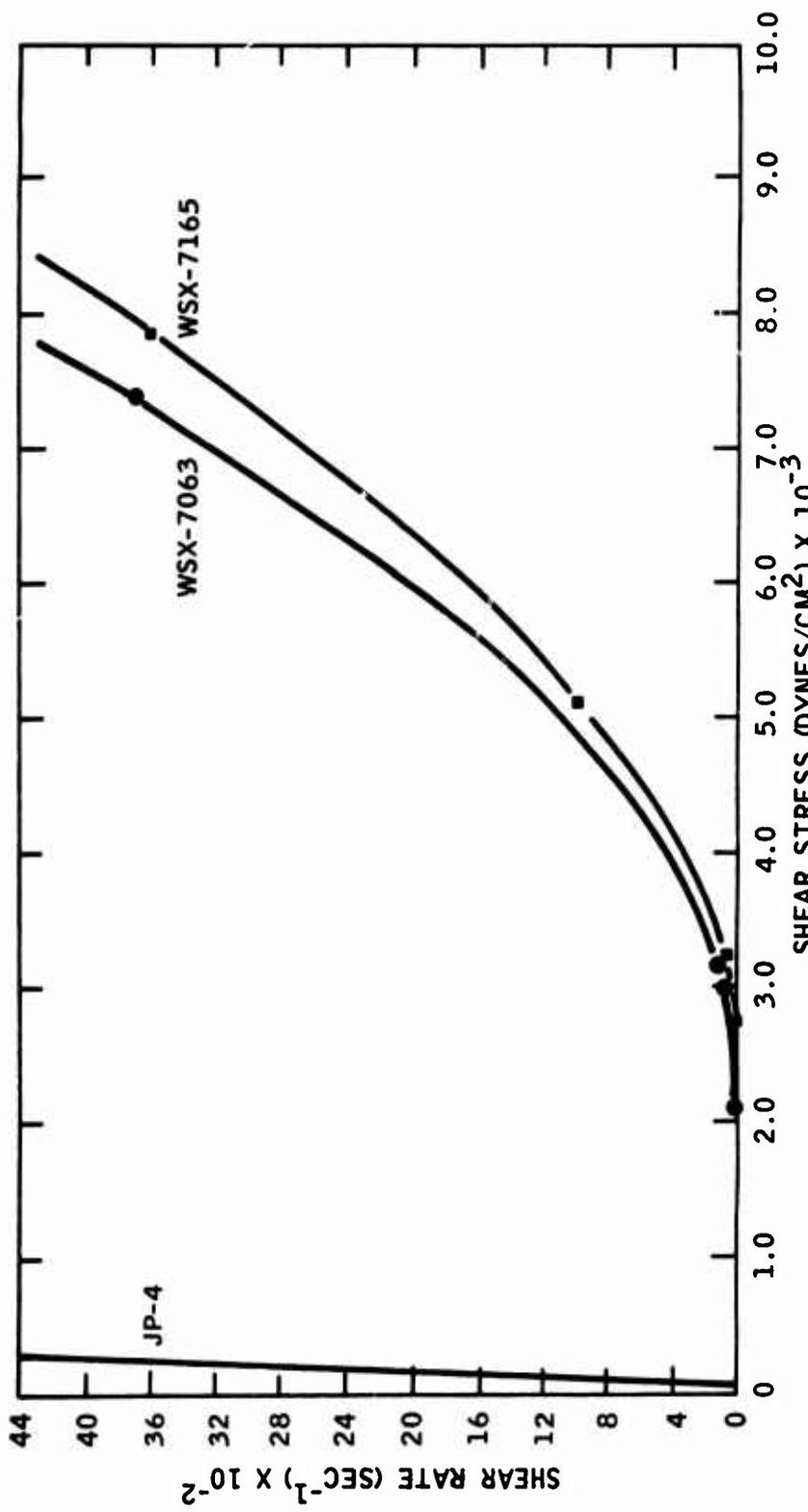
Figure 10. FLOW PROPERTIES OF WSX-7063 AND WSX-7165 AT 77°F

| TABLE 9 |
| EFFECT OF YIELD STRESS ON AMOUNT OF EMULSION WHICH FLOWS THROUGH A 2-INCH BY 1/2-INCH HOLE |

Yield Stress (dynes/cm^2)	Height (inches) of Emulsion After 5 Minutes*
1150	1.375
1325	2.75
1850	4.75
2000 (WSX-7063)	5.50
2300	5.50
2700 (WSX-7165)	5.50

*For all practical purposes,emulsions stopped flowing.

These data show that for an emulsion with a yield stress of 2000 dynes/cm^2 or greater, there will be essentially no flow of the fuel through a hole with dimensions of 2 inches by 1/2 inch under a static head of 5.50 inches. The data further show (see Figure 11) that an emulsion having a yield stress of about 1000 dynes/cm^2 would flow freely through a 2-inch by 1/2-inch hole. It appears that a yield stress of about 1500 dynes/cm^2 is the lower limit for minimizing the flow of emulsions through a .50-caliber bullet hole. However, it should be realized that under sufficient static head, any emulsion will flow through such a hole.

The effect of pressure on the flow of emulsions through a 2-inch by 1/2-inch hole was also investigated. For these studies, an emulsion having a yield stress of 2200 dynes/cm^2 was used. These data are summarized in Table 10.

| TABLE 10 |
| EFFECT OF PRESSURE ON FLOW OF FUEL EMULSION THROUGH A 2-INCH BY 1/2-INCH HOLE |

Psig	Grams/Sec
0.0	0
0.5	43
1.0	62.3

These data show that, if a tank containing a 2-inch by 1/2-inch hole is pressurized, the emulsion will flow from the tank. Nevertheless, the flow rate is still substantially less than what one would get with liquid JP-4.
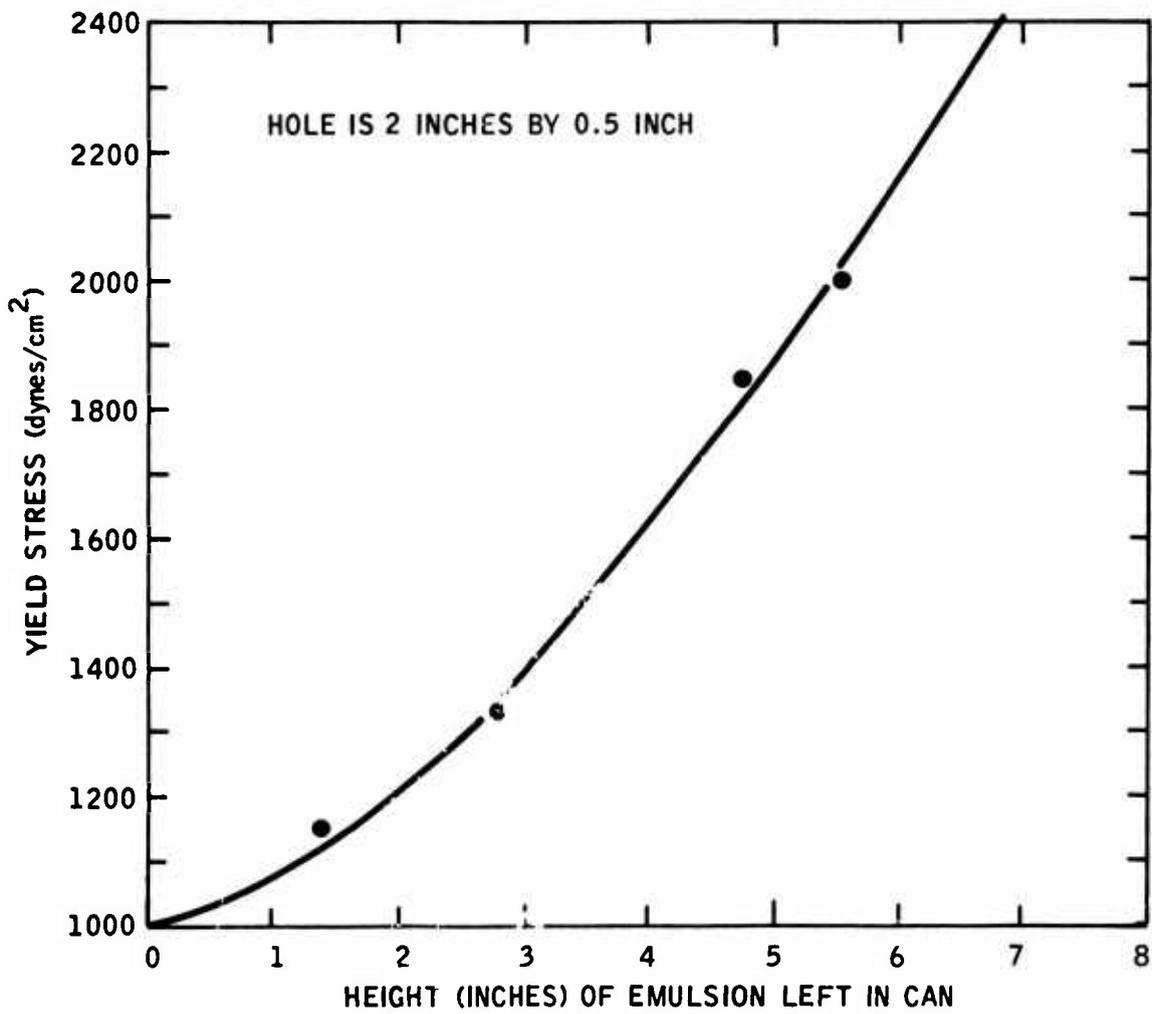
Figure 11. EFFECT OF EMULSION YIELD STRESS ON
FLOW FROM A CAN WITH A HOLE

Stability of WSX-7063 and WSX-7165

Both fuel emulsions, WSX-7063 and WSX-7165, also meet all the contractual requirements set for stability (Table 5). These emulsions have a shelf life of better than 30 days without any separation of JP-4; they are stable with respect to centrifugation at a relative centrifugal field of 500 g's; they are stable with respect to vibration over a frequency range of 0 to 32 cycles per second at a frequency amplitude of 0.4 g for 24 hours. These emulsions were also stable when they were dropped in a partially filled steel bomb from a height of 200 feet onto a concrete surface. There was no appreciable breakdown of the emulsion ($\sim$0.5 percent). The emulsions are stable to freeze-thaw conditions from -20°F to 130°F for WSX-7063 and from -65°F to 130°F and higher for WSX-7165 (Table 5). No separation was observed with these emulsions at 130°F for one week in a closed container. There was no separation of WSX-7165 at -65°F and 160°F after 30 days.

Pumpability

WSX-7063 and WSX-7165 were both pumped using a Blackmer pump and a Vickers pump at ambient temperature, 130°F, and -30°F, without any appreciable breakdown of the emulsion. These pumps are of the vane type, and they rotated at 480 rpm and 1200 rpm, respectively. The Blackmer vane pump pumped the emulsions at 100 gallons per minute without any breakdown, whereas the low output (2 gallons per minute) Vickers vane pump caused about a 3 percent breakdown of the emulsion. It seems that high shear pumps will tend to break down both of these fuel emulsions. Similar results were obtained when we tried to pump these emulsions with a 7000-rpm boost pump from a helicopter tank. It would appear that emulsions can easily be pumped with a low-shear positive displacement pump.

De-emulsification Studies

The effect of shear rate, temperature, and chemicals on the de-emulsification of WSX-7063 and WSX-7165 was investigated to assess the value of these emulsions for logistical hauling. This concept would involve hauling the fuel in the emulsified state from rear areas to forward areas in a combat environment, where the emulsion would be de-emulsified prior to use. These preliminary studies were carried out in the laboratory using a Waring blender. The effect of shear rate on the de-emulsification of WSX-7063 and WSX-7165 at room temperature (77°F) is summarized in Table 11.

31

TABLE 11 EFFECT OF SHEAR RATE ON DE-EMULSIFICATION OF WSX-7063 AND WSX-7165 AT 77°F			
		Wt.% JP-4 Separated	
Variac Setting (Volts)	RPM*	WSX-7063	WSX-7165
55	∿1,230	57.0	-
65	∿1,800	79.5	52.5
75	∿1,950	85.0	61.5
*Increasing RPM means increasing shear rate			

As one might expect, the de-emulsification of both WSX-7063 and WSX-7165 increases with increasing shear rate. It appears, however, that in this test WSX-7165 is more shear-stable than WSX-7063. The data in Table 11 were obtained when the emulsions were sheared for 15 minutes at the rpm levels indicated.

In the evaluation of WSX-7063 in a Lycoming T-55 engine fuel control system, de-emulsification data from the Lycoming report on WSX-7063 were also obtained (Appendix III). These data are summarized in Figures 12 and 13. Figure 12 shows that the emulsion could be completely broken down by shear (97 percent). The emulsion was de-emulsified completely by pumping in the gear pump of the fuel control system at 180 pounds per hour; the pump ran at 4200 rpm. Figure 13 shows the effect of recirculating the emulsion in the gear pump at moderate pump speeds. The emulsion is completely broken down by increasing the percent of the emulsion recirculated in the pump. This appears to represent a very effective way of de-emulsifying this emulsion on a continuous basis. Similar results are expected with WSX-7165.

The effect of temperature on the de-emulsification of WSX-7063 is shown in Table 12.

TABLE 12 EFFECT OF TEMPERATURE ON DE-EMULSIFICATION OF WSX-7063 AND WSX-7165						
	Wt.% JP-4 Separated					
	WSX-7165			WSX-7063		
Time (min)	77°F	-20°F	130°F	77°F	-20°F	130°F
5	61.2	77.0	65.0	84.0	93.0	72.0
10	-	-	-	84.0	95.0	74.0
15	61.5	-	-	80.5	96.0	77.0
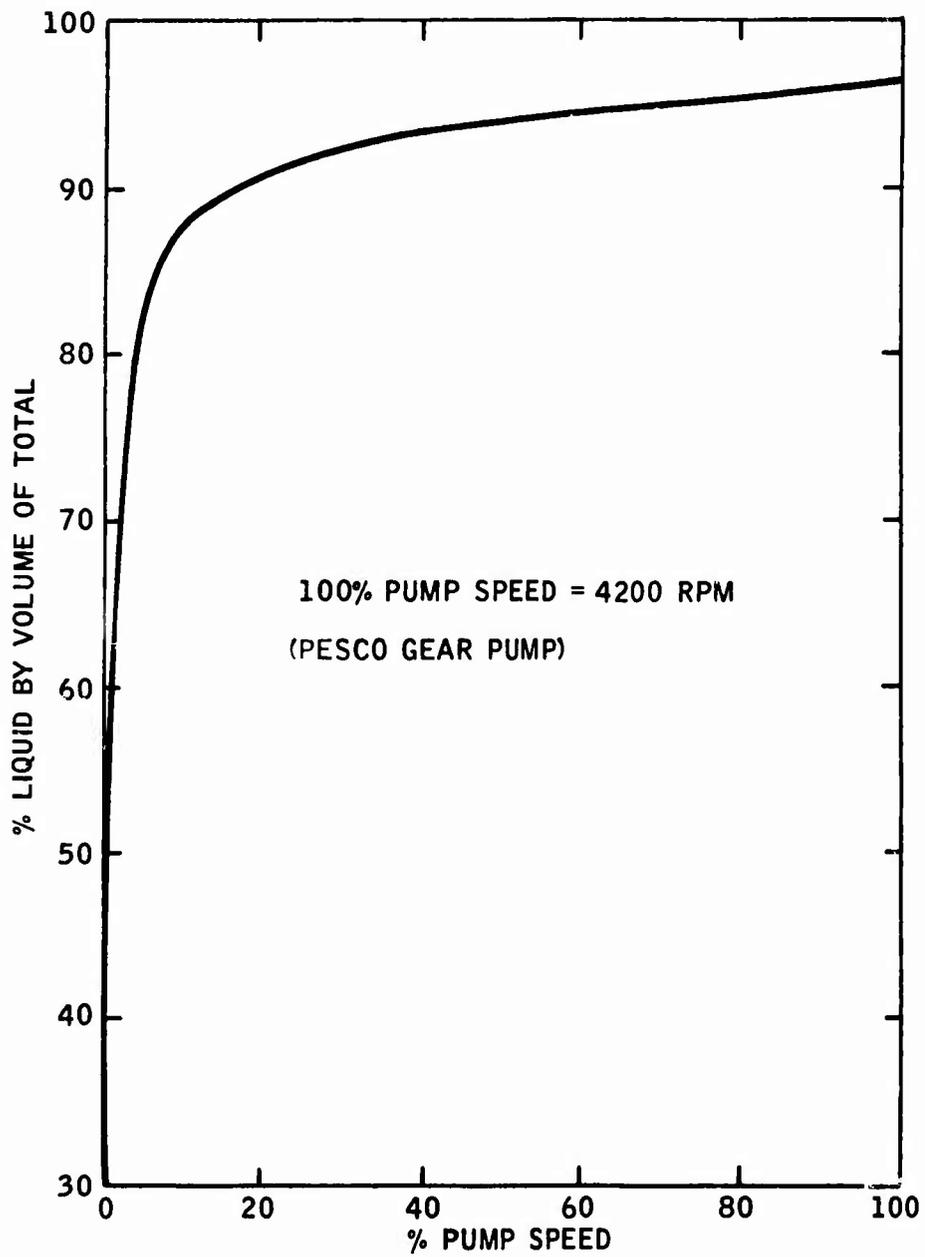
Figure 12. EFFECT OF PUMP SPEED ON DE-EMULSIFICATION
OF WSX-7063

DISCHARGE FLOW RATE OF 180 PPH
(PESCO GEAR PUMP)
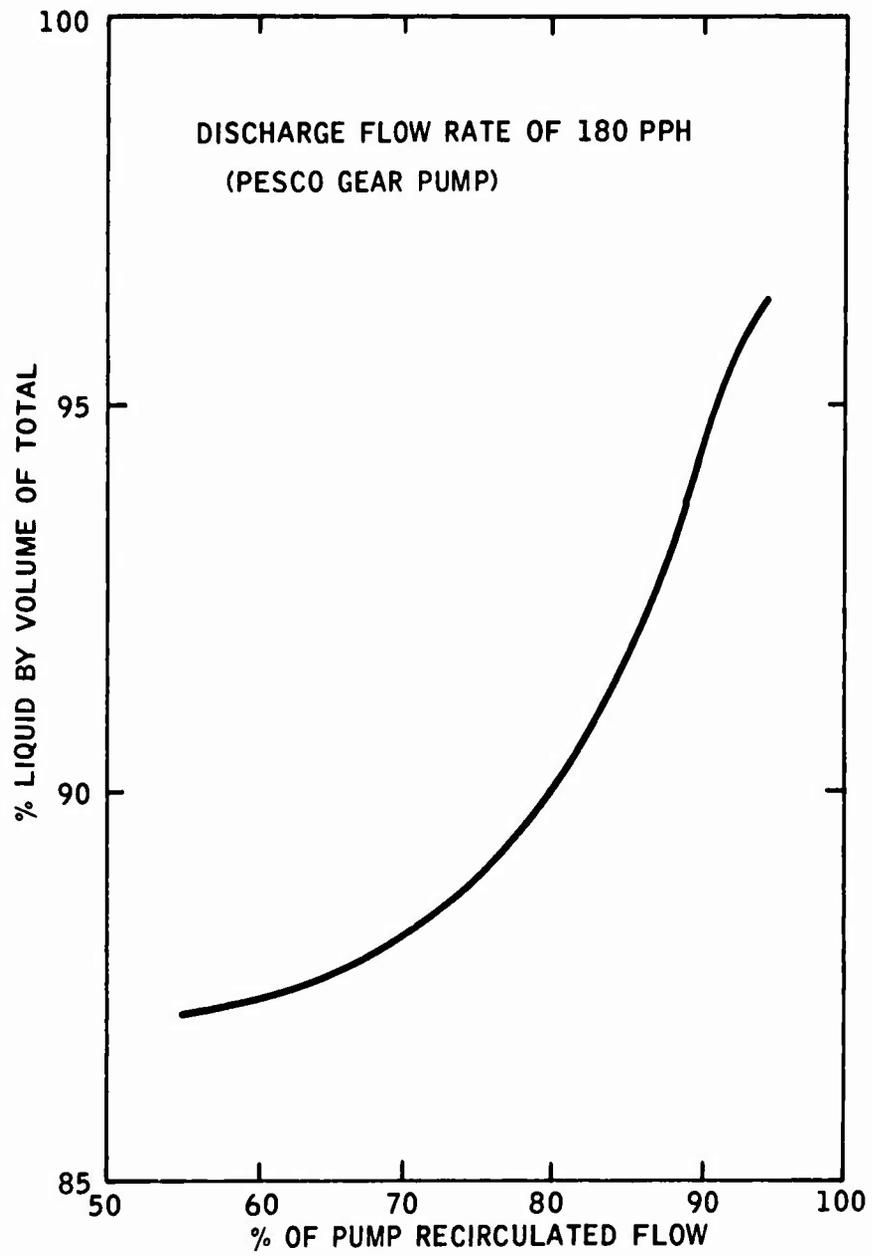
Figure 13. EFFECT OF RECIRCULATION BACK TO THE PUMP
ON DE-EMULSIFICATION OF WSX-7063

These data show that de-emulsification of both WSX-7063 and WSX-7165 is significantly more efficient at -20°F than at either room temperature (77°F) or 130°F. This effect is related to the solubility of the emulsifier; it is least soluble in both phases at -20°F and more soluble in both at the higher temperature. The latter tends to increase the stability of the emulsion, whereas the former tends to decrease its stability.

In our studies on the effect of chemicals on the de-emulsification of WSX-7063, two general classes were investigated: a surfactant and a polar solvent. These results have been summarized in Table 13.

TABLE 13
EFFECT OF CHEMICALS ON THE DE-EMULSIFICATION OF WSX-7063

		% JP-4 Separated			
		Triton X-102*		Isopropyl Alcohol	
Time (min)	0.0% Chemical	0.25%	1.0%	0.25%	2.0%
5	84.0	86.5	-	82.0	-
10	84.0	87.0	-	80.5	-
15	80.5	89·0	97.0	81.5	97.0

*Alkylaryl polyether alcohol

These data show that, even at the 0.25 percent level, the surfactant (Triton X-102), which upsets the HLB tends to increase the efficiency of de-emulsification of WSX-7063. At the 1.0 percent level, Triton X-102 completely de-emulsified WSX-7063. On the other hand, isopropyl alcohol at the 0.25 percent level has no appreciable effect on the de-emulsification of WSX-7063. However, if 2.0 percent of the isopropyl alcohol is used, complete de-emulsification of WSX-7063 can be achieved.

Similar chemical de-emulsification studies were carried out on WSX-7165. In general, these studies showed the same trend as those observed with WSX-7063. These data are summarized in Table 14.

TABLE 14
EFFECT OF CHEMICALS ON THE DE-EMULSIFICATION OF WSX-7165

	Wt% Separation				
	Triton X-102		Isopropyl Alcohol		
0.0% Chemical	0.50%	1.0%	1.0%	2.0%	5.0%
61.5	74.0	-	67.0	76.0	100

JP-4 Recovered From De-emulsification

The JP-4 recovered from the de-emulsification of WSX-7063 and WSX-7165 by shear was completely evaluated and compared with a typical JP-4 prior to emulsification. These results are summarized in Table 15.

TABLE 15

PROPERTIES OF MIL-T-5624 G JP-4 AND JP-4 RECOVERED FROM THE DE-EMULSIFICATION OF WSX-7063 AND WSX-7165

Distillation	Typical JP-4*	JP-4 Recovered from Emulsion	
		WSX-7063	WSX-7165
Initial boiling point, °F	-	250	210
10% Fuel evaporated		266	240
20% Fuel evaporated	20% min at 290°F	273	252
End point, °F	485	490	495
Residue, Vol Percent	1.5	1.5	1.5
Existent gum, mg/100 ml	7 max	2.0	2.0
Total potential residue, 16 hour aging, mg/100 ml	14 max	8.0	7.0
Sulfur, total, percent weight max	<200 ppm	<200 ppm	<200 ppm
Reid vapor pressure, 100°F psi	2.4	1.9	2.0
Heating value heat of combustion (BTU/lb min)	20,345	19,991	19,995
Copper strip corrosion, ASTM classification	1	1	1
Water separometer index	85 min	15	15
4-Ball wear (7.5 kg, 130°F, 1800 rpm, 1 hr)	0.450	0.436	0.449
Corrosion Data**(mg/in^2)			
Aluminum	0.0	0.0	0.0
304 Stainless Steel	+0.3	+0.3	+0.1
Titanium Alloy	+0.4	0.0	0.0
Bronze	0.2	0.3	0.1
Mild Steel	0.2	0.2	0.0

*A JP-4 that meets MIL-T-5624 G
**One week at 130°F

These data show that the de-emulsified fuel from both WSX-7063 and WSX-7165 meets all the specifications of JP-4 (MIL-T-5624 G) with the exception of water separometer index. The water separometer index for the de-emulsified fuel is 15 (the WSI for JP-4 is 85). This low water separometer index is due to the very small residual emulsifier remaining in the de-emulsified JP-4.

Effect of Static Electricity on the Emulsions

The effect of static electricity on WSX-7063 and WSX-7165 was investigated to ascertain whether static electricity has an affect on emulsion stability and whether these emulsions have a tendency to build up a static charge. To study the effect of the former, a field of 10 kilovolts was imposed on the emulsion as it flowed through a capillary at a constant flow rate. No change in the equilibrium pumping pressure was observed, nor was there any apparent change in the appearance of the egressed emulsion. Figure 14 shows that the electric field had no effect on the evaporation rate of the emulsion.

To determine if WSX-7063 or WSX-7165 would have any measurable tendency to produce static electricity, our modified charge tendency test was used. The system was set up with a radio frequency receiver equipped with a probe to detect the buildup of static electricity. There was no indication of any charge buildup with either of the emulsions. This is not surprising, since both of the emulsions are quite conductive in comparison to JP-4 (1.6×10^{-6} Mhos/cm for the emulsions; 10^{-13} Mhos/cm for JP-4).

Preliminary Systems Evaluation of the Emulsions

Both WSX-7165 and WSX-7063 were investigated in our rheology program, which was designed to evaluate the atomization properties of fuel emulsions. In addition to these two emulsions, two other emulsions formulated in this program were also evaluated from a rheological standpoint. These emulsions utilized either ethylene glycol-water or ethylene glycol-formamide-urea as the continuous phase mixtures. The compositions and properties of these two emulsions are shown in Table 16.

TABLE 16 COMPOSITION AND PROPERTIES OF TWO OF THE EMULSIONS EVALUATED IN THE RHEOLOGY PROGRAM		
Composition		
	Weight Percent	
	A	B
Ethylene glycol	1.14	1.60
Urea	-	0.575
Formamide	-	0.033
Water	1.36	-
Span 80	0.90	0.14
Tween 80	0.41	0.36
JP-4	97.0	97.0

TABLE 16 CONTINUED		
COMPOSITION AND PROPERTIES OF TWO OF THE		
EMULSIONS EVALUATED IN THE RHEOLOGY PROGRAM		
Properties		
	A	B
Yield Stress, Dynes/cm^2	1075	1900
Stability (Vol % Separation)		
● 30 days at room temp	0.0	0.0
● Six freeze-thaw cycles (-20°F to 130°F)	15.0	1.0

The program on the rheology of fuel emulsions was to evaluate the performance of fuel emulsions in nozzles. The specific objectives of this program were:

- Determine whether the emulsions are viscoelastic.

- Determine the drop-size distribution of the emulsions as they come out of the nozzle.

- Determine the extent of emulsion breakdown as it passes through the nozzle.

The four emulsions described above were evaluated in the thrust rheometer fitted with the actual helicopter nozzles. These nozzles are:

- Lycoming T-53 and T-55 Engine Nozzles

- Double-Staged G.E. T-64 Engine Nozzle

- Allison T-63 Engine Nozzle

In addition to an evaluation of the emulsions in these nozzles, studies were also carried out using a straight capillary. Studies were carried out with the capillary because it is more suitable for a precise theoretical description of the behavior of the emulsions than the nozzles. The results obtained in the capillary, however, are also valid for the nozzles.

On the basis of the studies carried out in this program on four emulsions in four nozzles and one straight capillary, the following conclusions were reached:

(1) At any given pressure, the flow rate and reaction thrust for the emulsions and JP-4 are identical. This demonstrates that the fuel emulsions are not viscoelastic under the nozzle conditions. In general, these conditions appear to be turbulent, as indicated by the experimental data, which show that the pressure is proportional to the square of the flow rate.
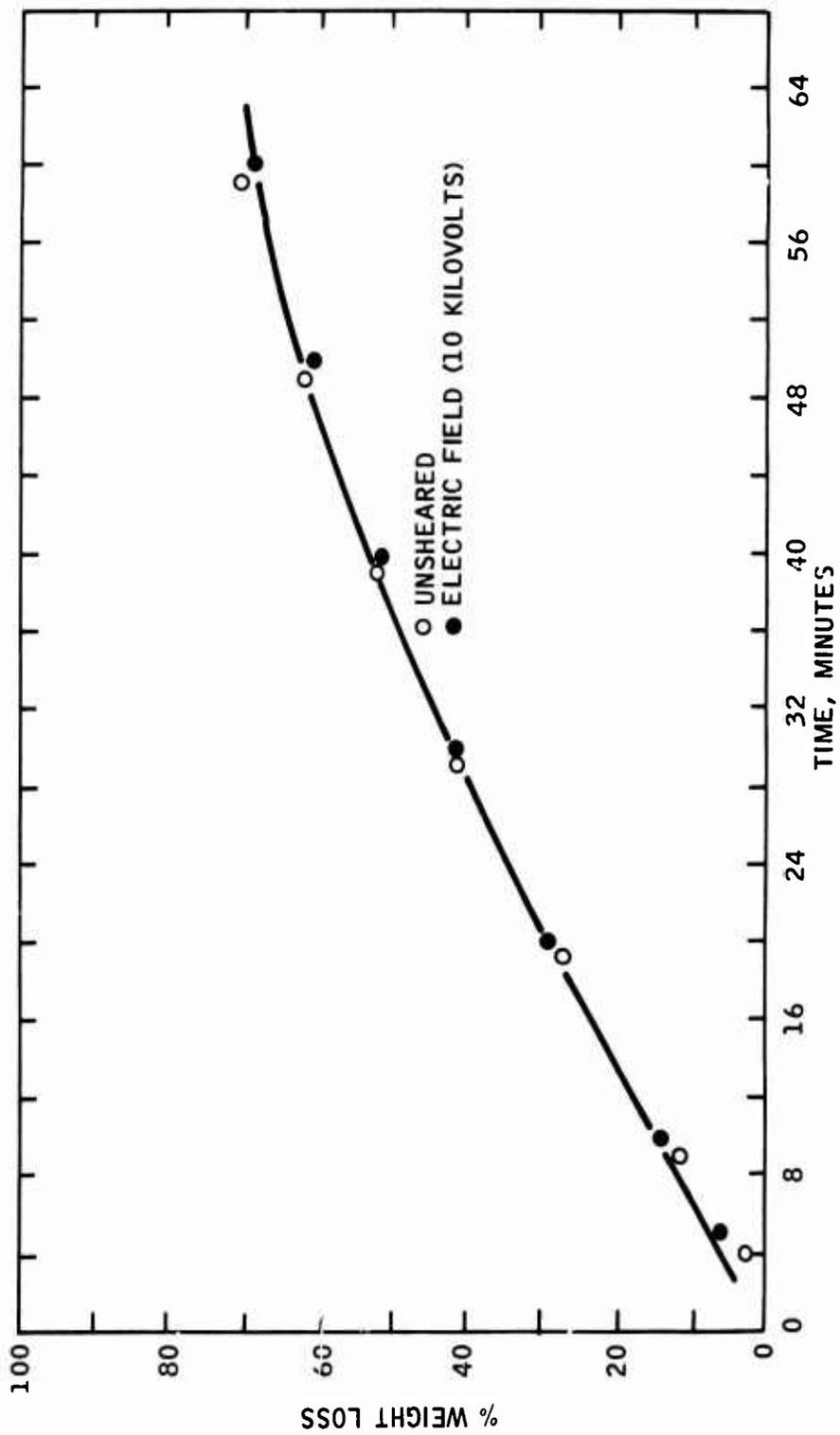
Figure 14. EFFECT OF ELECTRIC FIELD ON EVAPORATION OF WSX-7063 AT 77°F.

39

(2) All the emulsions evaluated broke down when passed through the four aircraft nozzles and capillary of similar pressure drop, but the degree of breakdown varied with the chemistry of the emulsion. Breakdown of the emulsion ranged from 97 percent separation (the ethylene glycol-water) to as low as 80 percent (the nonaqueous emulsions) at flow rates and pressures of 125 percent of the nozzle rating. At lower pressure drops, the breakdown decreased to the vanishing point at about 5 psi. The presence of unbroken emulsion in the spray from the nozzle could lead to undesirable combustion characteristics.

(3) In all cases, the drop size distribution of the emulsion passing through the nozzle was essentially identical to that of unthickened JP-4. This indicates that atomization of the emulsion in the nozzle is not a problem.

The main difficulty encountered in carrying out these studies involved severe plugging of the nozzles and capillary in the fuel emulsions. This problem, however, was overcome by filtering the emulsions through a cloth filter below a shear rate of 30,000 sec^{-1} prior to passing them through the nozzles. Plugging was not encountered when unthickened JP-4 was evaluated in the nozzles and capillary.

Detailed experimental data for this program are summarized in Appendix II.

WSX-7063 was also evaluated in a Lycoming T-55 engine fuel control system. There was no rust, bacterial or fungal growth, or sticking of valves, linkages and other moving parts in this test. In these runs, the fuel system response to the fuel emulsion was essentially the same as it was with the reference fuel. This work is discussed in detail in Appendix III.

WSX-7165 fuel emulsion has been made available to Lycoming for similar evaluations. The tests, however, have not as yet been run.

Scale-up of WSX-7063 and WSX-7165

About 6,000 gallons of WSX-7063 were prepared in 1,000-gallon batches. The quality of the material so produced was quite variable from batch to batch. The problems encountered were mainly associated with emulsion from some batches breaking down in transit; emulsion from other batches, however, has remained stable over several months. These problems were mainly due to inadequate mixing in the plant equipment and too rapid addition of the JP-4.

There have also been three 1,000-gallon batches of WSX-7165 produced to date. The first large scale batch of WSX-7165 was of poor quality; it broke down in transit. The second two batches were of acceptable quality, with all the first batch having arrived at its destinations without any sign of breakdown. The second batch has not as yet been

shipped. The WSX-7165 from the two batches is being used for evaluations in the Lycoming fuel control system, in a G.E. test, and for further testing by the Army. Even though the WSX-7165 prepared in the last two runs was of acceptable quality, its quality still was not as good as that of the laboratory-produced material.

Miscellaneous Items

As our experimental program progressed, it became obvious that there were a number of items that required investigation although they were outside the framework of the contract. Investigation of these items was necessary for success of the program. These included the detection and estimation of the degree of contamination in the emulsion, determination of the droplet size of the disperse phase of the emulsion, and a simple, uniform technique for the determination of yield stress for all candidates. Techniques for all of these have been developed. The particle size of WSX-7063 was measured using an ultraviolet fluorescence microscopic technique. The photographs show the polyhedric nature of the disperse phase of the emulsion; the WSX-7063 sample investigated had a particle size ranging from 1 to 2 microns. Detailed discussions of these items along with photographs appear in Appendix IV.

Parameters Affecting Formamide Emulsions

The effect of the emulsifier HLB on the yield stress and stability of formamide emulsions was investigated in this program. Table 17 summarizes the effect of HLB on the yield stress of these emulsions.

TABLE 17 EFFECT OF EMULSIFIER HLB ON THE YIELD STRESS OF FORMAMIDE EMULSIONS	
HLB	Yield Stress $(dynes/cm^2)$
11	1300
12	1900
13	1850
14	2200

The data show that as the HLB is increased from 11 to 12 and from 13 to 14, the yield stress is increased dramatically. Between HLB 12 and 13, however, the yield stress remains essentially constant. These results can be rationalized as follows. Emulsions are stabilized against coalescence by the formation of an interfacial film consisting of the emulsifier which is absorbed onto the surface of the dispersed droplets. The continuous phase is then tightly bound to the surface of this interfacial film (Reference 13).

As the hydrophile concentration of the emulsifier is increased (increasing emulsifier HLB), the hydrophile concentration in the interfacial film increases while the concentration of the lipophile in the interfacial film decreases. Increasing the concentration of the hydrophile in the interfacial film produces a stronger interfacial film because of the greater polarity of the hydrophile relative to the lipophile (Reference 13). The increased strength of the interfacial film manifests itself in terms of increased emulsion yield stress. This, therefore, accounts for the observed increase in emulsion yield stress in going from HLB 11 to 12 and in going from HLB 13 to 14.

The observed constancy of emulsion yield stress in going from HLB 12 to 13 can be explained as follows. HLB 12 is the required HLB for the system and represents the point where surface coverage and interfacial film strength are at an optimum and emulsion stability is at a maximum (References 13 and 6). That is, at HLB 12, surface coverage of the JP-4 droplets by emulsifier and interfacial film strength are such that the energy barrier to coalescence is a maximum (Reference 13). At optimum surface coverage and interfacial film strength, which is a minimum potential energy condition, the composition and thus the interfacial film strength are unaffected by a slight change in the hydrophile concentration, as is involved in going from HLB 12 to 13. Therefore, since the composition and thus the interfacial film strength are not changed in going from HLB 12 to 13, the yield stress of the emulsion remains ur changed.

As the hydrophile concentration, however, is further increased, as is involved in going from HLB 13 to 14, the composition and strength of the interfacial film are again altered. In going from HLB 13 to 14, the hydrophile concentration in the interfacial film is increased and the lipophile concentration is decreased. This causes (1) a decrease in surface coverage and (2) an increase in interfacial film strength (Reference 13). This is due, as stated before, to the larger size and greater polarity of the hydrophile relative to the lipophile. Therefore, the observed increase in yield stress in going from HLB 13 to 14 is due to an increase in the interfacial film strength caused by an increase in the concentration of the hydrophile in the interfacial film. The change in surface coverage does not affect emulsion yield stress, but rather emulsion stability. A decrease in surface coverage tends to decrease emulsion stability.

Studies were also carried out t determine the effect of the ratio of formamide to emulsifier on the yield stress and stability of the emulsions. In these studies, the JP-4 content was held constant at 97.0 percent. The results of these studies with respect to yield stress are summarized in Table 18.

42

TABLE 18		
EFFECT OF RATIO OF FORMAMIDE TO EMULSIFIER		
(HLB 11) ON YIELD STRESS		
Ratio of Formamide to Emulsifier (HLB 11)	Stability @ 130°F (vol % separation)	Yield Stress (dynes/cm^2)
1.0	1.0	1300
2.0	0.50	1300
5.0	4.0	1025

These studies show that when the emulsifier HLB is 11, the yield stress is unaffected by increasing the ratio of formamide to emulsifier from 1.0 to 2.0. This indicates that the interfacial film strength and composition are unaffected by the change. From these results, it can also be inferred that there was no change in surface coverage, since the composition of the film was not altered. Therefore, no decrease in stability is to be expected; if anything, there should be an increase in stability. Since enough emulsifier is present for the same surface coverage, increasing the continuous phase will increase emulsion stability by reducing the interfacial film strain due to the close packing of the emulsion droplets. The data above directionally support this conclusion and the data summarized in Table 19 show this effect more clearly.

TABLE 19	
EFFECT OF RATIO OF FORMAMIDE TO EMULSIFIER	
(HLB 13) ON EMULSION STABILITY	
Formamide/Emulsifier (HLB 13)	Stability @ 130°F Vol % Separation
1.0	2.0 - 3.0
2.0	0.25 - 0.50

The decrease in yield stress observed when the ratio of formamide to emulsifier was increased from 2.0 to 5.0 (Table 18) is due mainly to (1) a decrease in the concentration of the hydrophile in the interfacial film and (2) a reduction in packing of the disperse phase due to an increase in the continuous phase level. The effect of the former is to weaken the interfacial film and thereby cause a decrease in yield stress. The effect of the latter is to reduce the rigidity of the interfacial film which also tends to cause a decrease in the yield stress. Because interfacial film strength was reduced on increasing the ratio of formamide to emulsifier from 2.0 to 5.0 but not from 1.0 to 2.0, one can thus infer that in the former case the surface coverage of the dispersed droplets was also

decreased. A decrease in emulsion stability would therefore be expected because of a weaker interfacial film and decreased surface coverage. This is shown by the stability data for the above-mentioned emulsions in Table 20.

TABLE 20 EFFECT OF FORMAMIDE TO EMULSIFIER RATIO ON EMULSION STABILITY	
Formamide/Emulsifier	Stability at Room Temperature
1.0	Stable after 45 days
2.0	Stable after 45 days
5.0	Broken after 30 days

On the basis of these studies, formamide emulsions having a formamide to emulsifier ratio of two were prepared and characterized. The emulsifiers used were Span 80 and Tween 80 blended to HLB 12 and 13. The properties of these emulsions along with their compositions are shown in Table 21. These data show that at an emulsifier HLB 12 or 13, increasing the formamide to emulsifier ratio decreases the yield stress of the emulsion and significantly increases its stability. The stability of these emulsions in comparison to WSX-7063 (Table 21) shows that increasing the formamide to emulsifier ratio from 1.0 to 2.0 significantly increases the stability of the emulsion. This is further demonstrated by the evaporation rates of these emulsions under dynamic conditions at 130°F (Figure 15). In this test, the emulsions containing 2 percent formamide show a 40 percent reduction in evaporation rate (at 50 percent weight loss) relative to WSX-7063 (1.5 percent formamide) fuel emulsion. In all cases, the other properties of the emulsions are unchanged (compatibility with metals and elastomers).

Increasing the emulsifier HLB from 12 to 13 in the 2 percent formamide emulsions only increased the yield stress from 1600 dynes/cm^2 to 1725 dynes/cm^2; the other properties of the emulsion were unaffected.

As shown by the data in Table 21, when the HLB of the emulsifier was 12 or 13, increasing the formamide to emulsifier ratio from 1.0 to 2.0 caused a decrease in emulsion yield stress. However, when the HLB of the emulsifier was 11, the yield stress of the emulsion was unaffected by increasing the formamide to emulsifier ratio from 1.0 to 2.0 (Table 18). The different response of these systems to the same change in the ratio of formamide to emulsifier can be rationalized in the following manner. At emulsifier HLB 12 or 13, the interfacial film generated has a higher hydrophile concentration than that generated with emulsifier HLB 11. This is substantiated by the fact that the emulsion yield stress of the former (HLB 12 or 13) is greater than the yield stress of the latter (HLB 11). Because of this, increasing the ratio of formamide to emulsifier favors greater desorption of hydrophile (more soluble in the continuous phase)

TABLE 21				
EFFECT OF CONTINUOUS PHASE ON EMULSION PROPERTIES				

	Weight Percent		
	WSX-7063	B	C
Formamide	1.5	2.0	2.0
Span 80	0.42	0.28	0.19
Tween 80	1.08	0.72	0.81
JP-4	97.0	97.0	97.0
Formamide/Emulsifier Ratio	1.0	2.0	2.0
Emulsifier HLB	12.0	12.0	13.0
	Properties		
	WSX-7063	B	C
Yield Stress, Dynes/cm^2	2000	1600	1725
Stability (Vol % Separation)			
• 30 Days at Room Temperature	0.0	0.0	0.0
• Six 6-Hr Cycles at 130°F	2.0	0.50	0.50
• Six 16-Hr Cycles at -20°F	0.0	0.0	0.0
• After Centrifugation For 1 Hr at 500 g (RCF)	0.0	0.0	0.0
Vibration Stability After 8 Hrs At 6 Cycles/Sec and 2 g	No Change	No Change	No Change
Gross Heat of Combustion, BTU/lb	19,170	19,039	19,112
Ash Content, Wt %	<0.005	<0.005	<0.005
Sulfur Content	<200 ppm	<200 ppm	<200 ppm
Reid Vapor Pressure	1.9	2.0	2.0
Compatibility - Corrosion (One Week at 130°F) Of:			
Aluminum	0.0 mg/in^2	+0.1 mg/in^2	0.0 mg/in^2
Bronze	8.5 mg/in^2	6.2 mg/in^2	~7.0 mg/in^2
304 Stainless	0.0 mg/in^2	0.0 mg/in^2	0.0 mg/in^2
Titanium	0.1 mg/in^2	0.0 mg/in^2	0.0 mg/in^2
Swelling of (% Increase):			
Neoprene	19	46	42
Butyl Rubber	148	150	157
Buna N (MS-902)	22	22	22
Buna N (MS-29513)	43	44	47
210 Silicone	87	89	92
Viton	5.0	5.0	4.5
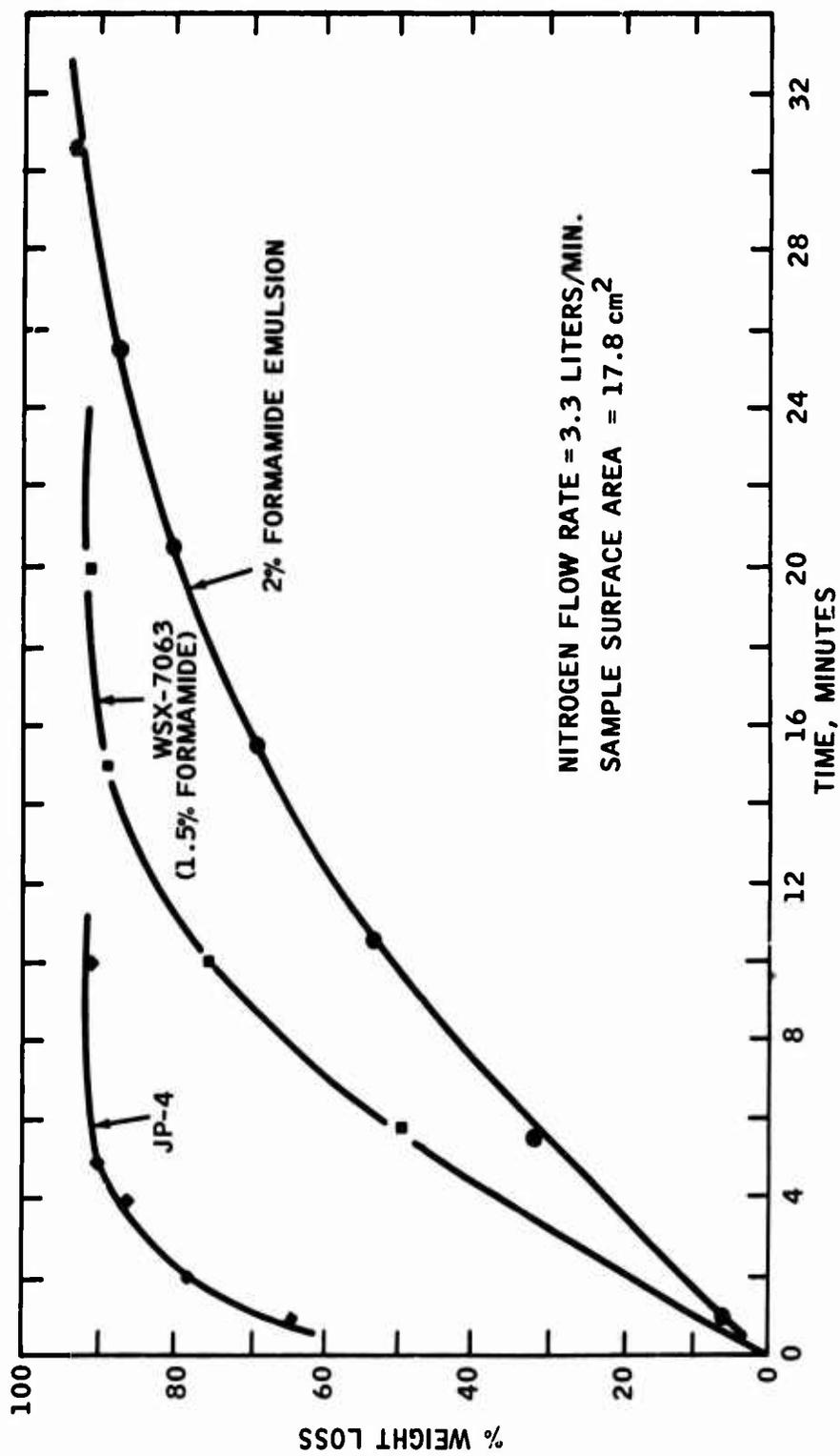
Figure 15. EFFECT OF CONTINUOUS PHASE LEVEL ON EVAPORATION RATES OF FORMAMIDE EMULSIONS AT 130°F

46

from the interfacial film containing the higher concentration of hydrophile. Since this is the interfacial film formed using emulsifier HLB 12 or 13, the response of this system to the change in formamide to emulsifier ratio is expected to be greater than that for the system using emulsifier HLB 11. At HLB 12 or 13, increasing the ratio of formamide to emulsifier from 1.0 to 2.0 is, therefore, sufficient to cause some desorption of hydrophile from the interfacial film, whereas at emulsifier HLB 11 it is not sufficient to cause any desorption of the hydrophile. Therefore, the decrease in the concentration of the hydrophile in the interfacial film formed with emulsifier HLB 12 or 13 causes a decrease in the strength of the interfacial film and thus a decrease in emulsion yield stress. One can infer from this that surface coverage is at the same time increased, since the smaller lipophile replaces the larger hydrophile in the interfacial film. Reduced film strength favors reduced emulsion stability, while increased surface coverage favors increased emulsion stability. Since increased emulsion stability was observed (Table 21), it is, therefore, apparent that reduced interfacial film strain (due to a higher continuous phase level) and increased surface coverage more than offset the decrease in interfacial film strength. Stated another way, at reduced interfacial film strain and greater surface coverage a somewhat weaker interfacial film can be tolerated without sacrificing emulsion stability (Reference 13).

Surface coverage and interfacial film composition are phenomena which are dependent on the number of emulsifier molecules. However, in the above discussions, emulsion properties related to surface coverage and interfacial film composition are explained in terms of weights and weight ratios of continuous phase and emulsifier. This is quite satisfactory, since these studies involved the use of a single emulsifier system, Span 80 and Tween 80. It is obvious, however, that the relationships developed on a weight or weight ratio basis for a single emulsifier system would have to be changed to a mole or mole ratio basis when applied to other emulsifier systems. This, of course, requires that the molecular weights of the emulsifiers be known.

Other Emulsion Systems

Several emulsions containing ethylene glycol-water as the continuous phase were prepared (Table 22). The one containing Span 80 and Tween 80 looked most promising. The properties of this emulsion along with the other less promising ones are summarized in Table 22. The main deficiencies of this emulsion were the extent of separation after six freeze-thaw cycles between -20°F and 130°F (5.0 percent) and the extent of separation (50 percent) in the vibration test (6 cycles per sec and 2 g amplitude). The emulsions were, however, compatible with the elastomers and materials of construction tested. Figure 16 shows evaporation loss data for this emulsion relative to WSX-7063. The data show that WSX-7063 is significantly more stable.

Emulsions were also prepared using pure glycerol or ethylene glycol as the continuous phase and a combination of diethanolamine sulfate and lauryl alcohol as the emulsifiers. The properties of the glycerol

47

TABLE 22
PROPERTIES OF ETHYLENE GLYCOL-WATER EMULSIONS

	Weight Percent		
	A	B	C
Ethylene Glycol	1.30	1.20	0.91
Water	0.70	0.80	1.09
Span 80	0.31	0.19	0.19
Tween 80	-	-	0.91
JP-4	97.0	97.0	97.0
Triton X-405	-	0.28	-
Triton X-100	-	0.53	-
Brij 35SP	0.69	-	-

	Properties		
	A	B	C
Yield Stress, Dynes/cm^2	2300	2000	1225

Stability (Vol % Separation)

	A	B	C
• 30 Days at Room Temperature	0.0	0.0	0.0
• Six 6-Hr Cycles at 130°F	0.5*	0.0*	5.0
• Six 16-Hr Cycles at -20°F	Broke*	Broke*	0.0
• After Centrifugation For 1 Hr at 500 g (RCF)			1.0
Vibration Stability After 8 Hrs At 6 Cycles/Sec and 2 g	-	-	50% Separation
Gross Heat of Combustion, BTU/lb	-	-	19,276
Four-Ball Wear (mm)	-	-	0.575
Ash Content, Wt %	-	-	0.005
Sulfur Content	-	-	200 ppm
Reid Vapor Pressure	-	-	2.0

Compatibility Corrosion
(One Week at 130°F) Of:

	A	B	C
Aluminum	-	-	0.1 mg/in^2
Bronze	-	-	0.2 mg/in^2
304 Stainless	-	-	0.0 mg/in^2
Titanium Alloy	-	-	0.0 mg/in^2

Swelling Of:

	A	B	C
Neoprene	-	-	39
Butyl Rubber	-	-	147
Buna N (MS-902)	-	-	20.0
Buna N (MS-29513)	-	-	40
Silicone	-	-	88
Viton	-	-	3.5

* After one cycle
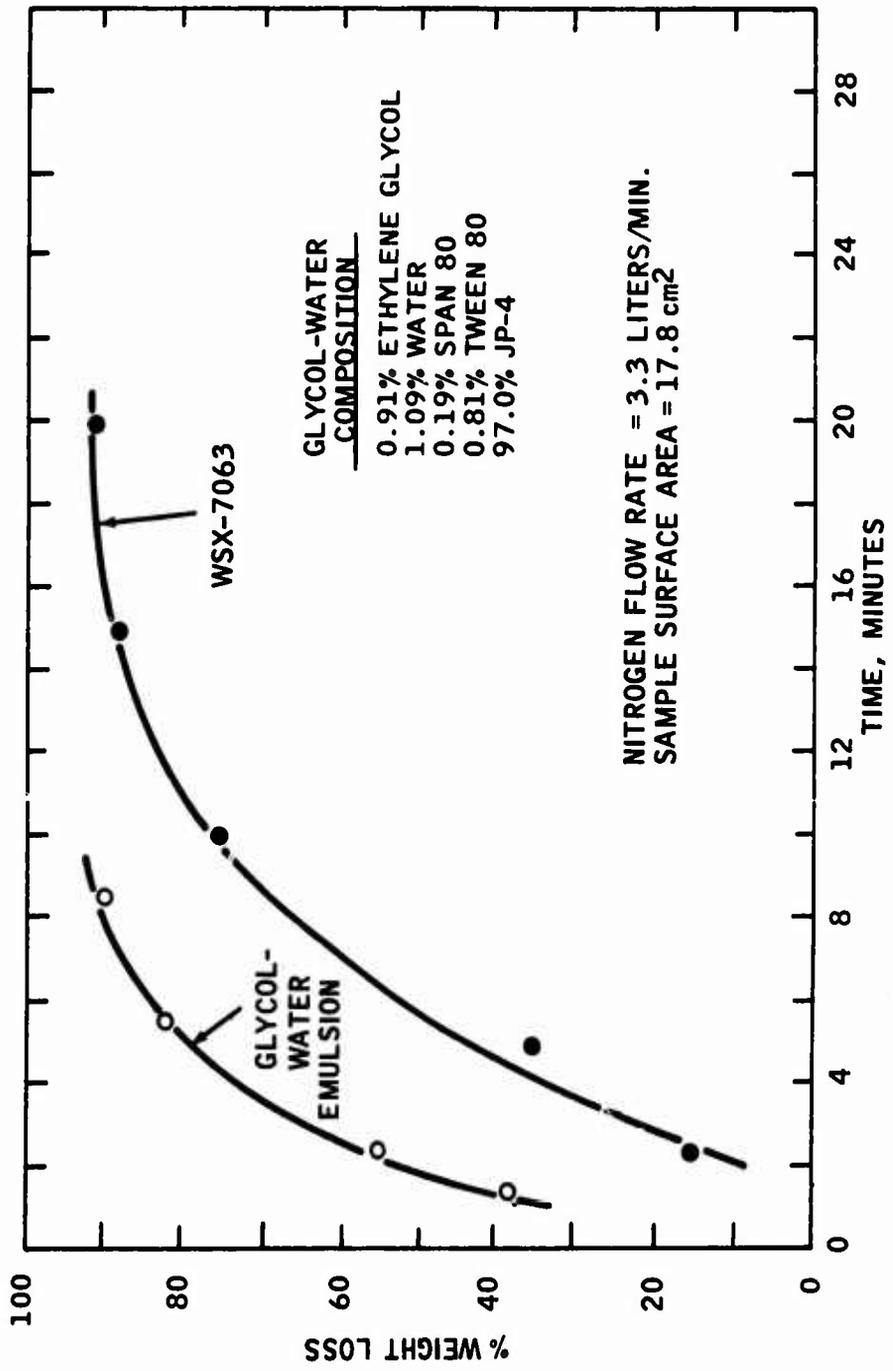
Figure 16. EVAPORATION RATE OF WATER-GLYCOL EMULSION AT 130°F

49

emulsion are shown in Table 23. This emulsion had a yield stress of 2400 dynes/cm^2, but had 15 percent separation of JP-4 after six freeze-thaw cycles. Since sulfates have been linked with excessive turbine corrosion, emulsions containing these would have to possess unusual stability or yield stress retention and storage stability to warrant serious consideration as a main candidate. Because they did not have these properties, the sulfate emulsifiers were not pursued further. These emulsions were compatible with materials of construction. No corrosion occurred with either aluminum, bronze, 304 stainless steel, or titanium alloy after one week at 130°F (Table 23).

Urea Containing Emulsions

During the course of this program, we found that the addition of urea to ethylene glycol, glycerol, and formamide produced more stable emulsions. The effect of urea on the stability and other properties of formamide emulsions at two levels or urea is shown in Table 24. Data for WSX-7063, which contains no urea, are shown for the purpose of comparison. The emulsions containing urea had a maximum of 0.5 percent separation after six freeze-thaw cycles as compared to 2 to 3 percent for WSX-7063. The effect of urea on stability is further substantiated by evaporation loss data (Figure 17). On the basis of these data, the urea-formamide emulsions are significantly more stable than either WSX-7063 or its 2 percent formamide modification. These data, which are shown in Figure 17, show a 65.5 percent reduction in evaporation rate (at a 50 percent weight loss) for the urea-formamide emulsion relative to WSX-7063. The urea-formamide emulsions show a 37.5 percent reduction in evaporation rate relative to the 2.0 percent formamide emulsions. The addition of the urea does not adversely affect any of the other emulsion properties investigated (Tables 24 and 25).

The ability of urea to induce emulsification of JP-4 with ethylene glycol was also investigated. It was found that urea in ethylene glycol allows one to form a nonaqueous emulsion using Span 80 and Tween 80 as emulsifiers. Without the presence of urea in ethylene glycol, emulsification with JP-4 cannot be induced with these emulsifiers. These emulsions have been characterized by high initial yield stresses, good thermal stability, and noncorrosiveness to aluminum, stainless steel, titanium alloy, bronze, copper, and mild steel (Table 26). These emulsions, however, require considerable care in their preparation. This is probably due to (1) the very high viscosity which develops early in the emulsification process and (2) the low potency of the emulsifiers (Span 80 and Tween 80) with respect to this system.

Emulsifiers other than Span 80 and Tween 80 were also investigated, and several showed promise. These emulsifiers are shown in Tables 27 and 28. Promising emulsions were prepared when we used a combination of emulsifiers consisting of Atlas IL-850 and IL-851 emulsifiers. The properties of these emulsions are shown in Table 27. The emulsions had one drawback: they tended to separate to the extent of 2 percent in our vibration test. This suggested that their stability in transit would not be acceptable. Table 28 shows the data on formamide emulsions containing a combination of the esters of ethoxylated polyols (Atlas IL-850, -851 and -852). The emulsions had rather high yield stress values on the whole.

50

TABLE 23
PROPERTIES OF GLYCEROL EMULSION

	Weight Percent
Glycerol (or Ethylene Glycol)	1.0
Sipon LD (Diethanolamine Sulfate)	1.25
Lauryl Alcohol	0.75
JP-4	97.0

Properties

Yield Stress, Dynes/cm^2	2900

Stability (Vol % Separation)

• 30 Days at Room Temperature	0.0
• Six 6-Hr Cycles at 130°F	15.0
• Six 16-Hr Cycles at -20°F	0.0
• After Centrifugation for 1 Hr at 500 g (RCF)	0.0

Vibration Stability After 8 Hrs at 6 Cycles/Sec and 2 g	No Separation
Gross Heat of Combustion, BTU/Lb	19,160
Four-Ball Wear (mm)	0.48
Ash Content, Wt %	< 0.005
Sulfur Content	< 200 ppm
Reid Vapor Pressure	2.0

Compatibility - Corrosion
(One Week at 130°F) of:

Aluminum	0.2 mg/in^2
Bronze	0.1 mg/in^2
304 Stainless	0.0 mg/in^2
Titanium Alloy	0.0 mg/in^2

TABLE 24
EFFECT OF UREA ON FORMAMIDE EMULSION PROPERTIES

	Weight Percent		
	A	B	C
Formamide	1.70	1.34	1.5
Urea	0.30	0.66	-
Span 80	0.28	0.28	0.42
Tween 80	0.72	0.72	1.08
JP-4	97.0	97.0	97.0

	Properties		
	A	B	C
Yield Stress, Dynes/cm^2	1700	2400	2000
Stability (Vol % Separation)			
● 30 Days at Room Temperature	0.0	0.0	0.0
● Six 6-Hr Cycles at 130°F	0.50	0.0	2.0
● Six 16-Hr Cycles at -20°F	0.0	0.0	0.0
● After Centrifugation for 1 Hr at 500 g (RCF)	0.0	0.0	0.0
Vibration Stability After 8 Hrs at 6 Cycles/Sec and 2 g	No Change	No Change	No Change
Gross Heat of Combustion, BTU/lb	19,163	19,147	19,170
Four-Ball Wear (mm)	-	-	0.55
Ash Content, Wt %	<0.005	<0.005	<0.005
Sulfur Content	<200 ppm	<200 ppm	<200 ppm
Reid Vapor Pressure	2.0	2.0	1.9
Compatibility - Corrosion (One Week at 130°F) of:			
Aluminum	+0.10 mg/in^2	0.0 mg/in^2	0.0 mg/in^2
Bronze	4.5 mg/in^2	5.0 mg/in^2	8.5 mg/in^2
304 Stainless	0.0 mg/in^2	0.0 mg/in^2	0.0 mg/in^2
Titanium Alloy	+0.2 mg/in^2	+0.1 mg/in^2	0.0 mg/in^2
Swelling of (% Increase):			
Neoprene	39	19	19
Butyl Rubber	143	137	148
Buna N (MS-902)	18	18	22
Buna N (MS-29513)	43	41	43
Silicone	85	79	87
Viton	4.0	4.2	5.0
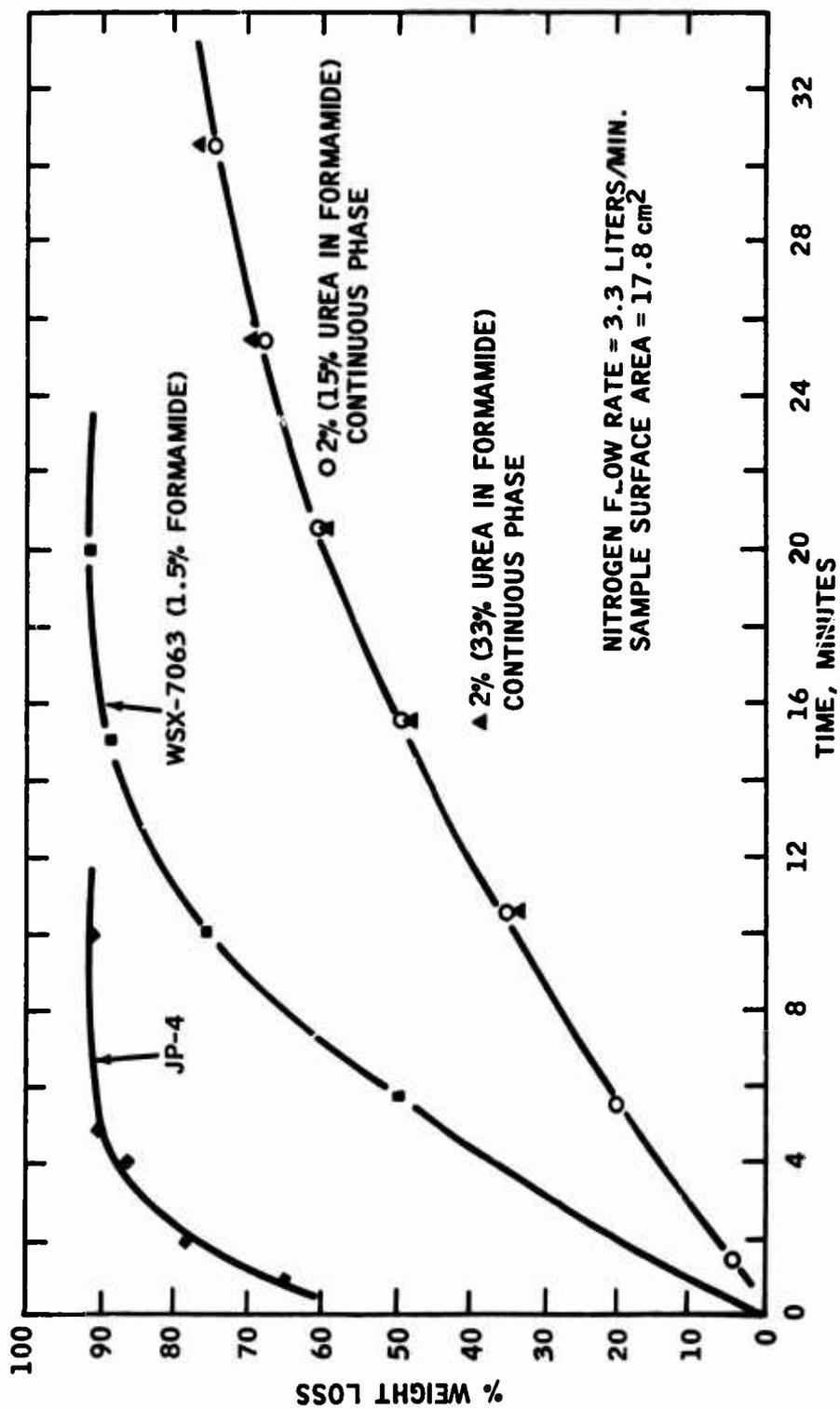
Figure 17. EFFECT OF UREA ON EVAPORATION RATE OF FORMAMIDE EMULSION AT 130°F

TABLE 25
PROPERTIES OF OTHER UREA-FORMAMIDE EMULSIONS

	Weight Percent	
	A	B
Formamide	1.28	1.01
Urea	0.22	0.49
Span 80	0.42	0.42
Tween 80	1.08	1.08
JP-4	97.0	97.0

	Properties	
	A	B
Yield Stress, Dynes/cm^2	2950	2200

Stability (Vol % Separation)

	A	B
● 30 Days at Room Temperature	0.0	0.0
● Six 6-Hour Cycles at 130°F	0.25	0.50
● Six 16-Hour Cycles at -20°F	0.0	0.0
● After Centrigugation for 1 Hr at 500 g (RCF)	0.0	0.0

Vibration Stability After 8 Hrs at 6 Cycles/Sec and 2 g	No Change	No Change
Gross Heat of Combustion, BTU/Lb	19,161	19,107
Ash Content, Wt %	<0.005	<0.005
Sulfur Content	<200 ppm	<200 ppm
Reid Vapor Pressure	1.8	1.8

Compatibility - Corrosion (One Week at 130°F) of:

	A	B
Aluminum	0.1 mg/in^2	+0.2 mg/in^2
Bronze	∼4.0 mg/in^2	5.0 mg/in^2
304 Stainless	0.0 mg/in^2	0.1 mg/in^2
Titanium Alloy	0.0 mg/in^2	+0.2 mg/in^2

Swelling of:

	A	B
Neoprene	19.0	37
Butyl Rubber	148	146
Buna N (MS-902)	23	18.6
Buna N (MS-29513)	42	42
Silicone	87	86
Viton	5.0	3.4

TABLE 26
EFFECT OF UREA ON ETHYLENE GLYCOL EMULSIONS

	Weight Percent		
	A	B	C
Ethylene Glycol	0.91	2.0	1.6
Water	1.09	-	-
Urea	-	0.5	0.4
Span 80	0.19	0.14	0.28
Tween 80	0.81	0.36	0.72
JP-4	97.0	97.0	97.0

	Properties		
	A	B	C
Yield Stress, Dynes/cm^2	1225	1850	2200
Stability (Vol % Separation)			
● 30 Days at Room Temperature	0.0	-	-
● Six 6-Hr Cycles at -130°F	5.0	0.0	0.5
● Six 16-Hr Cycles at -20°F	0.0	0.0	0.0
● After Centrifugation for 1 Hr at 500 g (RCF)	1.0	-	-
Vibration Stability After 8 Hrs At 6 Cycles/Sec and 2 g	50% Separation	<2% Separation	<2% Separation
Gross Heat of Combustion, BTU/lb	19,276	-	-
Four-Ball Wear (mm)	0.575	0.45	0.60
Ash Content, Wt %	<0.005	<0.005	<0.005
Sulfur Content	<200 ppm	<200 ppm	<200 ppm
Reid Vapor Pressure	2.0	-	-
Compatibility - Corrosion (One Week at 130°F) of:			
Aluminum	0.1 mg/in^2	0.0 mg/in^2	-
Bronze	0.2 mg/in^2	0.10 mg/in^2	-
304 Stainless	0.0 mg/in^2	0.0 mg/in^2	-
Titanium Alloy	0.0 mg/in^2	0.0 mg/in^2	-
Swelling Of:			
Neoprene	39	39	-
Butyl Rubber	147	148	-
Buna N (MS-902)	20.0	19.0	
Buna N (MS-29513)	40	43	-
Silicone	88	86	-
Viton	3.5	4.0	-

TABLE 27 PROPERTIES OF UREA-FORMAMIDE EMULSIONS WITH ESTERS OF ETHOXYLATED POLYOL EMULSIFIERS		
	Weight Percent	
	A	B
Formamide	1.60	1.60
Urea	0.40	0.40
Atlas IL-850 (HLB 11)	1.00	-
Atlas IL-851 (HLB 13)	-	1.00
JP-4	97.0	97.0
Properties		
Yield Stress, Dynes/cm^2	2250	2200
Stability (Vol % Separation)		
● 30 Days at Room Temperature	0.0	0.0
● Six 6-Hour Cycles at 130°F	1.0	0.0
● Six 16-Hour Cycles at -65°F	0.0	0.0
● After Centrifugation for 8 Hours at 500 Grams (RCF)	0.0	0.0
● After Vibration at 6 Cycles/Sec and 2 Grams for 1/2 Hour	∼2.0% Liquid	∼2.0% Liquid
Gross Heat of Combustion, BTU/Lb	19,174	19,180
Ash Content, Wt %	<0.005	<0.005
Compatibility-Corrosion (mg/in^2) (One Week at 130°F) of:		
Aluminum	0.25	0.20
Bronze	4.2	3.0
304 Stainless	0.0	0.0
Titanium Alloy	+0.20	0.0
Swelling of (% Increase):		
Neoprene	36.5	36.6
Butyl Rubber	135	135
Buna N(MS-902)	16.5	16.5
Buna N(MS-29513)	40.3	48.8
Silicone	81.7	81.8
Viton	4.7	4.7

TABLE 28 FORMAMIDE EMULSIONS WITH SPAN 80 AND ESTERS OF ETHOXYLATED POLYOLS AS EMULSIFIERS					

	Weight Percent				
	A	B	C	D	E
Formamide	1.5	1.5	1.5	2.0	2.0
Span 80	-	-	0.42	-	-
Atlas IL-850 (HLB-11)	1.5	-	-	1.0	-
Atlas IL-851 (HLB-13)	-	1.5	-	-	1.0
Atlas IL-852 (HLB-15)	-	-	1.08	-	-
JP-4	97.0	97.0	97.0	97.0	97.0

	Properties				
	A	B	C	D	E
Yield Stress, Dynes/cm^2	1800	2925	2075	2900	1900
Stability (Vol % Separation)					
• 30 Days at Room Temperature	0.0	0.0	0.0	0.0	0.0
• Six 6-Hr Cycles at 130°F	0.50	0.50	5.0	0.50	0.50
• Six 16-Hr Cycles at -20°F	0.0	0.0	0.0	0.0	0.0
• After Centrifugation for 1 Hr at 500 g (RCF)	0.0	0.0	0.0	0.0	0.0
Vibration Stability After 8 Hrs at 6 Cycles/Sec and 2 g	-	-	-	2.0% Liquid	2.0% Liquid
Gross Heat of Combustion, BTU/Lb	-	-	-	19,163	19,188
Four-Ball Wear (mm)	-	-	-	0.674	0.266
Ash Content, Wt %	<0.005	<0.005	<0.005	<0.005	<0.005
Sulfur Content	←————————— 200 PPM —————————→				
Reid Vapor Pressure	←————————— 2.0 —————————→				

Preliminary Process Studies

During the course of this program, it became obvious that the problems associated with the scale-up of fuel emulsions can be formidable. It is not an easy task to scale-up these fuel emulsions from 2500-gram laboratory batches to 1000-gallon batch sizes and higher. Our efforts to do this with the two most promising emulsions uncovered in this program have amply demonstrated this point. We feel that this will, in general, be the case for any high-internal-phase fuel emulsion. Thus, some preliminary process studies were carried out to define the important process parameters involved in the preparation of WSX-7165. These same parameters are applicable to WSX-7063. The two most important process parameters which have been defined are JP-4 addition rate and mixing energy. The time of mixing the finished emulsion can also affect the quality of the emulsion. These parameters alter the particle size distribution of the emulsion and thereby overall emulsion stability. Other factors being equal, the smaller the dispersed droplets, the greater the stability of the emulsion. The above parameters (mixing energy and JP-4 addition) are related to particle size as expressed by the following relationship:

$$E = \frac{3 \gamma V}{r}$$ (Reference 5)

where

  E is the energy of mixing

  γ is the interfacial tension between the disperse phase and the continuous phase

  V is the volume of the disperse phase

  r is the radius of the dispersed droplets

The interfacial tension of our system is fixed by the composition of the emulsion. It is obvious from the above relationship that improved stability, i.e., smaller droplets, can be achieved in two ways: (1) by increasing the mixing energy, and (2) by decreasing the volume of the disperse phase (decrease the rate of JP-4 addition). The volume of disperse phase here is the volume to be dispersed; it does not include the volume which is already dispersed.

The laboratory results confirm the above relationship. Several batches of WSX-7165 were made at the same mixing level but at different rates of addition. The data which show the effect of these parameters on emulsion stability are summarized in Table 29.

58

| TABLE 29 |
| EFFECT OF MIXING AND JP-4 ADDITION |
| RATE ON EMULSION STABILITY |

Emulsion	Mixing Level	JP-4 Rate (ml/min)	Vol % of Separation after Vibration for 1/2 hour	-65°F for 16 Hours
A	High	110	20.0	90.0
B	High	41	0.0	0.0
C	High	25	0.0	0.0
D	Low	41	25.0	90.0

These data show that good-quality emulsion is achieved by good mixing and an optimum JP-4 addition rate.

The absolute effect of these variables on particle size distribution can be determined from the haze level and conductivity of the emulsion. Both haze and conductivity reflect the droplet size of the disperse phase (References 1,2,and 7). The smaller the droplets, the greater the stability of the emulsion. Smaller droplets of the disperse phase are reflected in terms of higher conductivity (References 1,2,and 7) (higher current flow) and lower haze of the emulsions. Haze and conductivity data as they are affected by mixing energy and JP-4 addition rate are shown in Table 30.

| TABLE 30 |
| EFFECT OF MIXING AND JP-4 ADDITION RATE ON DROPLET SIZE |
| AS MEASURED VIA CONDUCTIVITY AND HAZE |

Emulsion	Mixing Level	JP-4 Rate (ml/min)	Conductivity (Current flow in MA)	Haze
A	High	110	0.08	>135
B	High	41	0.17	35
D	Low	41	0.08	>135

The results (Tables 29 and 30) show that as the conductivity of the emulsion increases, the haze level of the emulsion decreases and the stability of the emulsion improves. Also, the addition of small volumes of JP-4 (lower addition rates) and high mixing energy favor small droplets and greater emulsion stability. High JP-4 addition rates (addition of large volume of disperse phase) produce emulsions having larger droplets which are less stable.

Ingredient Quality and Levels

The process of emulsification involves surface properties which are greatly affected by low concentrations of material. It is mandatory that the quality of the ingredients of the emulsion be tightly controlled. In addition, the composition of the emulsion, particularly with respect to emulsifier and continuous phase, must also be carefully controlled. This point cannot be overemphasized, as the emulsifier and continuous phase compositions are balanced and a change in any one of these components upsets this balance and tends to promote instability of the emulsion. Upsetting the hydrophile-lipophile balance is one typical approach to de-emulsification of emulsions (References 2 and 6).

The specification on JP-4 is fairly broad, and this is further complicated by the fact that JP-4 may contain any one of seven different corrosion inhibitors. In addition, the JP-4 may contain an anti-icer. The rather broad specification on JP-4 should not, however, have any appreciable effect on the quality of our fuel emulsions as long as the JP-4 contains the same anti-icer and corrosion inhibitor. This is to be expected because the solubility parameters of all the possible constituents of JP-4 are not too different. Thus, the maximum variation in the solubility parameters of JP-4 will be only $\pm$ 0.5 (g cal/mole/cc)$^{1/2}$, which is insignificant. On the other hand, if the polar additives (corrosion inhibitor and anti-icer) in JP-4 were changed, this could have a significant effect on the HLB of the system. The polar additives have solubility parameters significantly greater than JP-4 (Reference 3). Therefore, a change in these polar additives would require adjustments in the emulsifier system, without which the stability of the emulsion would be adversely affected.

CONCLUSIONS

1. Two emulsions, designated WSX-7063 and WSX-7165, have been formulated which meet all the contractual requirements for a safety fuel emulsion.

2. Emulsion WSX-7165 is stable at -65°F and 160°F, the desired stability range for a safety fuel.

3. Both of the emulsions developed can be de-emulsified completely either by shear or by chemical means.

4. The de-emulsified fuel from both emulsions meets all the MIL-T-5624 G Specification requirements for JP-4 with the exception of the water separometer index.

5. Both emulsions inhibit the release of combustible vapors, reduce burning rates, and reduce flame propagation by a substantial amount; however, in all these respects, WSX-7165 is more effective than WSX-7063.

6. The production of the fuel emulsion in large batches (1000 gallons and greater) is a rather complex operation and requires further study.

7. Several other highly promising emulsions systems uncovered in this program require further study before they can be considered operational.

8. The emulsions uncovered in this program can be pumped using regular vane or gear pumps and other high-discharge pumps. Some high speed pumps, however, will cause emulsion breakdown.

9. WSX-7063 operated satisfactorily in the Lycoming T-55 engine fuel control system with no apparent difficulty; the fuel appeared to be compatible with the fuel system in all respects.

10. A method has been developed for measuring the level of contamination in fuel emulsions. Results obtained using this method were correlatable with tendency to cause plugging of engine nozzles.

11. A photographic technique has been developed which allows the internal details of emulsions to be studied. This technique can be used to measure average drop size of the disperse phase on the undisturbed emulsion.

12. In the atomization of JP-4 and the emulsions test, the thrust and output at constant pressure for both JP-4 and the emulsions are identical. This means that the emulsions show no elasticity under the conditions of atomization and ejection from the nozzle.

13. The breakdown of the emulsions after passing through the nozzle is not complete; as much as 20 percent of the emulsion passes through the nozzle without breakdown. This effect will probably alter the combustion characteristics of the fuel.

14. The drop size of the fuel emulsion passing through the nozzle appears to be identical to that of JP-4. Thus, atomization of the fuel emulsion will probably not present a problem.

RECOMMENDATIONS

1. WSX-7165 should be considered our best candidate at this time.

2. At least two versions of WSX-7165 (yield stresses of 1500 dynes/cm^2 and 3000 dynes/cm^2) should be evaluated in ballistic tests and impact tests in the presence of ignition sources. This information is needed to set a minimum on the yield stress for safety fuels.

3. Additional work is needed to improve emulsion stability with respect to pumping and handling at all temperatures (-65°F to 160°F) and with low-discharge high-speed pumps.

4. Additional work is needed to define the precise process parameters involved in the scale-up of emulsions.

5. The yield stress of emulsions, in general, decreases in storage; therefore, the effect of various parameters, e.g., emulsifiers, emulsifier level, continuous phase level, etc., on yield stress retention needs to be investigated further.

6. Further optimization studies on our best candidate and at least one of the other most promising candidates should be carried out. These studies would include the effect of (1) increasing JP-4 level, (2) increasing the ratio of continuous phase to emulsifier, and (3) emulsifiers of varying solubility in the continuous phase.

7. Additional rheological studies should be carried out in conjunction with the optimization studies to assess the effect of the parameters investigated in these studies on the atomization and breakdown of these emulsions.

8. Combustion studies should be carried out in conjunction with the optimization studies and rheological studies so that the effect of the various emulsion parameters can be related to their combustion properties.

BIBLIOGRAPHY

(1) Alexander, Philip, "Cosmetics and Toiletries," <u>Manufacturing Chemist and Aerosol News</u>, December 1966, pp. 67-68.

(2) Becher, Paul, <u>Emulsion Theory and Practice</u>, Second Edition, Reinhold Publishing Corporation, New York, N.Y., 1965.

(3) Burrell, Harry, "Solubility Parameters for Film Formers", <u>Official Digest</u>, October 1955, pp. 726-758.

(4) Ford, R. E., and Furmidge, C. G. L., "Studies at Phase Interfaces: The Stabilization of Water-in-Oil Emulsions Using Oil-Soluble Emulsifiers", <u>J. Colloid and Interface Science</u>, Volume 22, 1966, pp. 331-341.

(5) Greenwald, Harold L., "Theory of Emulsion Stability", <u>J. Soc. Cosmetic Chemists</u>, Volume 6, 1955, pp. 164-177.

(6) Griffin, William C., "Classification of Surface-Active Agents by HLB", <u>J. Society Cosmetic Chemists</u>, Volume One, 1949, pp. 311-326.

(7) Kaye, R. C., and Seager, H. "Measurement of Emulsion Stability", <u>Instrument Practice</u>, September 1966, pp. 733-738.

(8) Kudzakov, G. N., IZV. A. SSROCN <u>Bulletin Academy Science U.S.S.R.</u>, Volume 4, 1949, p. 509.

(9) Lissant, K. J., "The Geometry of High Internal Phase-Ratio Emulsions", <u>J. Colloid and Interface Science</u>, Volume 22, 1966, pp. 462-468.

(10) Lucas, J. R., "A Preliminary Evaluation of an Emulsified Fuel Mixture in the Model T-63 Turbine Engine", <u>S.A.E. Preprint 670368</u>, April 1967.

(11) Monarch, John, "Environmental Testing of a Gas Turbine Engine with Emulsified JP-4 Fuel", <u>S.A.E. Preprint 670367</u>, April 1967.

(12) Opdyke, George Jr., "Initial Experience With Emulsified Fuels at Avco Lycoming", <u>S.A.E. Preprint 670366</u>, April 1967.

(13) Osipow, Lloyd I., <u>Surface Chemistry: Theory and Industrial Applications</u>, Reinhold Publishing Corporation, New York, N.Y., 1962.

(14) Petersen, R. V., Hamill, R. D., and McMahon, J. D., "Emulsifying Effects of Some Nonionic Surfactants on a Nonaqueous Immiscible System", <u>J. Pharmaceutical Sciences</u>, Volume 53, No. 6, 1964, pp. 651-655.

(15) Posey, Ken, Jr., Schleicher, Richard, et al., <u>Feasibility Study of Crash Fire Hazards</u>, F.A.A. Aircraft Development Service, Atlantic City, N. J., February 1966.

(16) Robertson, S. Harry, and Turnbow, James W., <u>Aircraft Fuel Tank Design Criteria</u>, USAAVLABS Technical Report 66-24, U.S. Army Aviation Materiel Laboratories, Fort Eustis, Virginia, March 1966.

(17) Winsor, P. A., "Hydrotropy, Solubilisation and Related Emulsification Processes", <u>Trans. Faraday Society</u>, Volume 44, 1948, pp. 376-398.

(18) Yaffee, Michael L., "Thickened Fuels May Reduce Crash Fires", <u>Aviation Week and Space Technology</u>, July 4, 1966, pp. 36-41.

APPENDIX I

LITERATURE SURVEY

BACKGROUND

The present conflict in Viet Nam has shown that low-flying Army aircraft are vulnerable to small-arms fire. This vulnerability is largely due to the fire hazards associated with JP-4 fuel. When fuel tanks are punctured by enemy projectiles, the fuel mists, it comes into contact with local hot spots, it ignites, and flames spread rapidly. In May 1966, the Army awarded Esso Research and Engineering Company a contract (DA 44-177-AMC-387 (T)) to develop a safety fuel that will minimize and/or eliminate this problem in low-flying vehicles. The safety fuel will be an emulsion that contains a minimum of 97 percent JP-4. Thus, the continuous phase-emulsifier mixtures cannot exceed a total of 3 percent by weight. Other major requirements for the emulsified fuel are:

(1) It must be stable at room temperature for a minimum of 30 days.

(2) It must be stable and pumpable at -20° to 130°F.

(3) It must not corrode practical materials of construction.

(4) The rate of evaporation, rate of burning, and rate of flame spread must be reduced substantially.

(5) It should not impart serious performance penalties to engines.

The Esso safety fuel program involves a Phase I literature survey and a Phase II laboratory program on the formulation and evaluation of emulsified fuels. About 60 percent of Phase I was completed during the first two months of the program. The remainder of Phase I was completed during the next four months of the program. This report is a comprehensive summary of the literature survey on nonaqueous emulsion systems.

SUMMARY OF REFERENCE MATERIAL

A search of the literature was made for systems (i.e., continuous phase - emulsifier) which could be used to emulsify JP-4. The search was limited to nonaqueous or partially nonaqueous continuous phases because of the Army's requirement of emulsion stability from -20°F to +130°F. A number of pertinent references were found and are summarized in the attached annotated bibliography, arranged alphabetically by author.

Of the many systems cited in the bibliography, a few are of interest with respect to the emulsification of JP-4. Several continuous phases are suggested by this study; they are ethylene glycol, glycerol, propylene glycol, and formamide, as well as their aqueous solutions. The nonionic emulsifiers are preferred because they leave no ash on burning and are noncorrosive.

Based on studies with aqueous emulsions of JP-4, it was originally estimated that an HLB* value of about 11 would be required for an emulsifier or blend of emulsifiers in order to achieve a stable emulsion of JP-4 in a nonaqueous continuous phase. If this is indeed the case, a number of nonionic emulsifiers were found in this survey which would meet this HLB requirement; among these are polyoxyethylene sorbitan trioleate (HLB = 11), polyoxyethylene sorbitan tristearate (HLB = 10.5), polyoxyethylene sorbitan monooleate (HLB = 10.0), polyoxyethylene stearyl or oleyl ether (HLB = 12.4), and polyoxyethylene alkyl phenol (HLB = 12.8). Of course, it is desirable to blend some of the more promising emulsifiers in order to achieve the required HLB.

It may not be possible to directly utilize the HLB values derived from aqueous systems in a completely nonaqueous emulsion. In their studies of olive oil-glycerol emulsions using a number of nonionic emulsifiers (28), Petersen, Hamill and McMahon concluded that the HLB value of a given emulsifier or blend of emulsifiers could not be correlated with the emulsifier's ability to induce emulsification, with the emulsion type, or with the method of mixing the emulsion. This conclusion was made from a study of olive oil-glycerol emulsions that contained no water (except, perhaps, what would be present as an impurity in a component of the emulsion). This was the only study found in the literature which attempted to correlate HLB values with emulsifiability for emulsifiers in nonaqueous emulsions. It must be concluded, therefore, that there is not enough information in the published literature to make a firm decision concerning the applicability of the HLB concept in nonaqueous emulsions.

Several of the more interesting references uncovered in this search are discussed below.

The studies by Hamill, Petersen et al. (15,25,28) on olive oil-glycerol (equal weight) emulsions included an evaluation of different methods of preparing the emulsions. It was found that the emulsions formed most readily when the emulsifier was added to the glycerol prior to forming the emulsions. Emulsifiers of all types were used in these studies. Many of the emulsions were quite stable, some showing no phase separation after two years. Good stability was exhibited by emulsions prepared using as emulsifiers amine salts of the fatty acids available in olive oil.

The emulsion polymerization of styrene and styrene-butadiene was studied in formamide and formamide-water mixtures by Carr and Johnson of Firestone (5,6). The emulsifiers used for these polymerizations were primarily of the anionic type such as the alkali metal soaps and alkali metal alkyl sulfates or sulfonates, although such cationic emulsifiers as cetyldimethyl benzylammonium chloride were also used. Other work along the same lines was carried out by Carothers and by Dales and Downing of du Pont (3). These studies were concerned with the emulsion polymerization of chloroprene in formamide, ethylene glycol, and glycerol.

*HLB refers to Hydrophile-Lipophile Balance, which, for nonionic emulsifiers is defined as the weight percent of the hydrophilic portion of a molecule divided by 5.

Nonaqueous emulsion formulations containing Freon for use in aerosols were described by Sanders of du Pont (30). The continuous phases in these emulsions were glycols such as propylene glycol and polyethylene glycol 400. The emulsifiers used in these formulations were primarily nonionic; e.g., ethoxylated fatty alcohols, polyoxyethylene fatty ethers, propylene glycol monostearate, and sorbitan monostearate. One formulation contained as much as 90 weight percent Freon, 8 weight percent propylene glycol, and 2 weight percent propylene glycol monostearate (self-emulsifying).

Most of the continuous phases, disperse phases, and emulsifiers found in this search are listed in Tables 31 through 39.

TABLE 31 NONAQUEOUS CONTINUOUS PHASES	
Continuous Phase	Reference No.
Glycerol	3,15,25,28
Ethylene glycol	3
Propylene glycol	30
Polyethylene glycol 400	30
Alcohol	18
Formamide	3,5,6
Formamide - Glycerol	6
Formamide - Ethylene glycol	6
Anhydrous hydrogen fluoride	14

TABLE 32
AQUEOUS SOLUTIONS OF FREEZING POINT
DEPRESSANTS AS CONTINUOUS PHASES

Freezing Point Depressant	Reference No.
Methyl alcohol	2,10,11,31,34,35,39
Ethyl alcohol	2,10,19-21,31,34,35,39
Propyl alcohol	2
Isopropyl alcohol	2,10,32,34
Tert-butyl alcohol	2,33
Ethylene glycol	2,8-10,17,31,34,37-39,42
Propylene glycol	8,9
Glycerol	1,2,8-10,31,39
Sorbitol	8,36
Polyfunctional alcohols (not specified)	13
Formamide	5,6
Acetone	10,31,34,39
Acetonitrile	10
Dioxane	10
Methyl acetate	34,39
Tetrahydrofuran	34

TABLE 33	
"OIL" PHASES IN NONAQUEOUS EMULSIONS	
"Oil" Phase	Reference No.
JP-4	4,23
Gasoline	2,17,26
Kerosene	2
N-heptane	4
Benzene	12,22,27
White oil	2,8,9
Olive oil	15,25,28
Transformer oil	19-21
Freon propellant	30
Glue	13
Bitumen	16,18,36,38
Crude montan wax	35

TABLE 34 POLYMERS PREPARED BY EMULSION POLYMERIZATION IN NONAQUEOUS SYSTEMS	
Polymer	Reference No.
Polystyrene	5,6,39
Butadiene - Styrene Copolymer	5,6,10,11,39
Polyisoprene	32
Polyethylene	33
Polychloroprene	3
Polyvinyl Acetate	1
Polyvinyl Chloride	31,42
Vinyl Chloride Copolymers with unsaturated compounds such as bis (2-ethylhexyl) malate	34

TABLE 35
NONIONIC EMULSIFIERS USED IN NONAQUEOUS EMULSIONS

Emulsifier	Reference No.
Polyoxyethylene Sorbitan Monolaurate	4,28
Polyoxyethylene Sorbitan Monooleate	4,28
Polyoxyethylene Sorbitan Monopalmitate	28
Polyoxyethylene Sorbitan Monostearate	28
Polyoxyethylene Sorbitan Trioleate	4,9
Polyoxyethylene Sorbitol Lanolin derivative	30
Sorbitan Monolaurate	4,28
Sorbitan Monooleate	4,9,28
Sorbitan Monopalmitate	28
Sorbitan Monostearate	28,30
Sorbitan Trioleate	28
Sorbitan Sesquioleate	28
Condensation Products of Ethylene Oxide with Alkyl Phenols	1,4,23
Propylene Glycol Monostearate	30
Diethylene Glycol Stearate	30
Glyceryl Monostearate Products	28
Sucrose Dipalmitate	28
Octakis (2-Hydroxypropyl) Sucrose	28
Polyoxyethylene Fatty Ethers	28,30,34,35
Alkyl Phenoxypolyoxyethylene Ethanols	33
Fatty Alcohols	14,30
Fatty Acid Amide - Ethylene Oxide Condensates	30
Mercaptan - Ethylene Oxide Condensates	4

TABLE 36	
ANIONIC EMULSIFIERS USED IN NONAQUEOUS EMULSIONS	
Emulsifier	Reference No·
Alkali Metal Soaps (e.g., Sodium Oleate)	3,5,6.10,22,25,27,31,32
Ammonium Salts of Fatty Acids in Olive Oil	15,25
Ammonium and Alkali Metal Salts of Alkyl Sulfates (e.g., Sodium Lauryl Sulfate)	3-6,17,25,24
Sodium Alkyl Sulfonates	6,42
Ammonium and Sodium Salts of Aromatic Sulfonic Acids	3,6,8
Miscellaneous Soaps	5,10,11,16,18,39
Miscellaneous Sulfonated Compounds	4,6,25

TABLE 37	
CATIONIC EMULSIFIERS USED IN NONAQUEOUS EMULSIONS	
Emulsifier	Reference No.
Cetyldimethylbenzylammonium Chloride	5
Stearyldimethylbenzylammonium Chloride	25
C_{16}-C_{18} Alkyl Trimethylammonium Salts	37
Cetylpyridinium Chloride	25
Dodecylamine Hydrochloride	5
Octadecylamino-3-Propylamine Salts	38
Imidazolines	4,23

TABLE 38		
AMINE SALTS OF THE FATTY ACIDS AVAILABLE IN OLIVE OIL AS EMULSIFIERS IN NONAQUEOUS EMULSIONS(15,25)		

Amine
2-Amino-2-Methyl-1,3-Propanediol
Tris (Hydroxymethyl) Amino Methane
Ethanolamine
Triethanolamine

TABLE 39	
MISCELLANEOUS EMULSIFIERS USED IN NONAQUEOUS EMULSIONS	

Emulsifier	Reference No.
Gum Tragacanth	2
Casein	13,18
Polyacrylates	4,23
Bentonite Clay	36

Several solubilization studies have been carried out in organic systems including the glycols (27,29,40). These "solubilized systems" may well be examples of microemulsions*. Other miscellaneous studies that are of some interest are included in the list of references (12,19-22,26).

---

*L. I. Osipow: "Transparent Emulsions" _J. Soc. Cosmet. Chem._ 14:277-85 (1963).

LIST OF PERTINENT REFERENCES

(1) G. P. Belonôvskaya, Zh. D. Chernova, and L. A. Bessonova: "Emulsion Polymerization of Vinyl Acetate at Low Temperatures." J. Appl. Chem. U.S.S.R. 37 #11:2438-41 (November 1964)

Emulsifier - OP-10 (condensation product of ethylene oxide with alkyl phenols--$RC_6H_4(CH_2CH_2O)_nCH_2CH_2OH$, n = 9-10, R = C_8-C_{10} alkyl)

Continuous phase - water containing glycerol (55%)

System - vinyl acetate polymerization; polymerization temperature as low as -35°C; the ratio of aqueous to hydrocarbon phases was 3:1.

(2) D. F. Brown and H. C. DeHoff (Esso)
U.S. 1,927,916, i. 9/26/33, f. 5/15/30
U.S. 2,189,854, i. 2/13/40, f. 12/14/37

Emulsifier - gum tragacanth

Continuous phase - water containing alcohol

System - 30-50 percent alcohol, 0.1-5 percent gum tragacanth, 1.2 percent oil, 0.1-10 percent polyisobutylene (thickener), balance water

Comments - Oil can be white oil, gasoline, or kerosene. Alcohol can be methanol, ethanol, propanol, isopropanol, tertiary butanol, ethylene glycol, glycerol, etc.

(3) W. H. Carothers (du Pont), U.S. 2,080,558; B. Dales and F. B. Downing (du Pont), U.S. 2,080,561, i. 5/18/37, f. 8/8/34

Emulsifier - sodium oleate, alkali metal salts of alkyl naphthalene sulfonic acids, alkali metal salts of the sulfuric acid esters of the normal straight chain primary aliphatic alcohols > C_8.

Continuous phase - glycerol, ethylene glycol, formamide

System - emulsion polymerization of 2-chloro-1,3-butadiene, e.g., 2-chloro-1,3-butadiene--200 parts, sodium oleate--4 parts, glycerol--200 parts

(4) D. E. Carr (Phillips), U.S. 3,006,142, i. 10/31/61, f. 12/21/59

Emulsifier - polyoxyethylene sorbitan monolaurate (Tween 20); polyoxyethylene sorbitan monooleate (Tween 60); polyoxyethylene sorbitan trioleate (Tween 85); sorbitan monolaurate (Span 20); sorbitan monooleate (Span 60); 1-hydroxyethyl-2-heptadecenyl glyoxaldine (Amine 220); trihexyl sulfotricarbyllate (Nekal N.S.); sulfonated tallow (Napco 1497B); 80/20 copolymer of lauryl methacrylate/diethylaminoethyl methacrylate; sodium lauryl sulfate; ammonium lauryl sulfate; butylamine salt of dihexyl-4-sulfophthalate; mercaptan-ethylene oxide condensation products; phenol-ethylene oxide condensation products such as the condensation product of nonyl phenol with four mols of ethylene oxide (Igepal CO-430); and duomeen-T-dioleate (N-alkyl-trimethylene diamine)

System - thrust-augmenting and smoke-suppressing liquid for use
in jet engines operating on JP-4 Referee fuel or n-heptane.
Emulsion contains water, C_1-C_4 saturated aliphatic alcohol,
C_5-C_{12} paraffin hydrocarbon, and emulsifier (0.1-5 percent);
e.g., water--74.25 weight percent; ethanol--12.5 weight per-
cent; n-heptane--12.5 weight percent; emulsifier--0.75
weight percent

Comments - For this work, a stable emulsion is defined as one
having not more than 1 percent liquid separation upon
standing one hour at 75°F.

(5) E. L. Carr and P. H. Johnson (Firestone): "Nonaqueous Emulsion Poly-
merization Systems." Ind. Eng. Chem. 41 #8:1588-92 (August 1949)

Emulsifier - cetyldimethylbenzylammonium chloride as Triton
K-60 (a 25 percent paste in water), MP-189-EF (higher
alkyl sulfonic acid salt), dodecylamine hydrochloride,
sodium lauryl sulfate, sodium oleate, SF flakes, dodecyl-
isothiouronium hydrobromide (reacts with formamide)

Continuous phase - formamide, formamide-water.

System - styrene and butadiene-styrene polymerization
formamide; e.g., formamide--100 parts, sodium lauryl sul-
fate--5 parts, styrene--25 parts, butadiene--75 parts, mis-
cellaneous--1.5 parts
formamide-water - butadiene-styrene (75/25) polymerization
at -10°C in benzoyl peroxide-sugar redox recipe, using
MP-189-S as emulsifier. Sufficient formamide is used to
insure against freezing.

Comments - The use of formamide as an antifreeze as compared
with glycerol lowers viscosity.

(6) E. L. Carr (Firestone), U.S. 2,537,644, i. 1/9/51, f. 4/12/49

Emulsifier - alkali metal soaps of higher fatty acids (e.g.,
sodium oleate), alkali metal alkyl sulfates (e.g., sodium
lauryl sulfate), sodium alkyl sulfonates, alkali metal
salts of aryl and alkylated aryl sulfonic acids, alkali
metal salts of sulfonated α, β-dicarboxylic acid diesters,
alkali metal salts of monosulfated monoglycerides of C_8-
C_{22} fatty acids

Continuous phase - formamide

System - emulsion polmerization of styrene; e.g., styrene--100
parts, formamide--180 parts, sodium lauryl sulfate--5 parts,
potassium persulfate--100 parts

Comments - Formamide may be diluted with water, glycerol,
ethylene glycol, etc., for antifreeze purposes.

(7) N. V. Chemische Fabrieke "Andrelon" Brit. 891,631, publ. 3/14/62,
f. Neth. 8/2/57

Emulsifier - neutralization product of $C_{12}H_{25}(OCH_2CH_2)_nOSO_2OH$,
n = 2,3, and an amine; e.g., diethylamine, isopropylamine
butylethanolamine

Comments - Suggested for nonaqueous systems, e.g., in non-aqueous insecticidal compositions.

(8) L. V. Collings and D. B. Sheldahl (Sinclair) U.S. 3,235,510, i. 2/15/66, f. 4/17/62

Emulsifier - ammonium and sodium salts of oil-soluble aromatic sulfonic acids

Continuous phase - water containing a polyhydric alcohol having the formula $CH_2OH(CHOH)_xCH_2OH$ where x = 3-4, such as sorbitol, mannitol, arabitol, etc. A diol or triol may also be present; e.g., ethylene glycol, propylene glycol, glycerol, etc.

System - emulsified anti-corrosion composition; e.g., mineral oil--47.7 percent, sodium mahogany sulfonate--5.6 percent, isopropyl alcohol--1.1 percent, anti-foam agents--0.6 percent, sorbitol--3.5 percent, glycerol or ethylene glycol--10.0 percent, water--31.5 percent

Comments - Emulsions have low temperature cold storage stability and reduced pour point. Emulsion stability was tested by storage at room temperature for 30 days and low temperature storage at 10°F for 3 days followed by 27 days storage at room temperature.

(9) G. J. Colucci and J. F. Maxwell(E. F. Houghton & Co.) U.S. 3,039,969, i. 6/19/62, f. 8/29/58

Emulsifier - two emulsifying agents--one of which is water soluble (polyalkylene oxide condensates of fatty acids and fatty acid partial esters with polyhydric alcohols; condensates of ethylene oxide with fatty acids), and the other of which is oil soluble (esters of polyhydric alcohols with fatty acids)

Non-oil phase - water containing a polyhydric alcohol, e.g., ethylene glycol, glycerol, etc.

System - water/oil emulsions; e.g., oil phase--neutral oil--43 percent, Span 80 (sorbitan monooleate)--1.6 percent,methyl oleate--7.1 percent; "water" phase--Tween 85 (polyoxyethylene derivative of sorbitan trioleate)--3.1 percent; ethylene glycol--7.1 percent; water--38.1 percent

Comments - water/oil emulsions can be inverted to oil/water emulsions. Pour point of emulsions is -20°F.

(10) C. F. Fryling and A. E. Follett (Phillips): "New Oxidants for Initiation of Emulsion Polymerization in Antifreeze Recipes at -10°C." J. Polymer Sci. 6 #1:59-72 (January 1951)

Emulsifier - Dresinate 214 (disproportionated rosin soap), Dresinate S-134 (rosin soap), or rosin acid soap and potash soap (K-SF) (potassium salt of Rubber Reserve soap flakes)

Continuous phase - water containing methanol

System - butadiene-styrene emulsion polymerization; e.g., buta-
diene--70 parts, styrene--70 parts, water--192 parts,
methanol--48 parts, emulsifier--5 parts, miscellaneous~3
parts. Polymerization temperature was -10°C.

(11) C. F. Fryling, S. H. Landes, W. M St. John and C. A. Uraneck
(Phillips): "Emulsion Polymerizations at Low Temperatures." Ind.
Eng. Chem. 41: 986-91 (May 1949)

Emulsifier - Dresinate 731 (sodium salt of disproportionated
rosin acid); potassium oleate; potassium laurate, etc.
Continuous phase - water containing freezing point depressant,
such as methanol
System - butadiene-styrene polymerization; e.g., butadiene--
70 parts, styrene--30 parts, water--175 parts, methanol--
75 parts, emulsifier--5 parts, miscellaneous ~3 parts.
Polymerization temperature was -18°C
Comments - Other freezing point depressants--isopropanol,
ethanol, acetone, acetonitrile, dioxane, ethylene glycol,
glycerol--were also studied.

(12) T. Fujita and T. Sasaki: "The Nature of Emulsions" J. Chem. Soc.
Japan 64:1523-8 (1943); Chem. Abstr.-41:3343e.

Emulsions were prepared in the ternary systems: benzene, alco-
hol (ethyl, amyl, cetyl), water, by several means, and
the resulting phase inversion systems studied.

(13) F. V. Gehe and S. Dietze, Ger. (East) 40,949, open 9/15/65, f.
1/9/61 Chem. Abstr.-62:16089h

Emulsifier - casein
Continuous phase - water containing 10 weight percent polyfunc-
tional alcohols as antifreeze agents
System - glue emulsion containing 70 percent rosin

(14) W. T. Grubb, Jr. (General Electric Co.), U.S. 2,737,499, i. 3/6/56,
f. 4/28/53

Emulsifier - C_{12}-C_{22} aliphatic monohydric alcohols, aromatic
hydroxy compounds, aliphatic carboxylic acids, aliphatic
amines, aliphatic nitriles, aliphatic nitro compounds, ali-
phatic ketones and aliphatic ethers; e.g., n-octadecanol,
β-naphthol, n-octadecanoic acid, n-octadecyl amine, n-
octadecyl nitrile
Continuous phase - anhydrous hydrogen fluoride
System - emulsions of organic liquids in HF; some emulsions of
HF in organic liquids. Preferred concentrations--anhydrous
HF--49.0-49.5 weight percent, emulsifier--1-2 weight per-
cent, organic compound--49.0-49.5 weight percent
Comments - Organic liquids include carbon tetrachloride, n-
hexane, cyclohexane, benzene, trichloroethylene, benzo-
trifluoride, toluene, 1,2-dichloroethane. Emulsions are
uniformly stable over "relatively long periods of time."

(15) R. D. Hamill, F. A. Olson and R. V. Petersen (Univ. of Utah): "Some Interfacial Properties of a Nonaqueous Emulsion." _J. Pharm. Sci._ 54 #4:537-40 (April 1965); R. D. Hamill: "A Study of Some Factors Affecting Stability in a Nonaqueous Emulsion." Ph.D. Thesis, Univ. of Utah, 1965, _Dissertation Abstr._ 26 #10:5732-33 (1966), Order No. 65-13,043,117 p.

Emulsifier - condensation products of ammonia and of 2-amino-2-methyl-1,3-propane diol with the fatty acids available in olive oil
Continuous phase - glycerol
System - olive oil in glycerol emulsion
Comments - Emulsification occurs at a minimum concentration of 0.6 mg ammonia/100 ml and 2 mg 2-amino-2-methyl-1,3-propanediol/100 ml at a phase volume of 0.40. Effects of emulsifier concentration were studied. Interfacial viscosity and mechanical properties of the interfacial film can be correlated with the stability of an emulsion. An emulsion was considered stable if it did not separate after standing at room temperature for one week.

(16) L. Hemmer (Esso), Progress Report, September-October, 1951, RD.5P. 51, as discussed in D. A. Young: "Asphalt Road Emulsions: A Review of the Technology." RL-115M-65 (9/1/65), p. 30.

Emulsifier - tallow base potash soap
Comments - Anionic emulsions stable down to -15°F; typical formulation contains 0.5 weight percent bone fat, 0.2 percent potash and 0.1 percent potassium carbonate.

(17) P. S. Jones, S. J. Davenport, T. H. Tebben and L. D. Christensen (Stanford Research Inst.): "Evaluation of Fuel Handling Systems for Limited War." AD-448 448 (10/1/64), pp. 55-64.

Emulsifier - sodium lauryl sulfate
Continuous phase - water containing small amount of glycol
System - gasoline emulsion; e.g., 980 ml gasoline was emulsified in 20 ml of an aqueous solution (0.5 g sodium lauryl sulfate, 0.5 g polyvinyl alcohol, 3 ml ethylene glycol, 1 ml polyethylene glycol 400, water to make 20 ml)
Comments - Emulsion showed no instability after four weeks.

(18) R. M. Kerry (International Bitumen Emulsions, Ltd.), _Belg. 462,235_, g. February 1946, f. Brit. 7/31/44; _Rec. Brev. Inv. (1946):_ 141 (8/25/47)

Emulsifier - protein such as casein; fatty acids; soluble soaps
Continuous phase - alcohol
System - petroleum bitumen, tar, or pitch emulsion in alcohol

(19) S. E. Kharin and L. R. Takking: "Coagulation of (Transformer-Oil) Emulsions." Trudy Odess. Tekhnol. Inst. Pischevoi i. Kholodil. Prom. 6: 3-15 (1955); Chem. Abstr.-51:10886b.

   The rate of coagulation of transformer oil emulsions in aqueous
      ethanol was studied. No oil separated during coagulation.

(20) S. E. Kharin: "Equilibrium in a Heterogeneous Medium." (Emulsions of Oil in Aqueous Ethanol). Tr. Voronezhsk. Tekhnol. Inst. 16: 18-30 (1960); Chem. Abstr.-57:5326f.

(21) S. E. Kharin, L. R. Takking and I. V. Chaikovskaya: "Some Laws of Dispersed Colloidal Emulsions." Izv. Vysshikh Uchebn. Zavednii Pishchevaya Tekhnol. SSSR #2:70-73 (1965); (Abstr.) Chem. Ind. (Paris)-Genie Chim. 95 #5:1211 (May 1966)

   Oil droplet size was studied as a function of alcohol concentra-
      tion for a series of emulsions prepared from D-2 transformer
      oil and aqueous alcohol.

(22) L. Ya. Kremnev and Yu. G. Khazina: "Gelatinated (Foamy) Emulsions. III. Effect of Aliphatic Monatomic Alcohols on the Emulsion-Forming Properties of Sodium Oleate." Trudy LKKhTI (Lab. Kolloidnoi Khim.) #7:93-102 (1939); Chem. Abstr.-34:22304.

   The effect of the addition of ethyl, propyl, amyl, octyl and
      cetyl alcohols to solutions of sodium oleate used to emul-
      sify benzene was studied. A low concentration of alcohol
      resulted in an increased amount of emulsified benzene, but
      a further increase in alcohol concentration resulted in
      reduced emulsification.

(23) O. E. Larsen and E. D. Guth (Phillips), U.S. 3,058,301, i. 10/16/62, f. 12/24/58

   Emulsifier - should not react with nitric acid, e.g., imidazo-
      lines, polyacrylates, $C_{12}-C_{18}$ fatty amides
   System - liquid propellants, especially for ram jet engines.
      Emulsion of JP-4 (or other hydrocarbon fuel), nitric acid
      and an amine nitrate; e.g., amine nitrate--49.4 parts,
      anhydrous white fuming nitric acid--30.0 parts, hydrocarbon
      fuel--9.3 parts, emulsifier--11.3 parts
   Comments - Emulsions stable from 8 hours to more than 7 days.

(24) K. J. Lissant (Petrolite Corp.): "Emulsified Fuel Studies" Aircraft Fluids Fire Hazards Symposium (Fort Monroe, Va., 6/7-8/66)

   Emulsified fuel - EF 4-101 contains 2.8 percent external
      aqueous phase by weight; is stable between -40° and 130°F;
      is stable to vibration and normal shipping stresses; is
      stable for at least 2 months in normal fuel storage; can
      be pumped with standard equipment; has been burned directly
      in diesel and gas turbine engines on a limited basis. A
      comparison of Ef 4-101 with straight JP-4 shows that EF 4-
      101 has a lower evaporation rate; is more resistant to

dispersal from tank puncture, impact, and spillage; is less easily ignited and flame propagation is much slower than for JP-4; is water dilutable; does not film out on water; and is more readily extinguishable by water than JP-4.

(25) J. D. McMahon, R. D. Hamill and R. V. Petersen (Univ. of Utah): "Emulsifying Effects of Several Ionic Surfactants on a Nonaqueous Immiscible System." J. Pharm. Sci. 52 #12:1163-68 (December 1963)

> Emulsifier - oil in glycerol emulsions--tetrasodium-N-(1,2-dicarboxyethyl)-N-octadecyl-sulfosuccinamate, sodium lauryl ether sulfate, sodium lauryl sulfate, 2-amino-2-methyl-1,3-propanediol, tris(hydroxymethyl)amino methane, triethanolamine, ethanolamine, ammonia, cetylpyridinium chloride, stearyl dimethylbenzylammonium chloride; glycerol in oil emulsions--sodium stearate. Oil/glycerol to glycerol/oil inversion--stearyl dimethylammonium chloride
> System - equal weights olive oil and glycerol. Average emulsifier concentration was 0.5-5 percent
> Comments - A clear emulsion was produced with 0.15 percent 2-amino-2-methyl-1,3-propanediol and the other saponifying amines. Other emulsions were opaque. Emulsions formed most readily when the emulsifier was added to the glycerol. An emulsion was considered stable if there was no separation for 7 days. With the saponifying amine, some emulsions were stable for two years.

(26) V. I. Mogil'nyi and A. V. Stepanov: "Investigation of a Diethylene Glycol-Gasoline Emulsion and a Method for Designing Horizontal-Flow Emulsion Separators" Tr. Inst. Ispol'z. Gaza. Akad. Nauk Ukr. SSR #9: 90-96 (1961); Chem. Abstr.-57:7522d.

> The diethylene glycol-gasoline emulsions studied occur in installations for drying hydrocarbon gases with aqueous diethylene glycol at low temperatures.

(27) S. R. Palit and J. W. McBain (Stanford Univ.): "Effect of Soaps on Mutual Solubility of Organic Liquids" Ind. Eng. Chem. 38:741-44 (1946)

> Solubilization studies were conducted in propylene glycol using carboxylic soaps. A phase diagram is given for the propylene glycol-benzene-sodium oleate system. Temperature effects were also studied.

(28) R. V. Petersen, R. D. Hamill and J. D. McMahon (Univ. of Utah): "Emulsifying Effects of Some Nonionic Surfactants on a Nonaqueous Immiscible System" J. Pharm. Sci. 53 #6:651-55 (June 1964)

> Emulsifier - oil in glycerol emulsions--sorbitan monolaurate (S-20) polyoxyethylene sorbitan monolaurate (PS-20), sorbitan monopalmitate (S-40), polyoxyethylene sorbitan monopalmitate (PS-40), sorbitan monostearate (S-60), polyoxethylene sorbitan monostearate (PS-60), sorbitan monooleate(S-80)

polyoxethylene sorbitan monooleate (PS-80), sorbitan ses-
quioleate (S-83), sorbitan trioleate (S-85), polyoxethyl-
ene lauryl ether (POL 30), sucrose dipalmitate (DPM 600),
octakis (2-hydroxypropyl) sucrose (OHS 80). Glycerol in
oil emulsions--glyceryl monostearate (self-emulsifying)
(GMS 165), glyceryl monosteatate (non-self-emulsifying)
(GMS 169)

System - equal weights of olive oil and glycerol. Average emul-
sifier concentration was 4 percent

Comments - Most emulsions were clear, some opaque. Emulsions
formed most readily when the emulsifier was added to the
glycerol. A stable emulsion is one which does not separate
after standing at room temperature for 7 days. Some emul-
sions were stable after several months.

The HLB value of a given emulsifier, or blends of
emulsifiers, could not be correlated with the emulsifier's
ability to induce emulsification, the emulsion type, or
method of mixing the emulsion components.

(29) G. Rimlinger (C.N.A.M. Soc. Nivea, St.-Maur. France): "Emulsions
and Thermodynamics" Parfum., Cosmet., Savons 7 #9:396-402 (1964);
Transl. #C-2906.

The role of solubility in the formation of emulsion was studied.
The emulsifying power of the lower alcohols, ketones, and
glycols was determined with respect to toluene/water and
heptane/water emulsions. The emulsifying power of the
polyoxyethylene alcohols was also studied.

(30) P. A. Sanders (du Pont): "New Developments in Aerosol Foams" Amer.
Perf. Cosmet. 81:31-38 (February 1966), "Non-Aqueous Aerosol Foams"
Aerosol Age: 33-34,36,39,55,57-58 (November 1960)

Emulsifier - ethoxylated fatty alcohols (Polawax, Siponic sur-
factants), polyoxyethylene fatty ethers (Brij surfactants),
propylene glycol monostearate, Duponol WS (fatty alcohol
amine sulfate), Ethomid HT-15 (fatty acid amide-ethylene
oxide condensate), Arlacel 40 (sorbitan monostearate),
cetyl alcohol, diethylene glycol stearate, G-1441 (poly-
oxyethylene sorbitol lanolin derivative)

Continuous phase - glycols, e.g., propylene glycol, polyethylene
glycol 400

System - nonaqueous emulsion formulations for aerosols contain-
ing "Freon." Typical formulation contains 86 g propylene
glycol, 4 g emulsifier, 10 g Freon-12/Freon-114 (40/60)
propellant. Foams of excellent stability were obtained
with 90 weight percent Freon, 8 weight percent propylene
glycol, 2 weight percent propylene glycol monostearate
(self-emulsifying)

Comments - Variations of glycol type, emulsifier, and propellant
were studied.

(31) H. Scholz and W. Huebler (Badische Anilin- & Soda-Fabrik) Ger. 1,111,826, open 7/27/61, f. 6/25/59, addn. to Ger. 1,105,170

> Emulsifier - sodium palmitate
> Continuous phase - water containing up to 35 percent of a freezing point depressant
> System - vinyl chloride emulsion polymerization at -18°C
> Comments - Freezing point depressants include the lower aliphatic alcohols (e.g., methanol, ethanol, butanol, isobutanol), ketones (e.g., acetone), glycols (e.g., ethylene glycol and higher polyethylene glycols), and triols (e.g., glycerol, trimethylol propane).

(32) Shell Internationale Research Maatschappij N.V., Belg. 643,314, open 8/3/64, F. Neth. 2/5/63; Chem. Abstr.-63:5876d

> Emulsifier - potassium oleate
> Continuous phase - water containing isopropanol (e.g., 25 volume percent)
> System - rubber latex emulsion (polyisoprene)

(33) Spencer Chem. Intern., Brit. 949,722, publ. 2/19/64, f. U.S. 7/25/60

> Emulsifier - alkylphenoxypolyoxyethylene ethanol, e.g., Tergitol NPX (nonylphenyl polyethylene glycol ether); Igepal CO-730 (nonylphenoxy polyethyleneoxy ethanol); Triton N-101 (nonyl-phenoxy polyethoxy ethanol); Triton X-305, Triton X-100, Triton X-114 (octylphenoxypolyethoxy ethanol)
> Continuous phase - water containing up to 35 weight percent t-butanol
> System - polyethylene emulsion

(34) T. G. Swift (Armstrong Cork Co.) U.S. 3,085,889, i. 4/16/63, f. 3/17/60

> Emulsifier - polymerized fatty acid (600 molecular weight)-monoethanolamine; bentonite clay-sodium resinate; bentonite clay; tall oil fatty acids (6 percent rosin)-monoethanolamine
> Continuous phase - water containing d-sorbitol
> System - alphalt emulsions, resin emulsions, rubber emulsions, rubber-resin emulsions; e.g., triethylene ester of hydrogenated rosin--50 weight percent, toluene--5 percent; tall oil fatty acids (6 percent rosin)--2 percent, monoethanolamine--0.5 percent, commercial GR-S butadiene-styrene copolymer latex emulsion (60 percent solids)--20 percent d-sorbitol (powder)--15 percent, water--7.5 percent
> Comments - Emulsions in example did not break after being subjected to four freeze-thaw cycles. During one cycle, 100 g of the emulsion was subjected to a temperature of 0°F for approximately 18 hours and then allowed to thaw at room temperature for 6 hours.

(35) S. Terada (Nisshin Chem. Res. Inst. Co., Ltd.), Japan 598 ('66), open 1/21/66, f. 12/15/62; Chem. Abstr.-64:12841d

    Emulsifier - sodium dodecyl sulfate-polyoxyethylene lauryl ether

    Continuous phase - water containing 10 percent methanol, ethanol, isopropanol, ethylene glycol, acetone, methyl acetate, or tetrahydrofuran

    System - emulsion copolymerization of vinyl chloride with an unsaturated compound, e.g., bis(2-ethylhexyl)malate; sodium dodecyl sulfate--2.5 parts, polyoxyethylene lauryl ether--0.5 parts, bis(2-ethylhexyl)malate--30 parts, vinyl chloride--70 parts, water (containing 10 percent methanol)--150 parts, miscellaneous salts--0.7 parts

(36) E. Thiel, W. Presting, and E. Roettger, Ger. (East) 21,168, appl. 5/7/58; Chem. Abstr.-56:3583c

    Emulsifier - polyoxyethylene alkylphenol and polyoxyethylene oleyl alcohol

    System - self-polishing emulsion from crude montan wax; e.g., 10-14 parts crude montan wax, 2.5-3.0 parts polyoxyethylene alkylphenol, 2.5-3.0 parts polyoxyethylene oleyl alcohol, 100 parts water

    Comments - 3 parts of a methanol-ethanol mixture is added to the finished emulsion to improve freezing resistance.

(37) L. Valla (Esso): "Frost-Resistant Agricultural Mulches." Progress Report on Asphalts. Paper No. SF.1B.63

    Emulsifier - quaternary ammonium salts (C_{16}-C_{18} alkyl trimethyl ammonium salts)

    System - agricultural mulch

    Comments - Emulsions stabilized against freezing down to -17°C after 24 hours by adding aqueous ethylene glycol to the finished emulsion.

(38) L. Valla (Esso) Fr. 1,372,616, open 9/18/64, f. 8/6/63

    Emulsifier - (bitumen) octadecylamino-3-propylamine salts

    System - bituminous emulsion

    Comments - Emulsions stable after 24 hours down to -15° to -20°C by adding aqueous ethylene glycol or glycerol to the finished emulsion.

(39) E. J. Vandenberg (Hercules Powder) U.S. 2,648,655-6, i. 8/11/53, f. 11/24/48; U.S. 2,682,528, i. 6/29/54, f. 3/18/53

    Emulsifier - potassium salt of dehydrogenated rosin

    Continuous phase - water containing methanol, ethanol, glycerol, ethylene glycol, acetone, methyl acetate, etc.

    System - butadiene-styrene or styrene emulsion polymerization; e.g., 1,3-butadiene--72 parts, styrene--28 parts, water--150 parts, methanol--50 parts, potassium salt of dehydrogenated rosin--5 parts, miscellaneous--1.2 parts. Polymerization temperatures from -5° to -70°C.

(40) P. A. Winsor: "Solvent Properties of Amphiphilic Compounds." Chapt. 6 ("Solutions Containing Amphiphilic Compounds, Ethylene Glycol and Hydrocarbons not Miscible with Ethylene Glycol.") p. 129-34, Butterworths Sci. Publ., London, 1954; "Hydrotropy, Solubilization and Related Emulsification Processes." Parts I-VIII. Trans. Faraday Soc. 44: 376-98, 451-71 (1948)

> The mutual solubilization of various organic liquids and aqueous
> solutions was studied. For example, solubilization studies
> were carried out in ethylene glycol with Aerosol OT (sodium
> bisulfite compound of di-(2-ethylhexyl) maleate);
> e.g., study of effects of alternate addition of glycol and
> water to solutions of Aerosol OT in benzene;
> e.g., study of effect of gradual addition of 1-dodecanol to
> solutions of Aerosol OT in benzene with pure ethylene
> glycol or solution of sodium sulfate in ethylene
> glycol
> Solubilization studies were also carried out in ethylene
> glycol with 1-undecane ammonium chloride;
> e.g., study of effect of addition of 1-dodecanol and of
> calcium chloride to systems of cyclohexane, ethylene
> glycol, and 1-undecane ammonium chloride
> These data give an indication of concentrations of components and conditions necessary for the existence of one,
> two, or three phases, phase inversion, etc.

(41) D. A. Young (Esso): "Asphalt Road Emulsions: A Review of the Technology." RL-115M-65 (9/1/65)

> Emulsifier - hexadecyltrimethyl ammonium chlorhydrate
> Comments - Cationic emulsions stable down to -15°F; an excessive
> amount of emulsifier was required.

(42) V. I. Zegel'man, E. N. Zil'berman, I. B. Kotlyar and S. V. Svetozarskii: "Low-Temperature Emulsion Polymerization of Vinyl Chloride." Plasticheskie Massy #4:3-4 (1966); Chem. Abstr.-65:5541b

> Emulsifier - sodium C_{14}-C_{18} alkyl sulfonate
> Continuous phase - 50 percent aqueous ethylene glycol
> System - vinyl chloride emulsion polymerization. Polymerization
> temperature was -20°C; 1-2 percent emulsifier

APPENDIX II

INVESTIGATION OF THE RHEOLOGY OF FUEL EMULSIONS

Introduction

If fuel emulsions are to be burned directly in turbine engines (Concept 2), a knowledge of their behavior in nozzles is essential. The Army funded a rheological study [as an extension of Contract DA 44-177-AMC-387(T)] of the most promising fuel emulsions formulated under this contract. These studies were carried out in our Reaction Thrust Rheometer equipped with the actual engine nozzles. The purpose of these studies was to investigate the flow of emulsions through nozzles and to compare their flow with that for JP-4. The specific objectives of this program were:

(1) To determine if the fuel emulsions were viscoelastic.

(2) To determine how the drop size distribution of the fuel emulsions compared with JP-4 after passing through the nozzles.

(3) To determine the extent of emulsion breakdown on passage through the nozzles.

List of Test Equipment

The following equipment was utilized in this program:

(1) The Reaction Thrust Rheometer and the following nozzles:

- Lycoming T-53 and T-55 engine nozzles
- Allison T-63 engine nozzle
- Double-staged G.E. T-64 engine nozzle
- A straight capillary

(2) Short-Time Photography which involved the use of the following accessories:

- One-half microsecond flash unit
- 8 mm film objective
- Polaroid Land-camera
- Sliding Microscope

Materials

In this study, four fuel emulsions were evaluated. These were WSX-7063, WSX-7165, an ethylene glycol-water continuous phase emulsion, and an ethylene glycol-urea-formamide continuous phase emulsion. The composition and properties of these four emulsions are shown in Tables 4, 5 and 17 which are in the main body of this report.

86

Experimental Approach

To investigate the possible elastic properties of the fuel emulsions, use was made of an instrument termed "Reaction Thrust Rheometer". The instrument is shown schematically in Figure 18. A schematic of the entire installation, including accessory equipment, is shown in Figure 19.

When a liquid leaves a nozzle with an appreciable velocity, a thrust is produced. The thrust produced is related to the "momentum flux", which is given by the flow rate of the liquid. According to first principles, if one passes a Newtonian liquid and a viscoelastic liquid through a nozzle at the same flow rate, the difference in thrust can be directly related to the elastic tension in the emerging jet; i.e., the difference in thrust equals the elastic force in the emerging jet. Before using this relationship to obtain "normal" stresses or other mechanical parameters, it is first necessary to determine if an elastic force is produced. This is done by determining if the thrust generated with the emulsion is different from that generated by the JP-4 (Newtonian) at the same throughput.

A small difference in thrust between the two fluids can also be caused by a difference in their velocity profiles as they emerge from the nozzle. This effect is usually much smaller than the effect due to the elasticity of the fluid. Therefore, for all practical purposes, the difference in thrust between JP-4 and the fuel emulsion is equal to the elastic force of the emerging jet of emulsion from the nozzle.

Description of Apparatus

A. Thrust Rheometer Setup

In order to investigate the thrust produced by JP-4 and the fuel emulsions, the thrust rheometer was adapted so that the actual helicopter nozzles could be fitted to the unit. The nozzles were attached to the pendulum-like part of the thrust rheometer with the nozzle exit normal to the pendulum. Thus, the thrust developed by the emerging liquid was perpendicular to the pendulum (30-inch tubes) of the rheometer. The resulting thrust caused a deflection of the pendulum. The magnitude of the pendulum deflection was measured with the aid of a traveling microscope. This technique allowed us to measure the extent of deflection to within ± 0.001 inch. The thrust down to 0.1 g (equal to 0.1 mm deflection) could be determined with acceptable precision. However, below a deflection of 0.1 mm, the scatter in the data was too large to be of any use. The largest deflections encountered in these studies were of the order of 20 mm, or the equivalent of 200 g thrust.

The thrust rheometer was calibrated by exerting a pull of a given weight perpendicular to the pendulum at the point where the nozzle is attached and in the same direction as the thrust caused by fluids emerging from the nozzle. A straight-line calibration curve with a slope of 11.70 grams/mm was obtained when the data were plotted as deflection (mm) versus added weight (grams) (Figure 20).
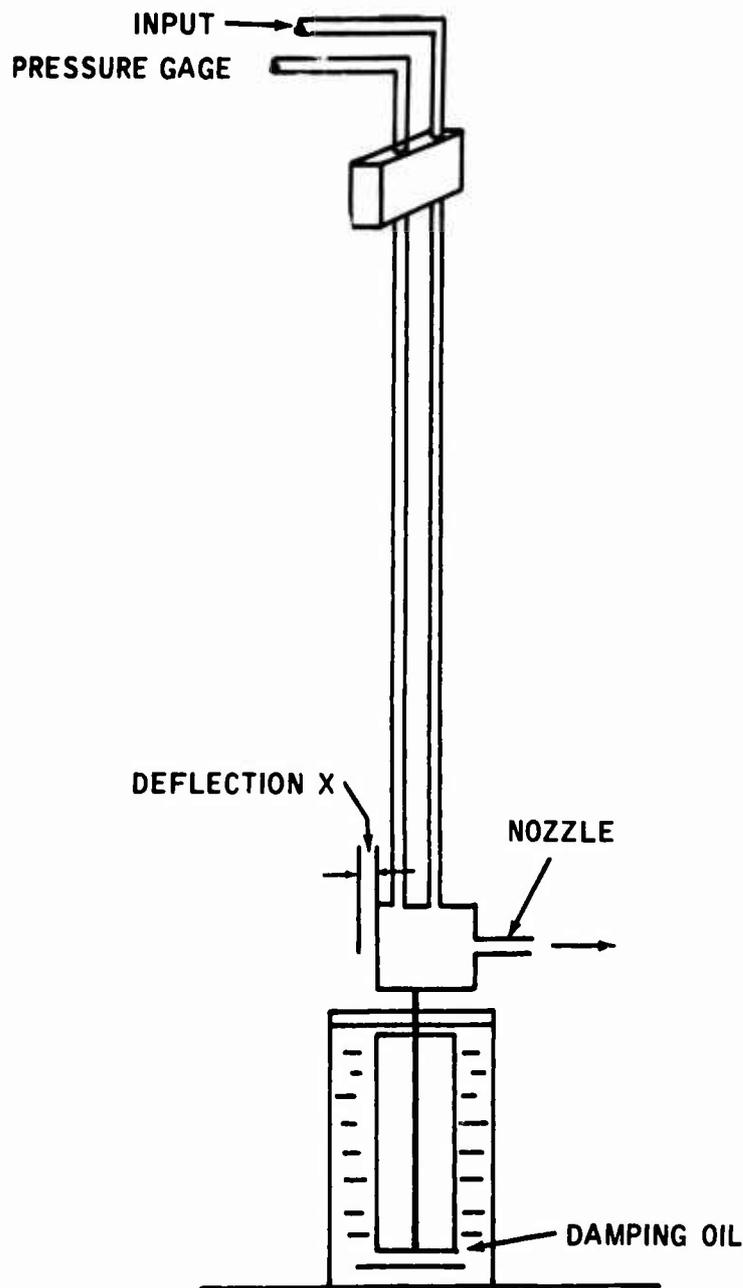
Figure 18. SCHEMATIC DRAWING OF THRUST RHEOMETER
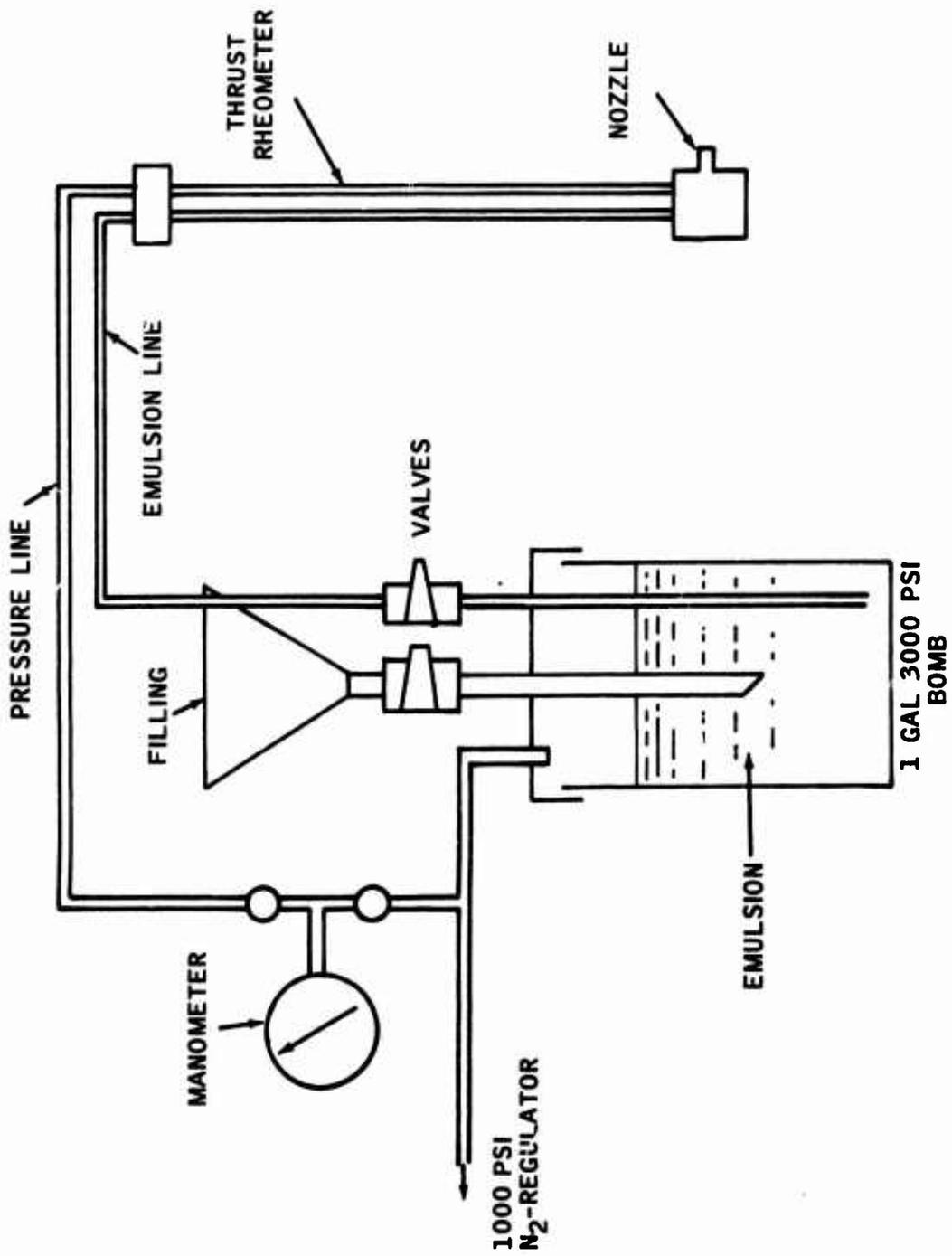
Figure 19. SCHEMATIC OF THRUST RHEOMETER SETUP
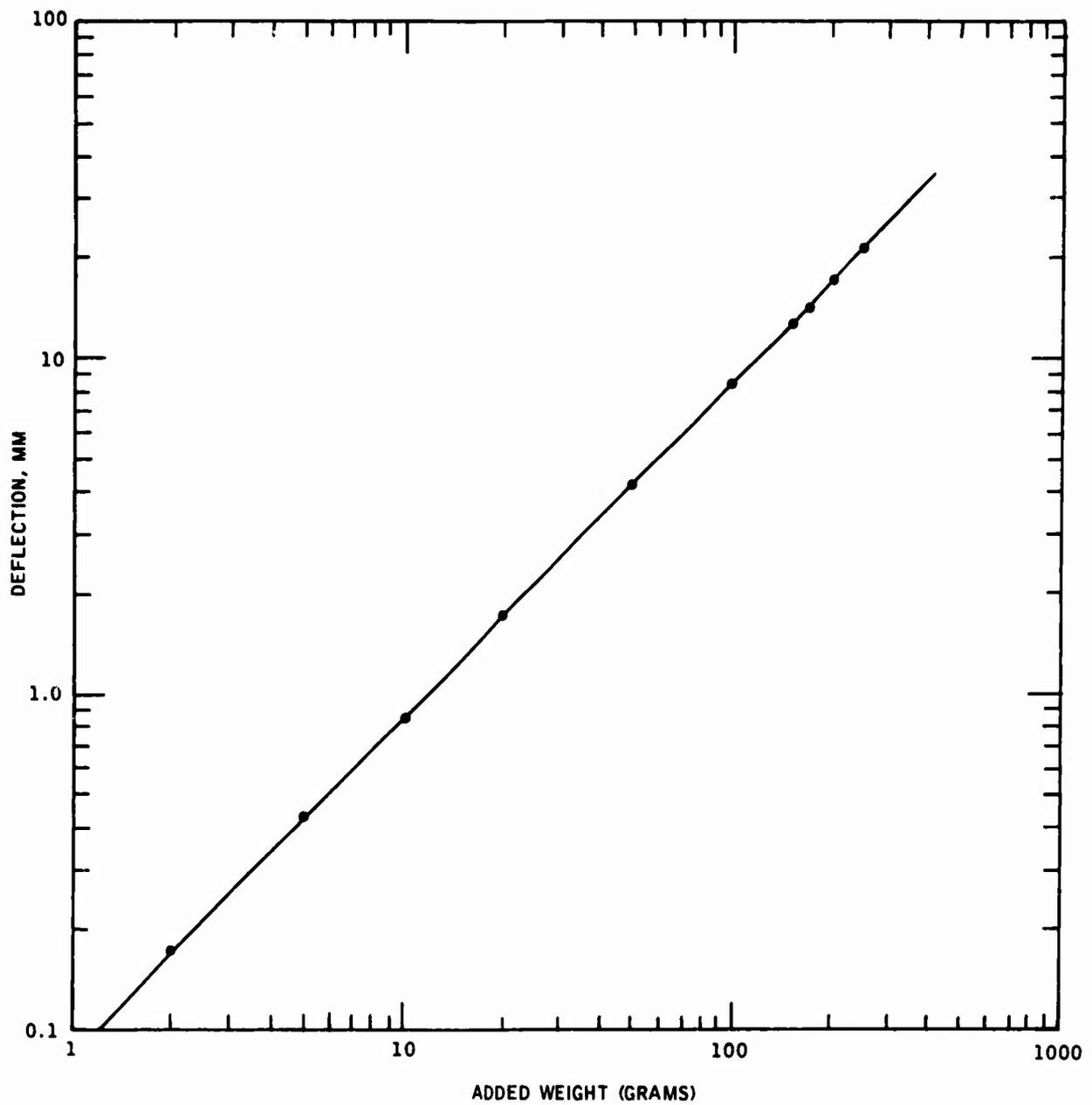
Figure 20. CALIBRATION CURVE FOR THE THRUST RHEOMETER

90

To determine the magnification achieved in the experimental optical setup, a small cylinder having a diameter of 1060 microns was accurately positioned to produce a sharp image. The size of the image produced was measured and compared to the actual size of the small cylinder. As long as the camera position was unchanged, a sharp image could be obtained in only a single position. This obviates having to calibrate the setup after each measurement. The calibration cylinder was not left in place during the experimental studies because it would have been wetted by the emulsion or JP-4; this would have rendered it useless as an internal standard for determining the degree of magnification.

Experimental Results

A. Thrust Measurements

A lubricating oil (Solvent 100 Neutral) which has a viscosity of about 35 cp at room temperature and JP-4 were investigated first in this program. The studies were first made using a capillary having a diameter of 0.86 mm and a length of 2 inches. At the completion of these studies, the two liquids were investigated in each of the four nozzles.

In the capillary it was found that the relation between applied pressure and throughput was not linear. Rather, it was roughly proportional to the square root of the pressure. Figure 21 shows throughput (M) versus thrust data for JP-4, Solvent 100 Neutral base oil, and two polymer-containing oils, E_1 and E_2 as obtained in the capillary for each of these systems. Over the entire range investigated, a plot of throughput versus thrust for JP-4 and base oil produces a straight line with a slope of 1/2 as required by theory. The difference in thrust between the lubricating oil and the JP-4 can be accounted for quantitatively by the difference in densities of the two liquids. This difference amounted to about 14 percent.

Thrust is given by the following expression:

$$\text{Thrust} = \frac{M^2}{PA} \qquad (1)$$

where

M = throughput in grams/sec
P = density in grams/cc
A = area of the capillary or nozzle in cm^2

The nozzles and the capillary at equal throughputs gave nearly identical thrusts. This was the case because the total area of the small holes of the nozzles was equivalent to the area of the hole in the capillary and because the throughput (M) is an average value. The T-63 engine nozzle did not produce a linear relationship between thrust and throughput (Figure 22). A linear relationship was observed with the other nozzles. The T-63 engine nozzle contained a check valve which opened at about 100 psi and thereby increased the throughput at this point; the thrust obviously increases dramatically at this point. After the check valve opened, i.e.,
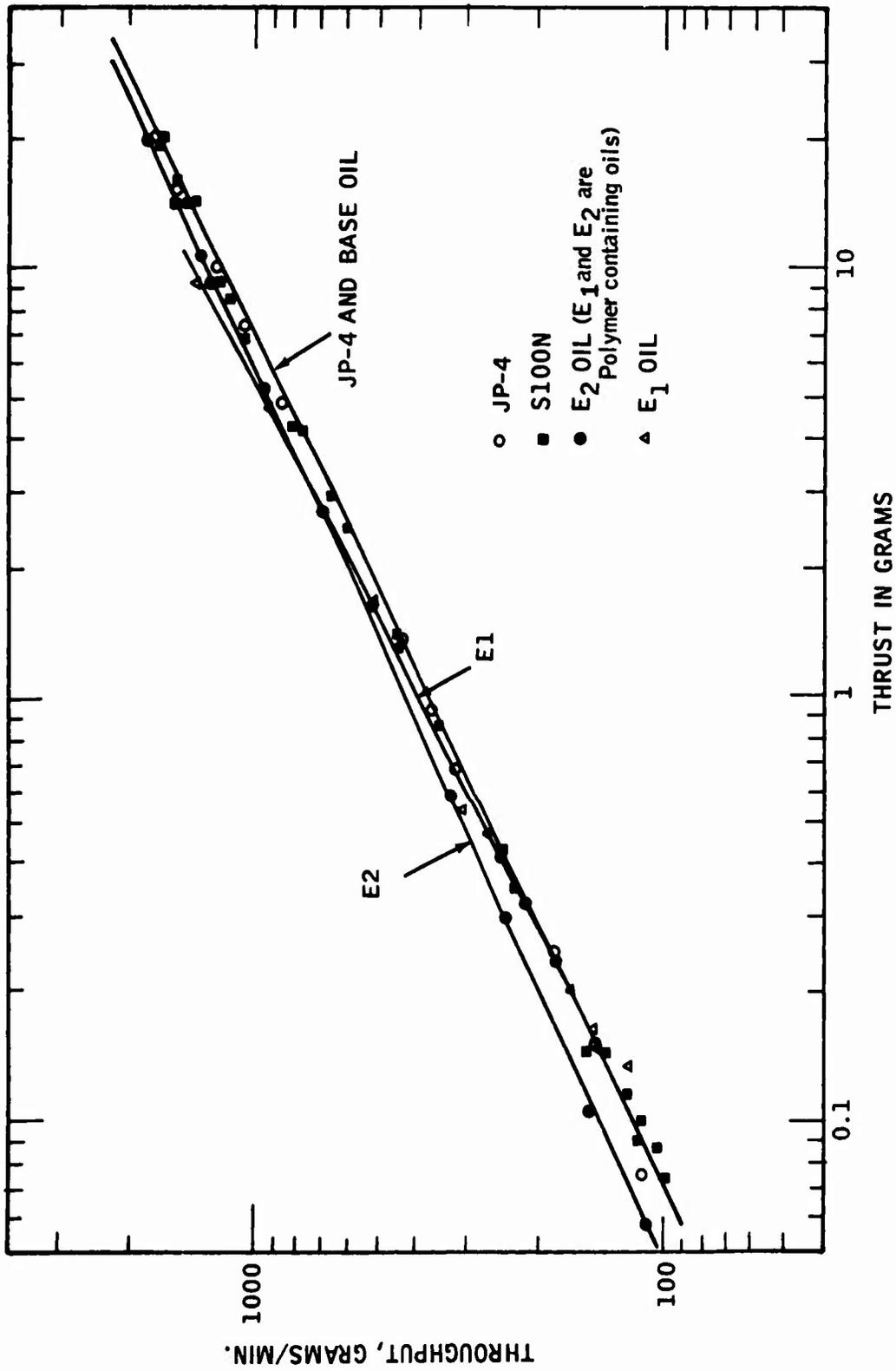
Figure 21. RELATION BETWEEN THROUGHPUT AND THRUST FOR NEWTONIAN AND NON-NEWTONIAN LIQUIDS

THRUST IN GRAMS

THROUGHPUT, GRAMS/MIN.

JP-4 AND BASE OIL

E1

E2

○ JP-4
■ S100N
● E_2 OIL (E_1 and E_2 are Polymer containing oils)
▲ E_1 OIL
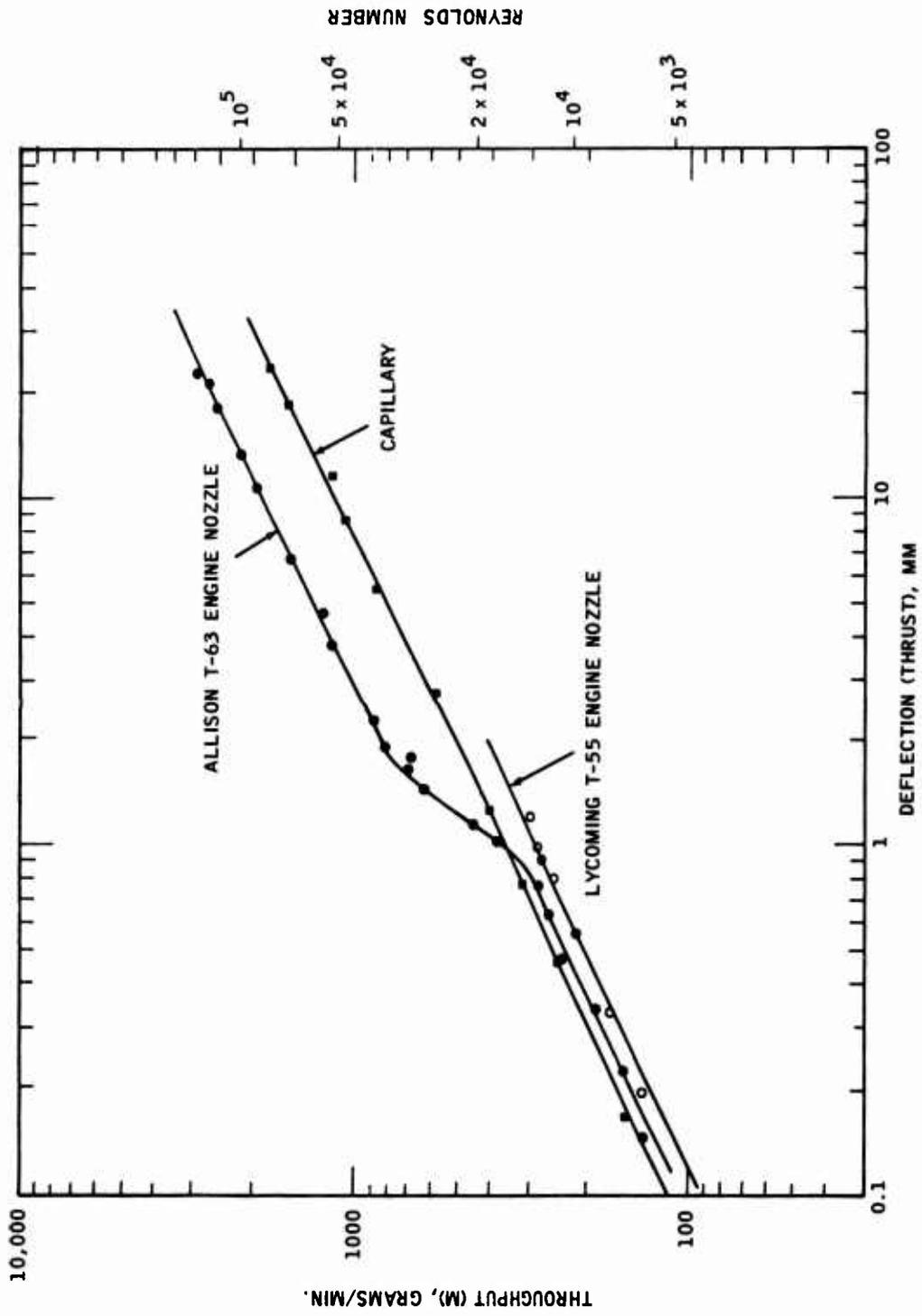
Figure 22. RELATION BETWEEN THROUGHPUT AND THRUST FOR JP-4 IN A CAPILLARY AND ENGINE NOZZLES (REYNOLDS NUMBERS ARE ALSO SHOWN)

at pressures above 100 psi, the square relationship between thrust and pressure was again established. The ratio of the curves describing the low-pressure region to that describing the high-pressure region (according to equation 1) should be the ratio of the areas over which flow occurs in the two operating regimes.

After completion of the studies with the two Newtonian liquids (Solvent 100 Neutral and JP-4), elasticity in flow was investigated with two polymer-containing oils (non-Newtonian) in the thrust rheometer using the capillary. The results of this study are shown in Figure 21. The data readily show the difference between the polymer-containing oils and the Solvent 100 Neutral. It is also apparent that the difference increases with rate of shear. Since these data were only obtained to demonstrate the difference between viscoelastic (non-Newtonian) and Newtonian liquids, no further analysis of the results is warranted.

The data in Figure 23 show the results obtained with fuel emulsion WSX-7063 using the capillary in the thrust rheometer. It is obvious that there is no difference between the thrust measured for the emulsion and JP-4 at the same throughput. Based on theory and our observations with the non-Newtonian and Newtonian oils, this obviously means that the emulsion is not viscoelastic in the thrust rheometer up to shear rates of 500,000 sec^{-1}. Several check measurements were performed with emulsion WSX-7063 in the nozzles. The thrust measured for both JP-4 and WSX-7063 was identical for all the nozzles. This obviously means that the emulsion is not viscoelastic under the conditions of shear encountered in the nozzles of jet engines. At low rates of shear, however, the emulsions are pseudoplastic with yield values of 2000 to 4000 dynes/cm^2. This finding allowed us to modify our experimental procedure. After ascertaining that the emulsions were not elastic, thrust measurements in the Rheometer were discontinued. The fact that the emulsions lose their elasticity at high rates of shear could not be anticipated intuitively from measurements at low shear rates or from just handling the emulsions. It is of considerable value to know that the behavior of fuel emulsions at high shear rates is identical to that of JP-4.

B. Pressure - Throughput Studies

After the investigations related to the elastic properties of fuel emulsions were completed, three other areas were pursued:

(A) Obtaining pressure - throughput data for the four emulsions in the four nozzles and the capillary

(B) Determining the extent of emulsion degradation in the nozzles and capillary

(C) Determining the particle size distribution of the WSX-7063 fuel emulsion after passing through the nozzles and capillary

94
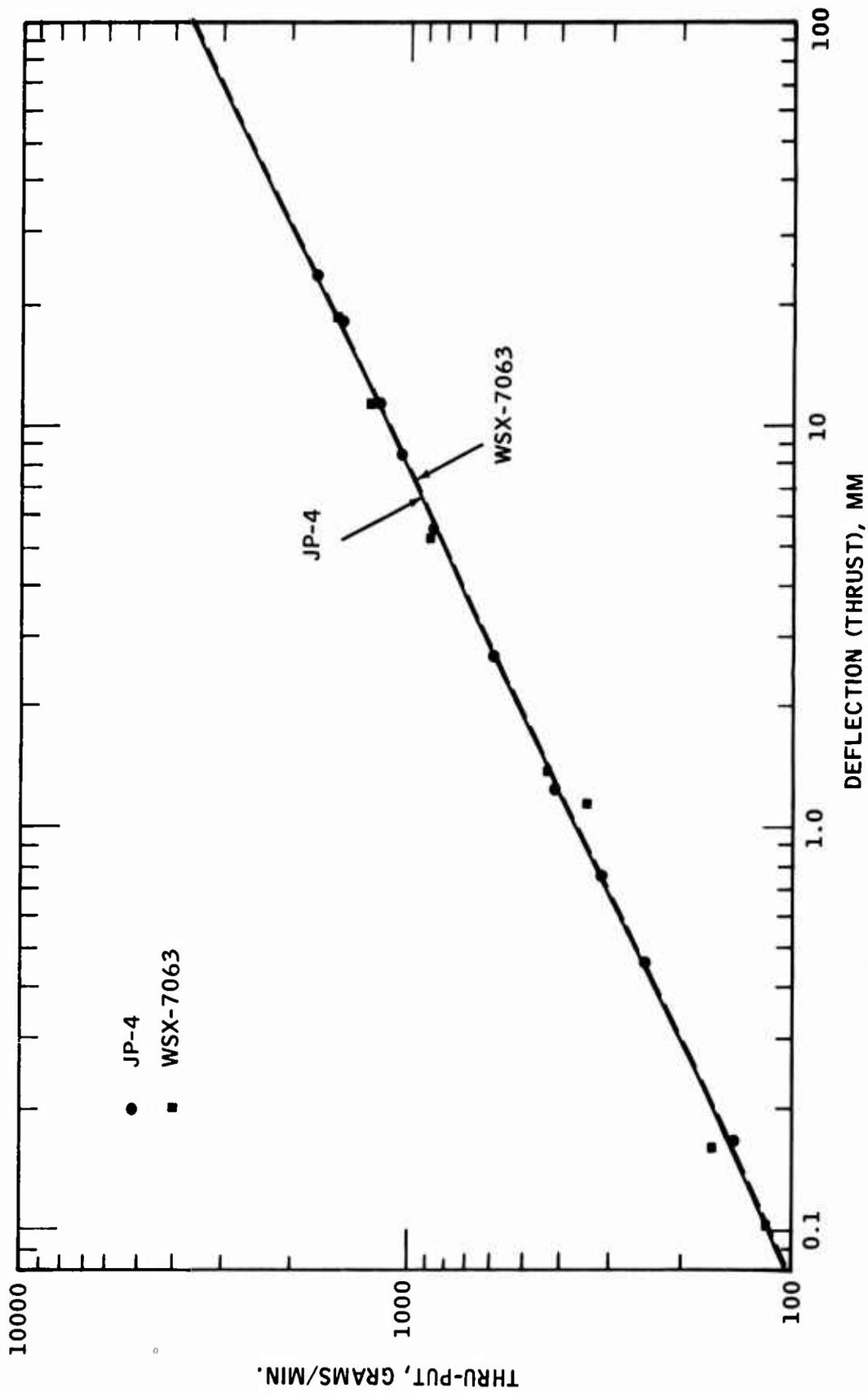
Figure 23. RELATION BETWEEN THROUGHPUT AND THRUST FOR JP-4 AND WSX-7063 IN A CAPILLARY

95

The pendulum-like device used on the thrust rheometer is quite sensitive to vibration. Therefore, in order to obtain meaningful measurements with this device, it was necessary to dampen out all extraneous vibrations not related to the thrust produced by fluid passing through the nozzle. This was accomplished by attaching a cross made of steel plates to the bottom of the pendulum and immersing it in a large beaker which contained oil (Bright Stock) having a viscosity of about 10 poises. The height of the oil in the beaker was adjusted so as to roughly produce periodic deflection of the pendulum under the influence of the emerging fluid from the nozzle. This experimental setup proved to be entirely satisfactory for all the studies carried out in this program.

B. Photographic Attachments

In order to determine the particle size distribution and the shape of the jet emerging from the nozzles, a photographic attachment capable of stopping this action was used. This was achieved by using a photo-flash unit that produced a very intense spark discharge over a time span of one-half microsecond. Even with a linear velocity of 100 ft/sec, which is greater than the maximum linear velocity used to force the emulsions and JP-4 through the nozzles, the fluids traveled a distance less than one-thousandth of an inch during the photographic process. This did not have any appreciable influence on the sharpness of the photographs. The jet emerging from the nozzle was directed horizontally, and the photo-flash unit was situated so as to produce a sharp photograph in the horizontal plane.

In order to eliminate wetting of the flash unit by the emerging spray from the nozzles, it was necessary to place the entire flash unit in a 5-gallon can. A 1-inch hole was made in the can to allow the light from the unit to reach the photographic objective. The objective used to photograph the emerging jet from the nozzles was an 8 mm film objective with an opening of 1:1.2 and a 14 mm focal length. With the Polaroid land-camera used, a 30-fold magnification was possible. To achieve a 30-fold magnification, the objective was placed at about 14 mm (focal length) away from the jet emerging from the nozzle. The camera without any other lens was moved to about 18 inches from the objective. Therefore, magnification was achieved by distance only and not by any complicated optical arrangements. Other investigators have used longer focal length objectives which require enlargement of the photographs. Because of the graininess of the film, enlargement of photographs to give a 30-fold magnification would result in pictures too fuzzy to be of value.

The camera and objective were mounted on the cross-support of a lathe bed which was positioned parallel to the emerging jet. In this way, photographs of the emerging jet as a function of distance from the nozzle could be made. The camera could be moved over a distance of 2 feet using this setup; however, at such distances from the nozzle, sharp photographs are impossible to get because the position of the emerging jet is too unstable. The position of the jet varied between the focusing period and the actual photographic period. The limit of resolution with this equipment and experimental setup is about one micron. It was possible to determine drop size with an accuracy of ± 10 percent of the diameter of the drops.

96

Pressure - Throughput Results

It is well known that the Hagen-Poiseuille Pressure Law describes the pressure drop associated with the laminar flow of a liquid through a capillary which in its simplest form is given by:

$$D = \frac{4}{\pi} \frac{Q}{R^3} \quad \text{or} \quad D = \frac{4}{\pi} \times \frac{M}{\rho R^3} \times \frac{1}{60} \quad (2)$$

$$\text{and} \quad T_R = \frac{Rp}{2L} \quad (3)$$

where

D = shear rate in sec^{-1}

T_R = shear stress at the capillary wall in dynes/cm^2

R, L = radius and length of the capillary, respectively, in cm

M = $Q \rho \times 60$ = throughput in grams/minute

ρ = density in gm /cc

Q = throughput in cc/second

P = applied pressure drop in dynes/cm^2
(1 psi = 69000 dynes/cm^2)

Plotting M or Q over P should result in a straight line or, if a log-log plot is made, a straight line having a slope of one should result. However, this is not the case where the fuel flows through the nozzles. First of all, the "active" pressure drop is smaller than the applied one by an amount of energy equal to the kinetic energy available in the jet. This energy is proportional to the square of the throughput (grams/minute), i.e., $M \sim \sqrt{P}$. This condition is more or less true for JP-4 involving flow through the nozzles and the capillary. Furthermore, it is also well known that under the conditions of turbulent flow, the throughput (M) is not linear with respect to the pressure. The increase in throughput under turbulent flow is less than the corresponding increase in the applied pressure. Turbulent flow, however, requires a certain length of travel to be fully established. As shown in Figure 24, throughput (M) corresponds to a square root dependence on pressure (P). This means that under the hydraulic conditions encountered in the nozzle, the conditions are best described by the theory which involves a large amount of kinetic energy in the emerging jet rather than the theory which involves just turbulent flow.
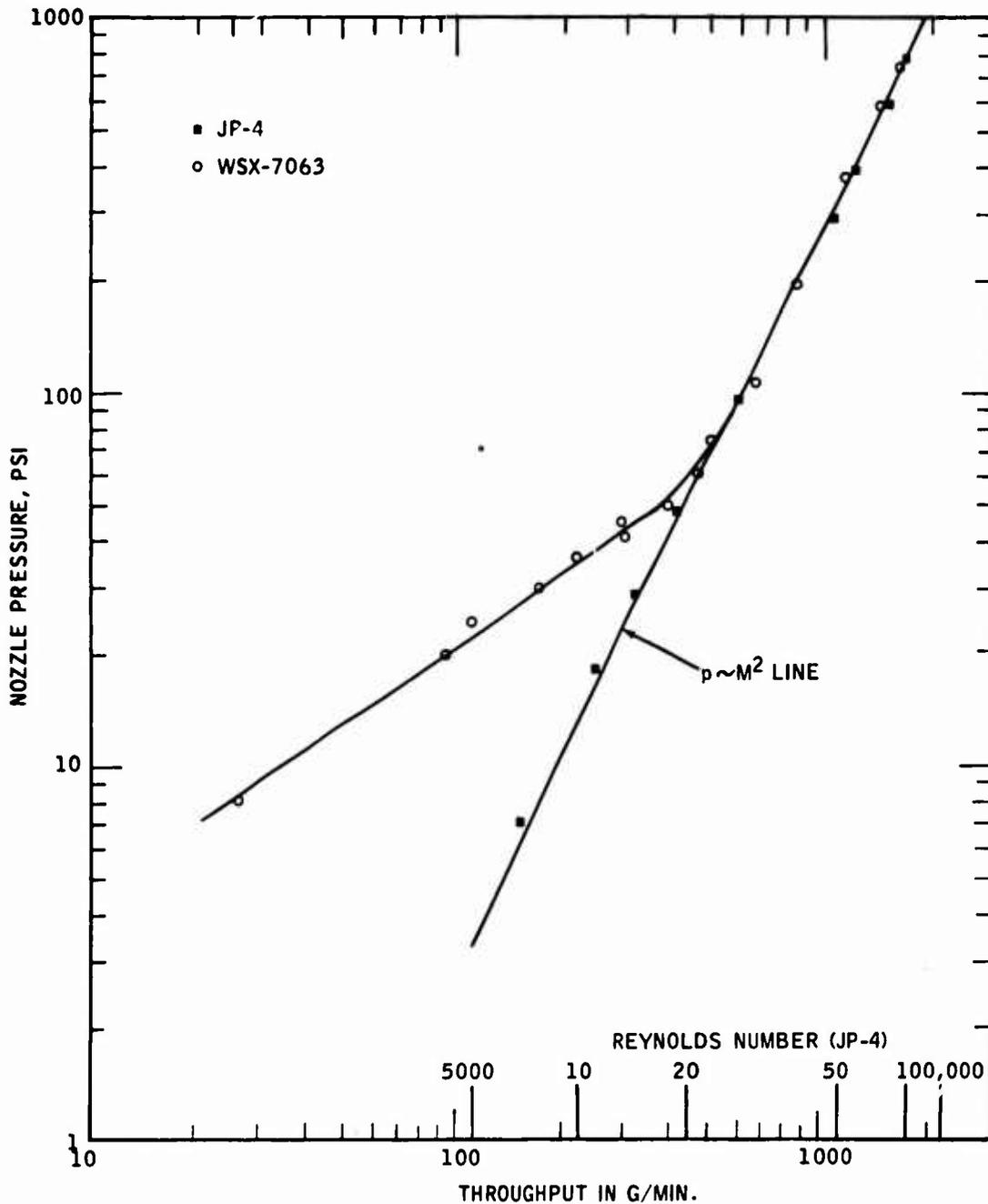
Figure 24. RELATION BETWEEN NOZZLE PRESSURE AND THROUGHPUT FOR JP-4 AND
WSX-7063 IN A CAPILLARY (REYNOLDS NUMBERS ARE ALSO SHOWN)

98

The Reynolds number (R_e) is given by the ratio of the inertial forces to frictional forces. When these forces are approximately the same magnitude, a transition from laminar to turbulent flow occurs. This transition is described by the critical Reynolds number (R_{ecr}), which is 2,300 for tube flow. However, the significance of the Reynolds number (R_e) is maintained even if the critical Reynolds number (R_{ecr}) is not observed. Reynolds numbers calculated for JP-4 in the capillary are as high as 80,000, which is considerably higher than the critical Reynolds number of 2,300. Therefore, the energies involved in accelerating the emerging jet are more than 10 times greater than the frictional forces associated with forcing the liquid through the capillary. Under these conditions, the "viscous drop" over the nozzle is negligible as compared to the pressure drop necessary to accelerate the emerging jet. Therefore, the viscosity of the liquid should not have any appreciable effect on the pressure drop measured across the capillary at the very high shear rates encountered in the capillary. This is indicated by the data shown in Figure 24, where the pressure drop (P) versus throughput (M) is plotted. The Reynolds number for JP-4 in the capillary is also presented. This is interpreted to mean that all the energy associated with the pressure drop is used to accelerate the emerging jet, with a negligible amount of this energy being dissipated in the form of frictional loss in the capillary. This also holds for flow through the nozzles as we shall see later.

Figure 24 also shows pressure drop versus throughput data for the capillary using fuel emulsion WSX-7063. The data show that there is no difference between the pressure drop at a given throughput (M) above 500 grams/minute for JP-4 and the fuel emulsion in the capillary. Below a throughput of 500 grams/minute, the viscosity of the emulsion increases with diminishing throughput, which is a non-Newtonian behavior. Therefore, the pressure is considerably higher for the emulsion than it is for JP-4 at low throughputs ($<$ 500 grams/minute). Figure 24 shows this divergence of the plots for JP-4 and WSX-7063 at throughputs below 500 grams/minute. The capillary was used for these measurements because the conditions in the capillary are more easily defined theoretically. Therefore, it is easier to calculate Reynolds number and rate of shear in the capillary than in the nozzles. Because the geometry of the nozzles is much more complicated than the capillary, it is almost impossible to calculate the hydraulic variables involved to any rigorous degree.

The data in Figures 25 through 28 show the flow behavior of the four fuel emulsions in the four helicopter nozzles and the capillary investigated in this program. Once again the data are plotted as pressure drop (P) versus throughput (M). As shown, there is no difference in the behavior between the four fuel emulsions and the JP-4.
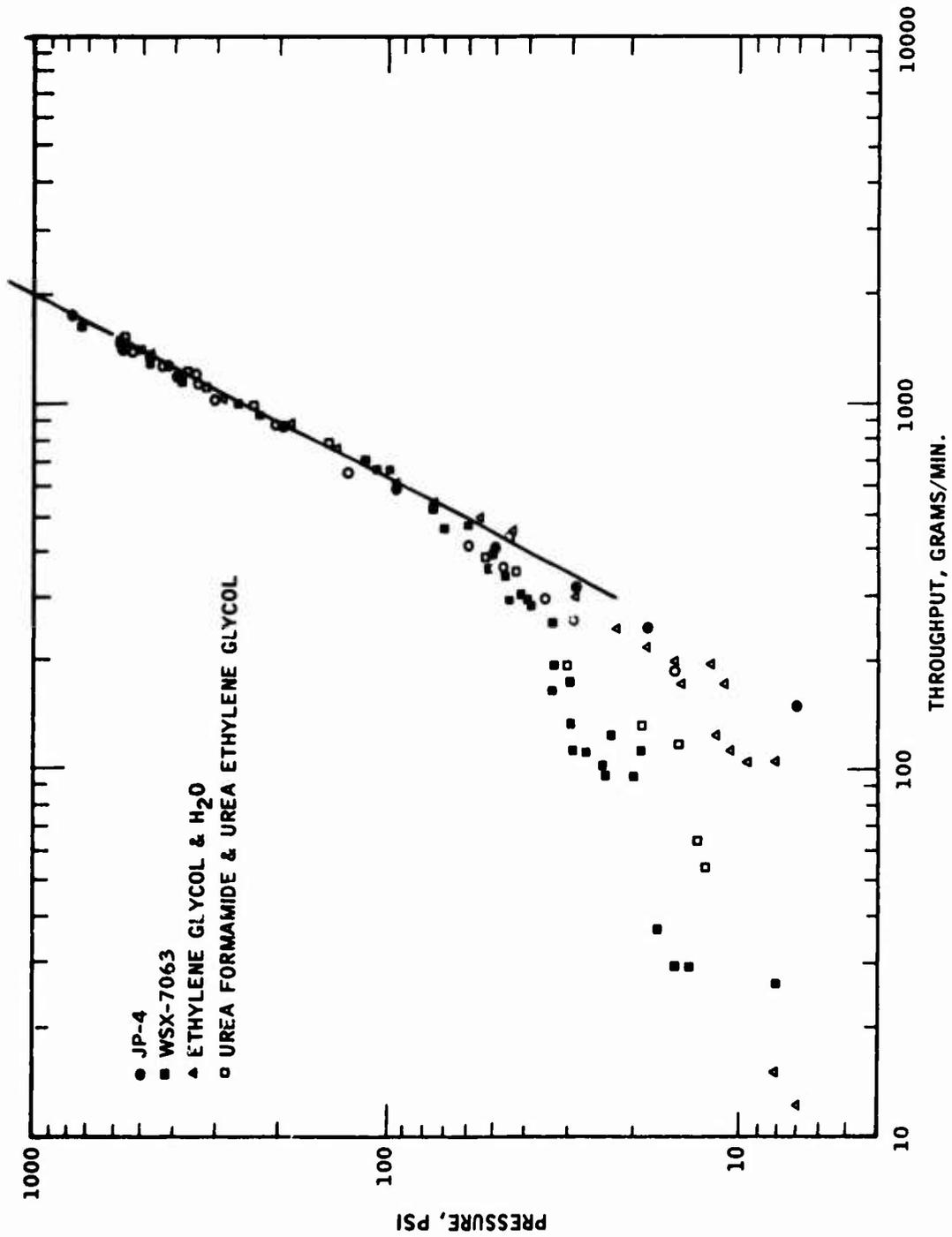
Figure 25. RELATION BETWEEN NOZZLE PRESSURE AND THROUGHPUT FOR FUEL EMULSIONS AND JP-4 IN A CAPILLARY

100
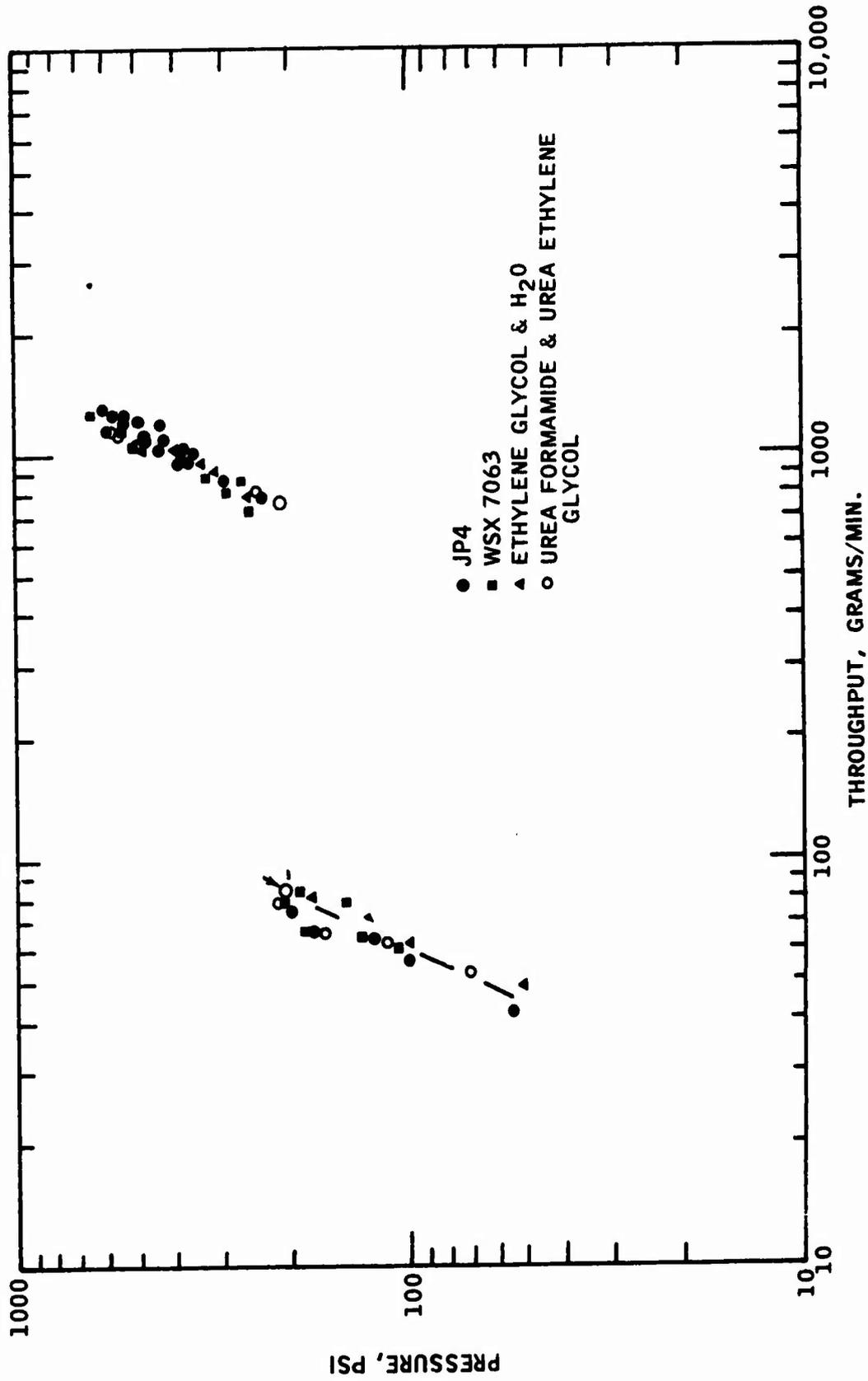
Figure 26. RELATION BETWEEN NOZZLE PRESSURE AND THROUGHPUT FOR FUEL EMULSIONS AND JP-4 IN A G.E. T-64 ENGINE NOZZLE

● JP4
■ WSX 7063
▲ ETHYLENE GLYCOL & H₂0
○ UREA FORMAMIDE & UREA ETHYLENE GLYCOL

THROUGHPUT, GRAMS/MIN.

PRESSURE, PSI

101
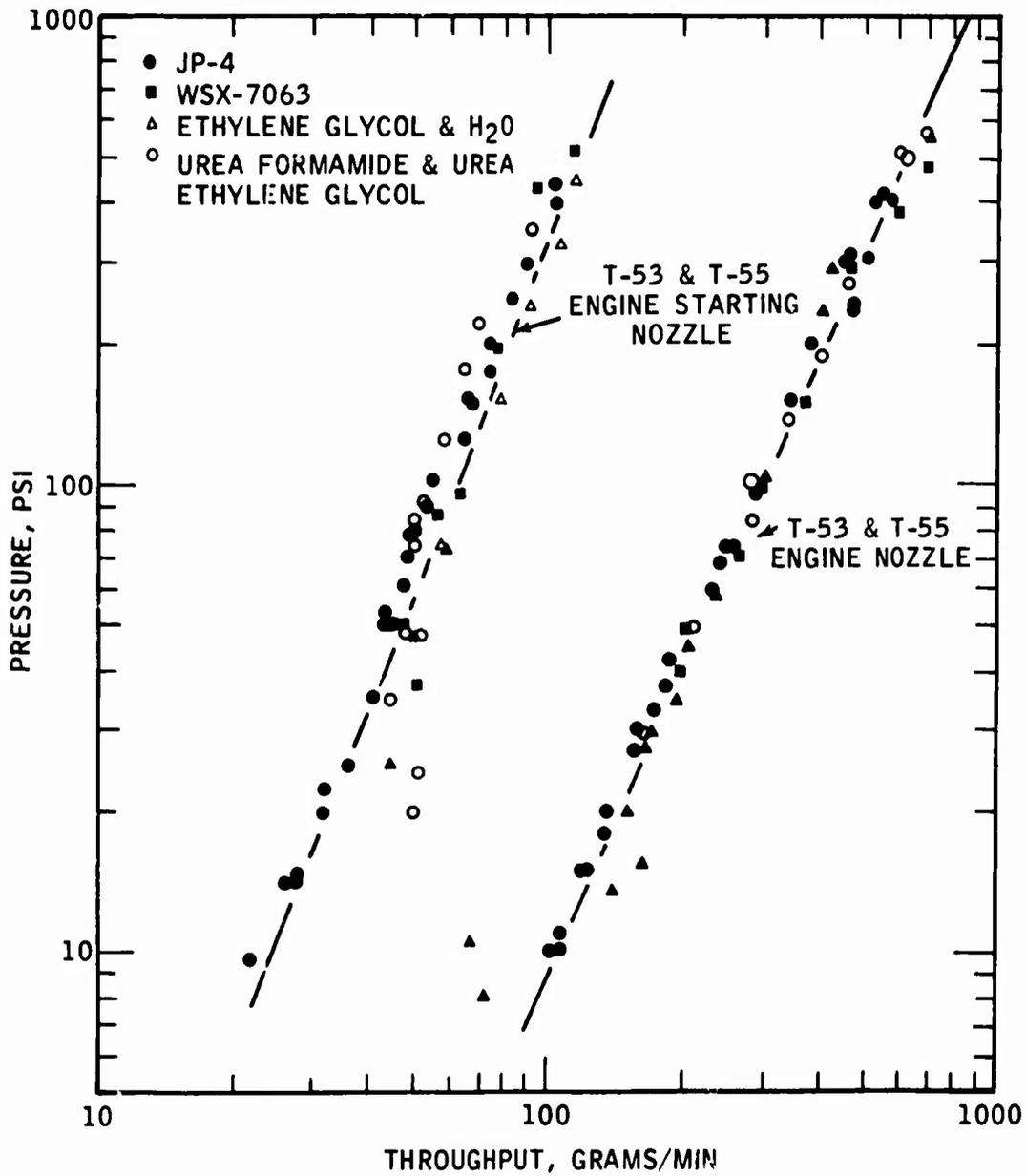
Figure 27. RELATION BETWEEN NOZZLE PRESSURE AND THROUGHPUT FOR FUEL EMULSIONS AND JP-4 IN LYCOMING T-53 AND T-55 ENGINE NOZZLES
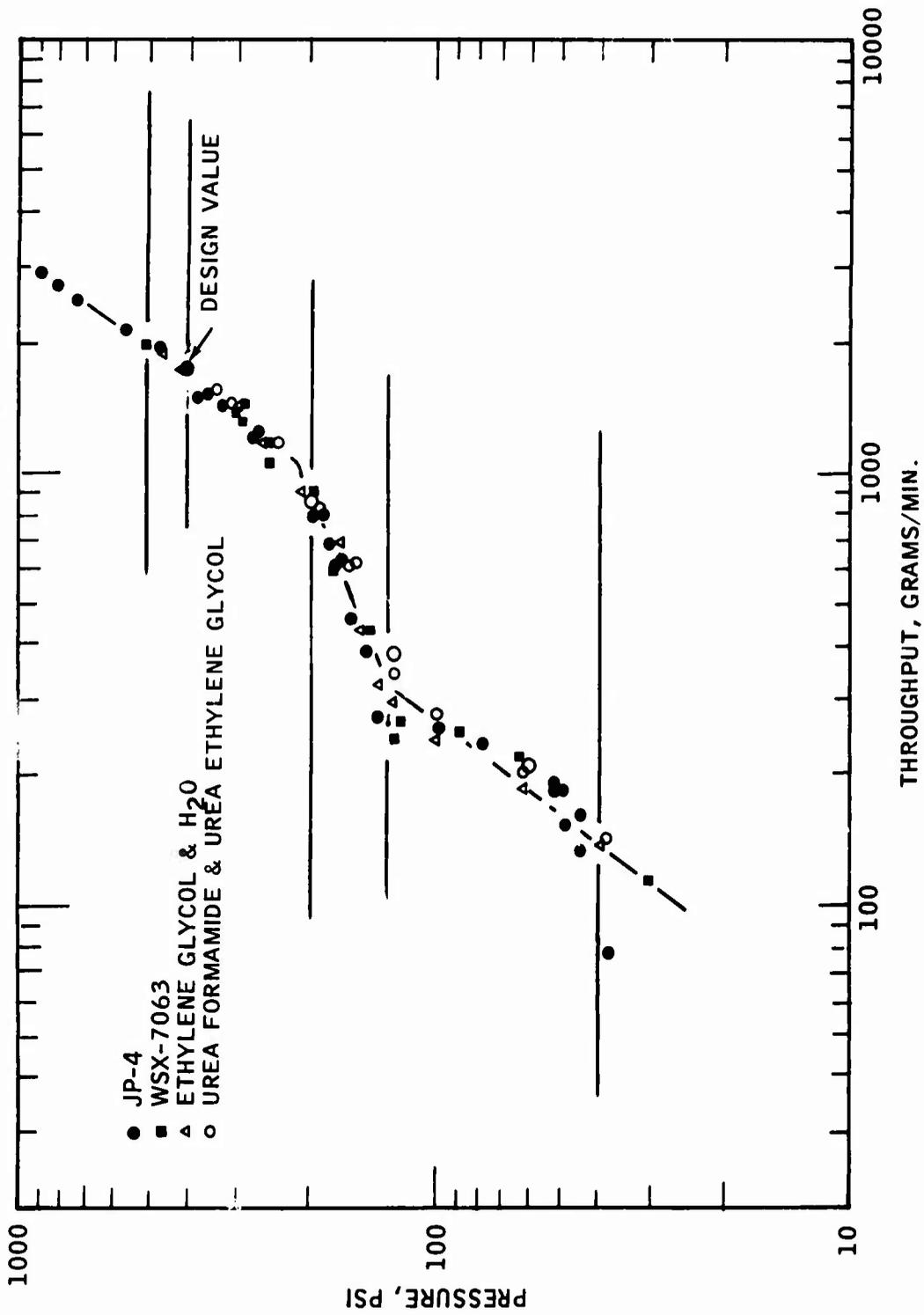
Figure 28. RELATION BETWEEN NOZZLE PRESSURE AND THROUGHPUT FOR FUEL EMULSIONS AND JP-4 IN AN ALLISON T-63 ENGINE NOZZLE

C. Emulsion Degradation

The emulsion is required to remain firm in the tanks of the aircraft in order to minimize and/or eliminate fire. For the safest possible condition, it should also remain intact right up to the nozzle. It would appear, however, that if the emulsion is to burn in the same manner as JP-4, the emulsion should enter the combustor completely broken down. Should the emulsion not be broken down, the undestroyed emulsion would have a much slower evaporation rate, which would cause a "long flame". This has actually been observed in experiments carried out by G. Opdyke of the Lycoming Division of Avco Corporation. Therefore, it would seem desirable to have complete breakdown of the emulsion when it passes through the nozzle. In addition, the particle size distribution of the atomized emulsion should also be equivalent to that of JP-4. It would seem that these conditions are required if the fuel emulsion is to operate in a manner equivalent to that of JP-4 in the combustor. Thus, degradation studies were carried out. Amount of breakdown was measured by catching the emulsion emerging from the capillary and the nozzles and filtering the free JP-4 from the unbroken emulsion.

The degradation studies were also carried out with the capillary because it was possible to calculate she   ates. The results of this study are summarized in Figure 29. The data show that the overall degradation of the emulsion increases with the rate of shear. For the ethylene glycol-water continuous phase emulsion and the urea-ethylene glycol-formamide continuous phase emulsion, breakdown is essentially complete at the high rates of shear in the capillary. However, in the case of WSX-7063 and WSX-7165, breakdown occurs only to the extent of 80-85 percent at high rates of shear in the capillary. Figure 30 shows the extent of degradation of WSX-7165 fuel emulsion as it is forced through the four different helicopter nozzles. For the G.E. and Allison engine nozzles, the degradation of the emulsions is similar to that achieved in the capillary. For the Lycoming engine nozzles, where the flow rates are lower than in the Allison or G.E. engine nozzles, the amount of emulsions breakdown was only 40 percent at the equivalent of idling speed. This condition represents the lowest rated throughput for the two Lycoming engine nozzles. A 40 percent breakdown of the emulsion could cause trouble in the operation of the engine at idling speed. Whether or not 40 percent residual emulsion is detrimental to proper engine operation cannot be ascertained from these studies. Actual combustion studies are required to answer this important question. A priori, however, it would seem that the less unbroken emulsion emerging from the nozzle, the better the engine performance.
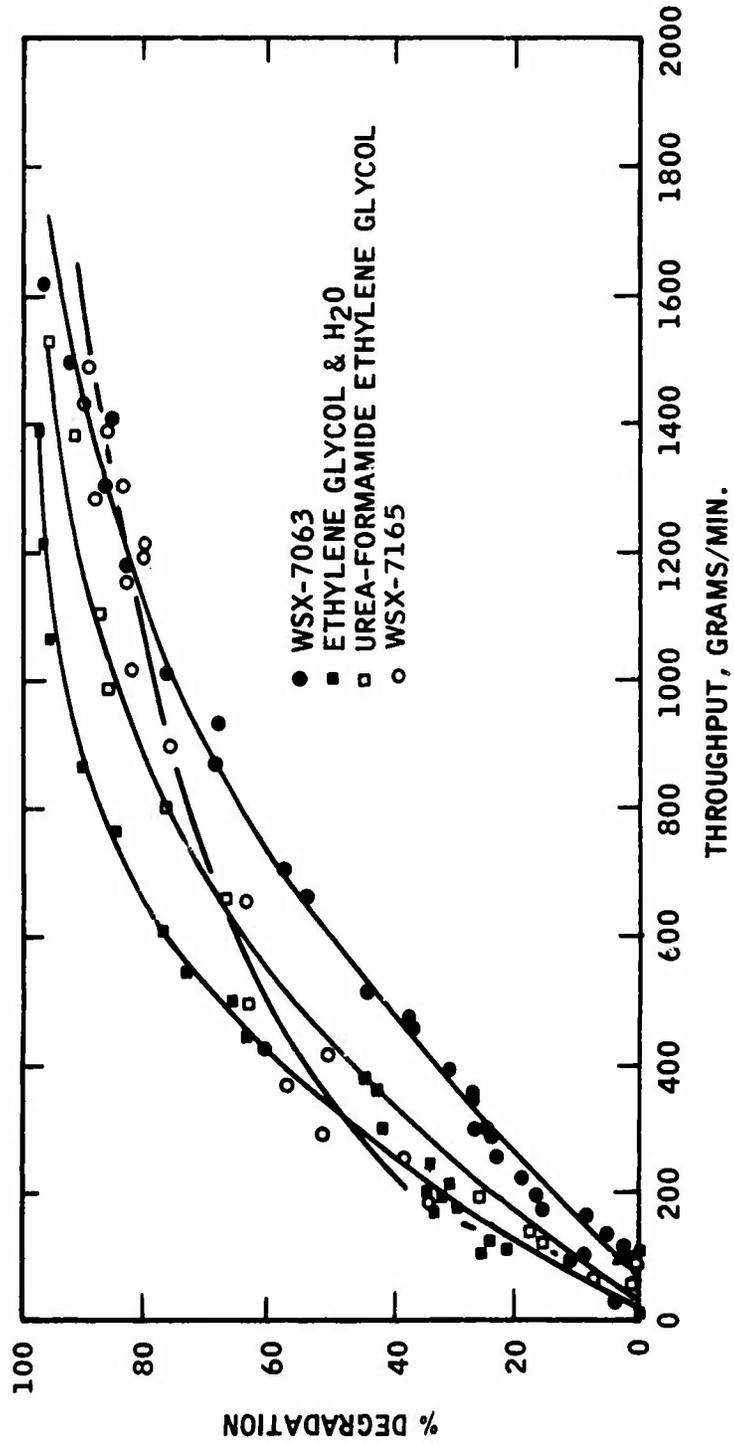
Figure 29. EFFECT OF SHEAR RATE (THROUGHPUT) ON EMULSION BREAKDOWN
IN A CAPILLARY

105
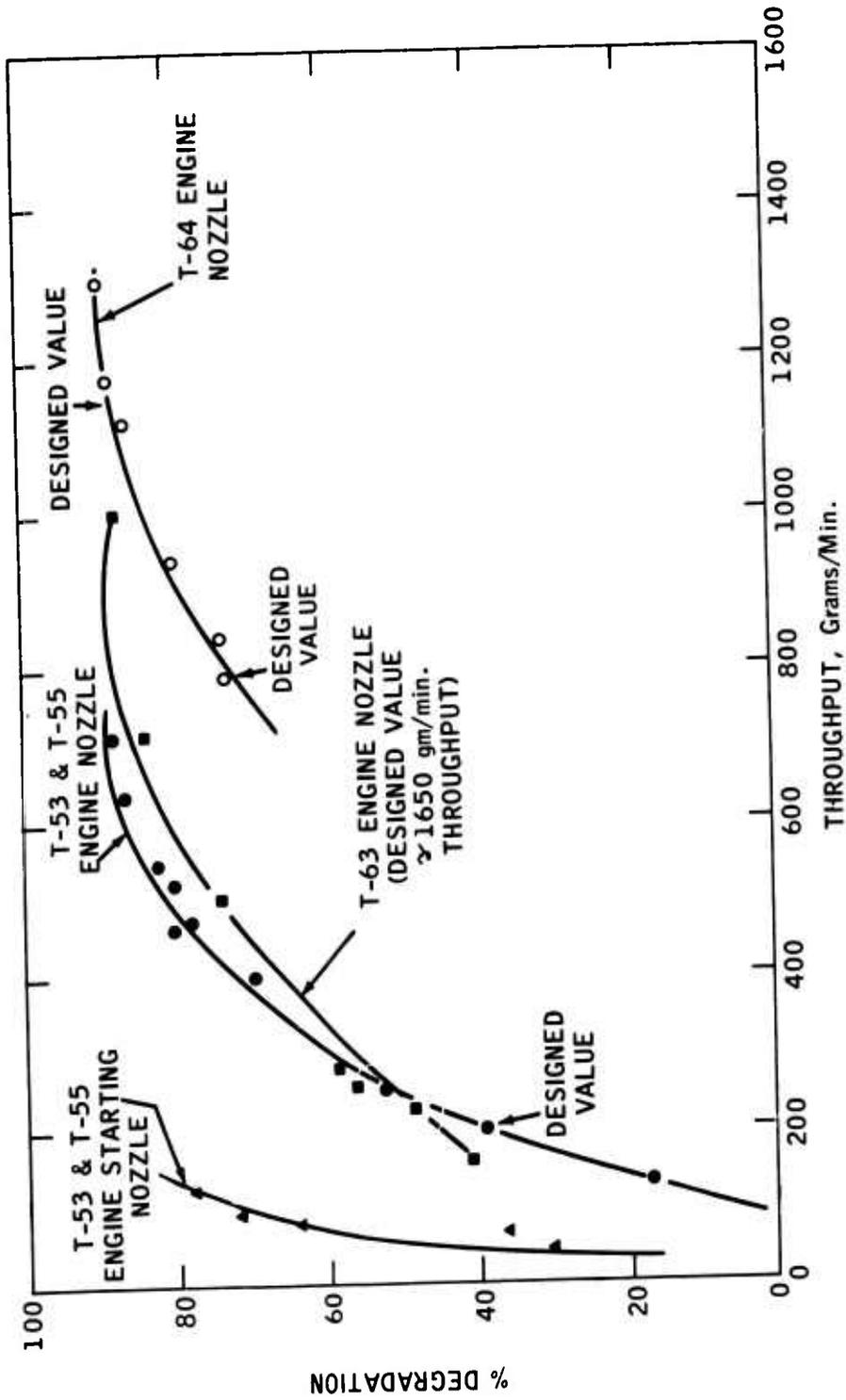
Figure 30. EXTENT OF BREAKDOWN OF WSX-7165 IN ENGINE NOZZLES

D. Particle Size Distribution

As seen from Figure 31, the JP-4 emerged from the capillary in the form of a corregated cylinder and remained coherent without disintegration for an appreciable distance from the capillary. At greater distances from the capillary, the emulsion broke up into a spray; however, its motion was so unstable that it was impossible to obtain sharp pictures with the existing equipment. The fuel emulsion emerged through the capillary in the form of a glass-clear cylinder (Figure 32) and remained coherent over the entire distance from the capillary to the collection pan.

The difficulty associated with investigating drop size of the atomized fuel as it emerged from the nozzles is due to the fact that the nozzles sprayed the fuel in a 90° cone. Therefore, at a 45° angle to the axis, there were a considerable number of drops. However, due to the scatter of the drops, it was impossible to get any appreciable number of drops in the same photograph. In addition to this problem, because of the position and close proximity of the objective and flash unit to the spray, they became completely coated with the fuel, making it impossible to get meaningful photographs. The spark unit was placed in a 5-gallon can fitted with a 1-inch straight pipe which took the light to the vicinity of the objective. In this manner, a series of photographs was made in which JP-4 and WSX-7063 were the fuels. These photographs, which appear in Figures 33 through 36, show that the particle size for both JP-4 and WSX-7063 is about the same. Because of the difficulties already discussed, the number of drops per photograph is small and therefore cannot be used for a statistical treatment of the data. However, it is safe to conclude that the drop size for atomized JP-4 and WSX-7063 is about the same. Further studies would be required to determine the drop size of the emerging JP-4 and emulsion quantitatively.

A more detailed investigation of drop size distribution could not be done with actual nozzles. However, this could be done with capillaries that have diameters equivalent to the holes in the nozzles. A higher magnification objective would also be required for such a study.

As shown, about 10 to 20 percent of the emulsion passes through the nozzle unbroken. The question arises as to whether the unbroken emulsion is uniformly distributed or whether it constitutes mainly the larger drops. To study this problem, the continuous phase was treated with a red dye which was insoluble in the JP-4. A series of color photographs was taken of the atomized red emulsion. Figure 37 shows that the emulsion is mainly distributed in the form of the larger drops. Additional studies are required to determine whether this condition prevails with other emulsions.
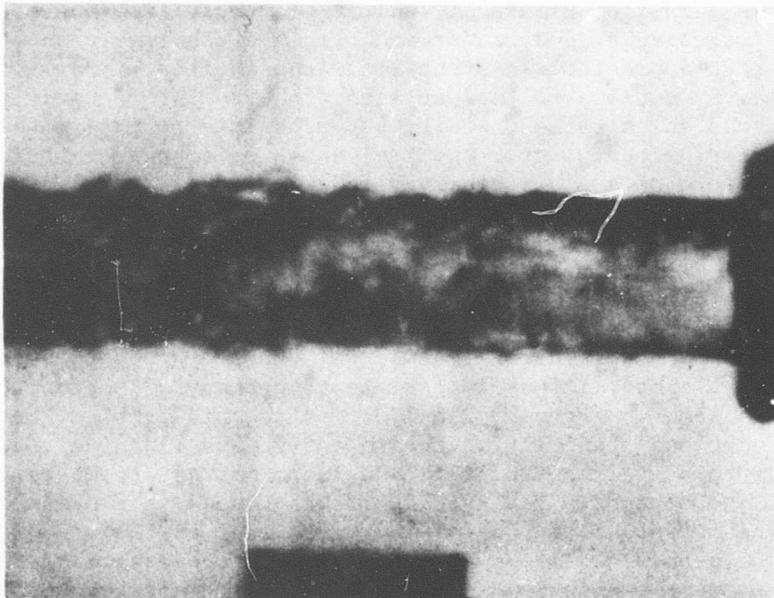
Figure 31. Emerging Jet of JP-4 From the Capillary
(30X Magnification).
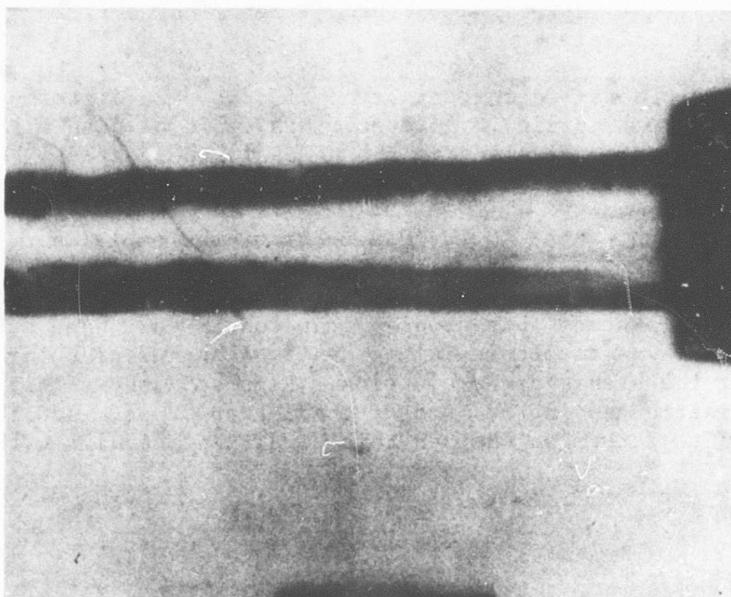
Figure 32. Emerging Jet of Emulsion From the Capillary
(30X Magnification).
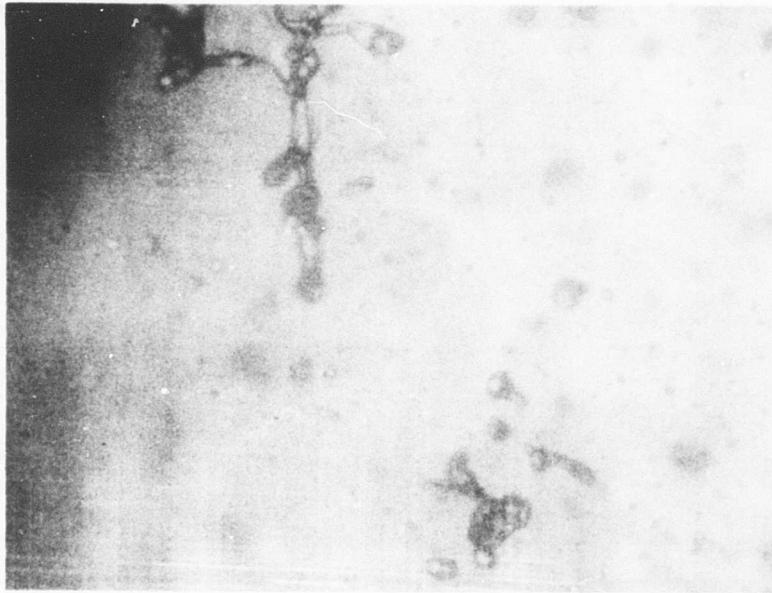
Figure 33. Atomized JP-4 Viewed at a 30° Angle From the Nozzle
(Very Close to Nozzle; 30X Magnification).
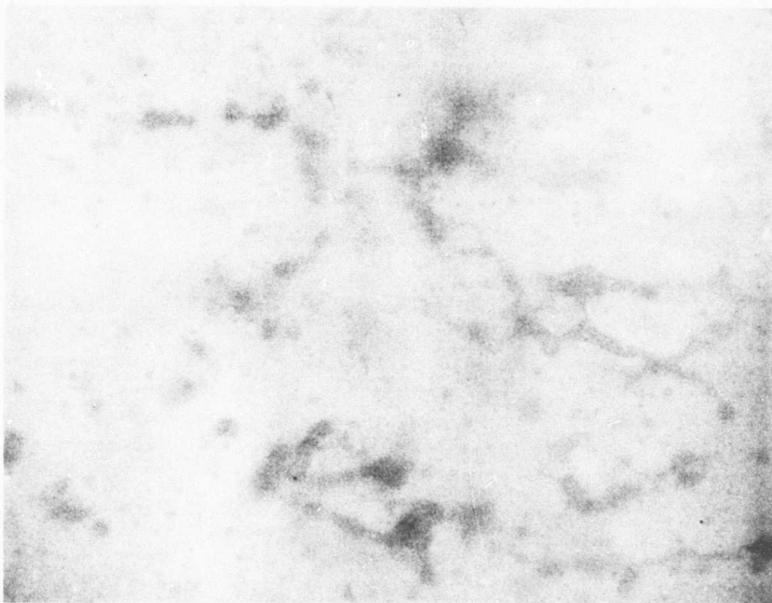
Figure 34. Atomized WSX-7063 Viewed at a 30° Angle From the Nozzle
(Very Close to Nozzle; 30X Magnification).

Figure 35. Atomized JP-4 Viewed at 30° Angle From
the Nozzle (25 mm From the Nozzle;
30X Magnification).
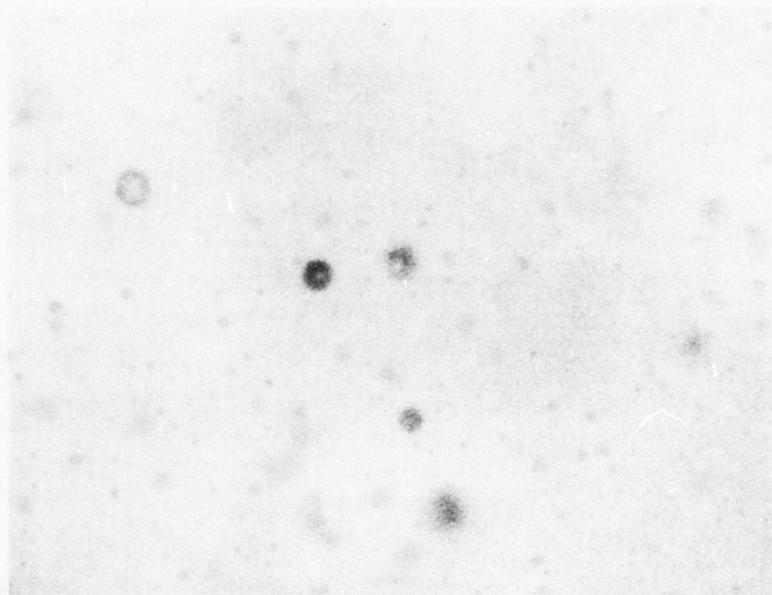
Figure 36. Atomized WSX-7063 Viewed at 30° Angle From
the Nozzle (25 mm From the Nozzle;
30X Magnification).

110
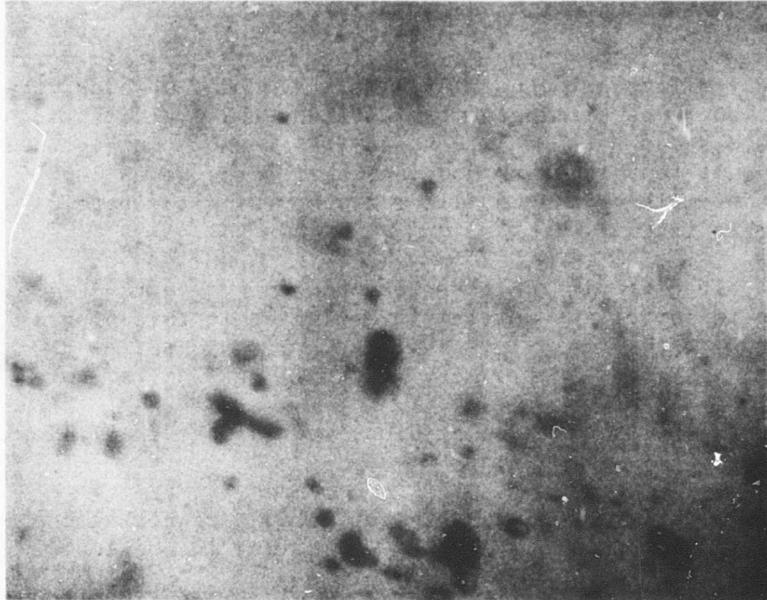
Figure 37. Atomized Fuel Emulsion Containing
Dye Soluble in Continuous Phase
(Large Drops Are Emulsion;
30X Magnification).

111

Problems Encountered

The main difficulty encountered during the course of this program was plugging of the nozzles and capillaries by contaminants present in the emulsion. A more detailed investigation showed that the contaminants were hair and fibers. The most severe plugging always occurred during the operation of the Lycoming engine nozzles. It was found, however, that the plugging problem could be eliminated by filtering the emulsion through a cloth filter below a shear rate of 30,000 sec^{-1}. As shown in Figure 29, the emulsions do not tend to break down at shear rates below 30,000 sec^{-1}. Therefore, the emulsion can be filtered, providing the rate of shear is kept below this level.

No plugging difficulties were encountered with JP-4 either in the capillary or in any of the nozzles investigated in this program.

Conclusions

On the basis of these studies, we can make the following conclusions:

(1) The fuel emulsions investigated were not viscoelastic under the conditions of high-speed flow in nozzles.

(2) The pressure drop for JP-4 and the fuel emulsions is identical at the same throughput.

(3) The particle size of the JP-4 and fuel emulsions droplets emerging from the nozzles appears to be identical. Further work is needed to determine this quantitatively.

(4) As much as 20 percent of the emulsions passes through the nozzles unbroken.

(5) The emulsions can be filtered to remove contaminants without breakdown of the emulsion.

Recommendations

The work under this phase of the contract suggests that the following areas should be investigated:

(1) The mechanism of emulsion breakdown should be investigated to ascertain how shear affects the mechanical properties and structure of the emulsions.

(2) The development of emulsions is a compromise between having the emulsion highly stable at low rates of shear and having the emulsion unstable at high rates of shear. Stability in this respect has not been optimized. Rheological studies should be carried out in conjunction with formulation studies to optimize the emulsions in this respect.

APPENDIX III

EVALUATION OF WSX-7063 BY LYCOMING
IN THE JFC 31 FUEL CONTROL SYSTEM

PURPOSE

The purpose of the test was to determine the feasibility of using WSX-7063 fuel emulsion in existing fuel control systems with a minimum of modifications.

BACKGROUND

The testing of the emulsion was conducted on December 9, 1966, in accordance with Contract No. P.O. E.R. 105.91-D. Dr. J. Nixon of Esso Research and Engineering Company observed the tests.

SUMMARY

The JFC 31 fuel control is capable of pumping and metering the Esso emulsion, WSX-7063. The fuel flow schedules metered by the control with the emulsion and with E 2074A Type II calibration fluid were compared and found to be acceptable and within the normal tolerance limits.

TEST ITEMS

1. Hamilton Standard
2. Experimental Barrier Type Filter (40-micron rating)
3. Esso (WSX-7036) Emulsion

TEST SETUP

Figure 38 is a schematic that defines the test setup used in the evaluation of the emulsified fuel for the control calibration. The emulsion was pumped to the fuel control pump from 50-gallon storage tanks with a pneumatically powered piston pump. The fuel discharge from the system was measured by the weight/time method.

Figure 39 is a schematic that defines the pump flow path for the JFC 31 fuel control pump.

TEST PROCEDURE

Fuel Control Calibration

The JFC 31 fuel control was calibrated for 59°F day sea level conditions. The following schedules were generated with both test fluids:
- Starting schedule
- Acceleration schedule
- Military droop schedule
- Ground idle droop schedule
- Deceleration schedule

LEGEND
P₁-Filter Inlet   PSI
P₂-Pump Inlet   PSI
P₃-Gear Pump Inlet   PSI
P₄-Pump Discharge   PSI
P₅-Pump Discharge   PSI
P₆-Back Pressure   PSI
T₁-Fuel Inlet Temp.   °F
T₂-Fuel Control Case Temp. °F
T₃-Fuel Outlet Temp.   °F
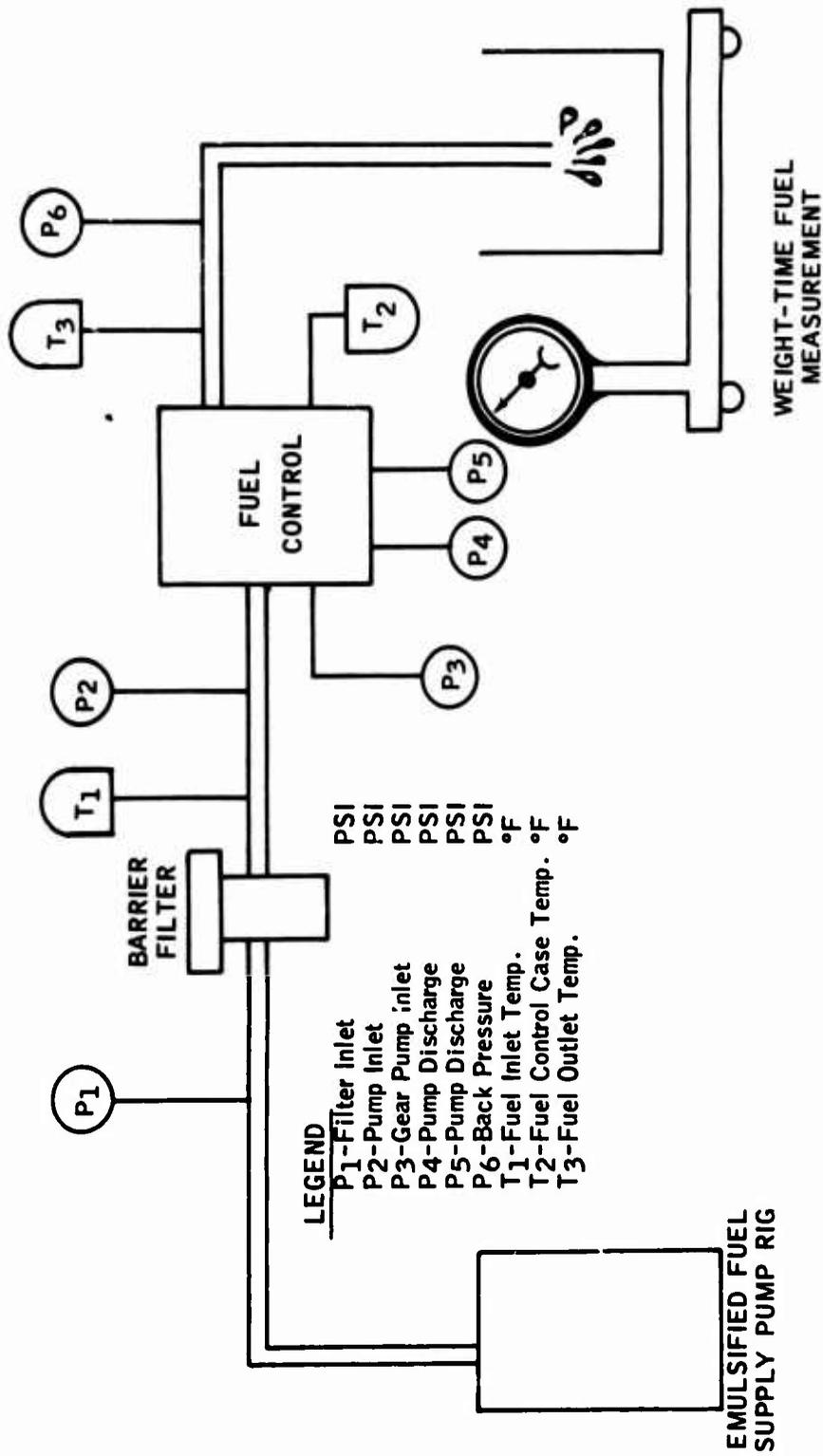
Figure 38. SCHEMATIC OF THE TEST SETUP FOR EVALUATING EMULSION IN THE JFC 31 FUEL CONTROL SYSTEM

114
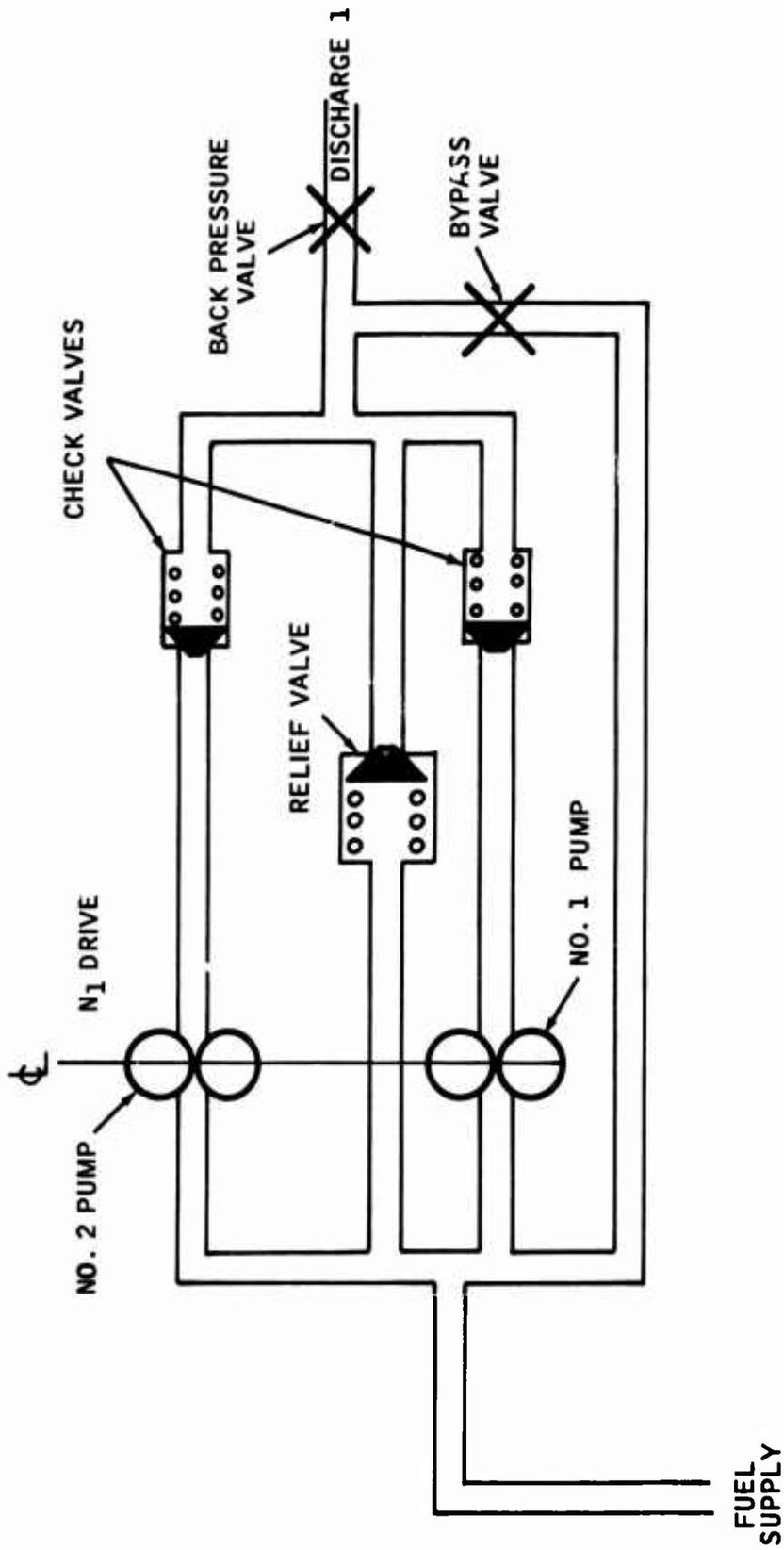
Figure 39. SCHEMATIC DEFINING FLOW PATH FOR THE JFC 31 FUEL CONTROL PUMP

115

Upon completion of the testing, the control computer was opened for inspection and photographs.

Pump Evaluation

The sandwich pump was removed from the computer section of the fuel control and fixtured with a test block used for pump calibrations.

TEST I

At a fixed pump speed of 10 percent of the maximum (maximum = 4200 RPM), the emulsion was pumped through the gear pump at a flow rate of 810 pounds per hour (PPH). This was a single flow pass through the gear pump with the bypass back to the pump inlet circuit closed. At this test point, samples of the emulsion were extracted at the following three stations in the fuel system:

1. Discharge of piston supply pump
2. Discharge from 40-micron filter elements
3. Discharge from fuel control gear pump

The samples were taken merely to assess the degree to which the emulsion was being broken down at each station.

TEST II

At 10, 20, 30, 50 and 100 percent speeds with the metered discharge flow at a fixed rate of 180 PPH, samples of the emulsion were extracted from the pump discharge port. This 180 PPM flow rate was held constant by opening the bypass valve in the return to the pump inlet line. This allowed the pump outlet flow in excess of the 180 PPH to be returned to the pump inlet. This test simulates the control operation of bypassing excessive pump flow during normal scheduling of metered flow to the engine. The samples taken were allowed to settle for 72 hours before determining percentage of separation.

TEST RESULTS

Control Calibration

The fuel control is capable of metering the WSX-7063 emulsion. Figure 40 shows that the response of the system with the emulsion was identical to that of the reference calibration fluid.

Pump Evaluation

TEST I

The amount of shear of the emulsion, caused by the gear pump when the emulsion is allowed only a single pass through the pump at the various stations, is shown in Table 40.
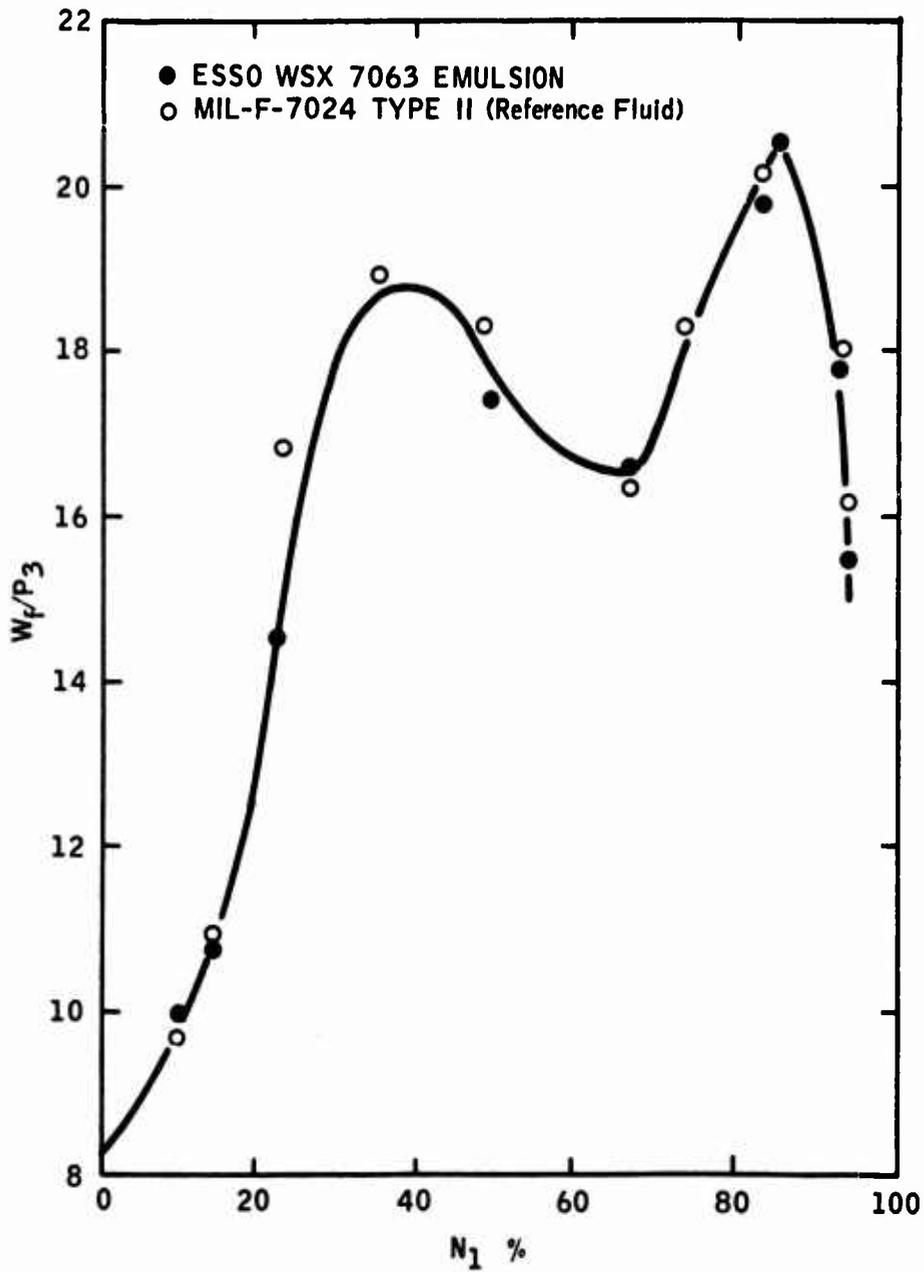
Figure 40. ESSO WSX-7063 EMULSION EVALUATION RATIO UNITS VS.
5 N_1 (GAS PRODUCER SPEED) FOR 59°F. DAY

TABLE 40	
EFFECT OF THE VARIOUS SYSTEMS ON EMULSION BREAKDOWN	
Stations	% Breakdown
Piston Pump	61
40-Micron Filter	63
Pesco Gear Pump	75

The data indicate that at a flow rate of 810 PPH, the fuel control sees about 75 percent JP-4 and only 25 percent emulsion. This apparently accounts for the fact that the fuel control response to the emulsion was essentially identical to that of the calibration fluid.

TEST II

This test involved determining the effect of pump speed on breakdown of emulsion at a constant flow rate of 180 PPH. The results are summarized in Figures 41 and 42. These show that as the pump speed increases, the emulsion is broken down to a greater extent. At 100 percent of the pump speed (4200 RPM), the emulsion is broken down completely. Figure 42 shows the effect of breakdown in terms of percent of the emulsion flow which gets recirculated back through the pump.

CONCLUSIONS

Control Calibration

1. The JFC 31 fuel control is capable of pumping and metering the WSX-7063 emulsion.

2. The emulsion does not cause any chemical reaction with the fuel control housing and linkages. This can be seen by the pictures shown in Figures 43 through 46. There were no indications of sticking of any moving parts, rust, or growth of bacteria.

3. The WSX-7063 emulsion as pumped from the 50-gallon supply drum for these tests exhibited approximately a 60 percent breakdown to a liquid by volume.

4. The amount of shear of the emulsion caused by the gear pump is a minimum when the emulsion is allowed only a single pass through the gear pump. This condition represents a limit which does not occur under normal operation of the pump on the T-55 engine.

118

5. Increasing the percentage of recirculated pump flow produces a higher percent of liquid by volume in the emulsion.

6. Figure 42 shows the percent liquid by volume of the emulsion that could be expected for a typical T55-L-7C gas turbine engine load line. It is interesting to note that the pump-control combination would deliver between 88 percent and 94 percent liquid by volume to the engine.
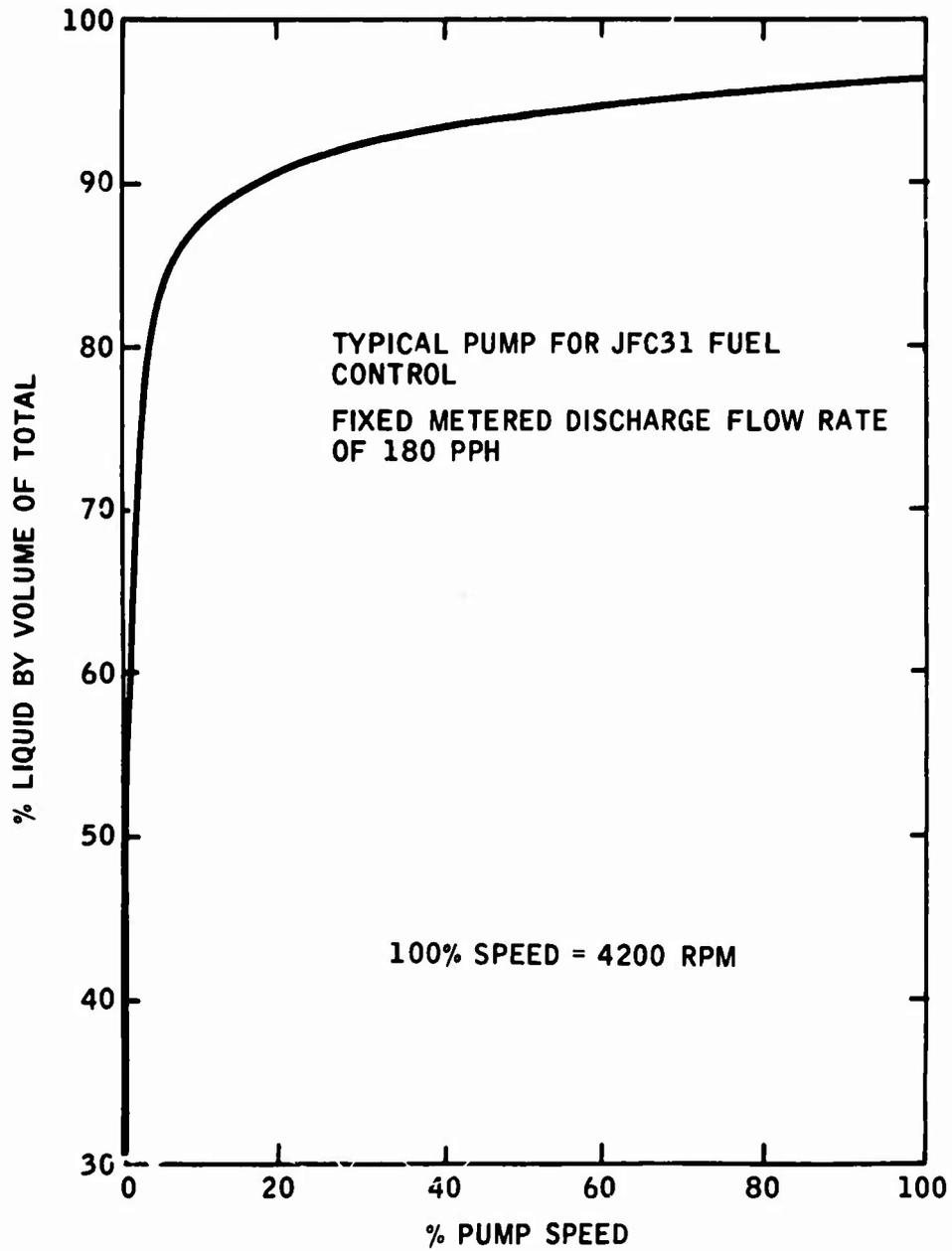
Figure 41. PERCENT LIQUID OF WSX-7063 EMULSION VS.
PERCENT OF MAXIMUM PUMP SPEED
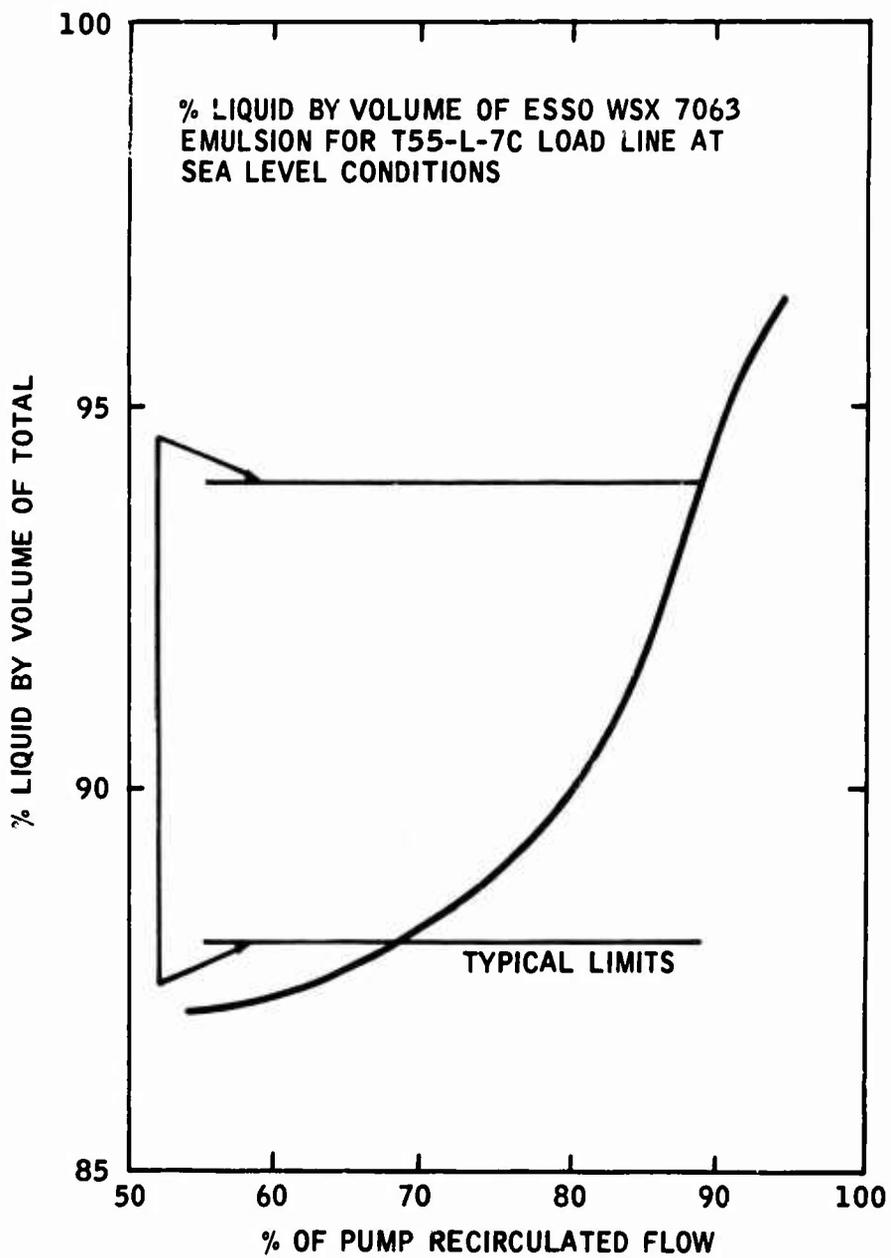
Figure 42. PERCENT LIQUID OF WSX-7063 EMULSION VS.
PERCENT OF PUMP FLOW RECIRCULATED FOR
JFC 31 FUEL CONTROLS
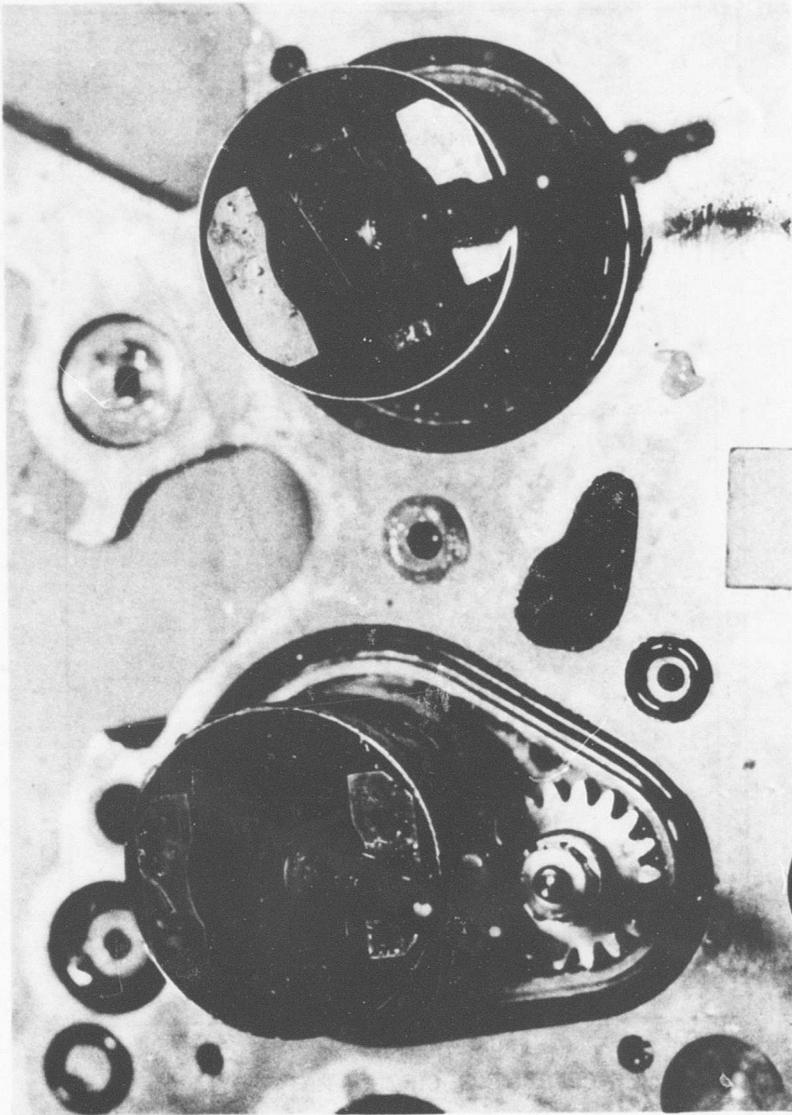
Figure 43. JFC 31 - Fuel Control Flyweights Assemblies (After 100 Gallons of WSX-7063 Being Metered Through Control).

122
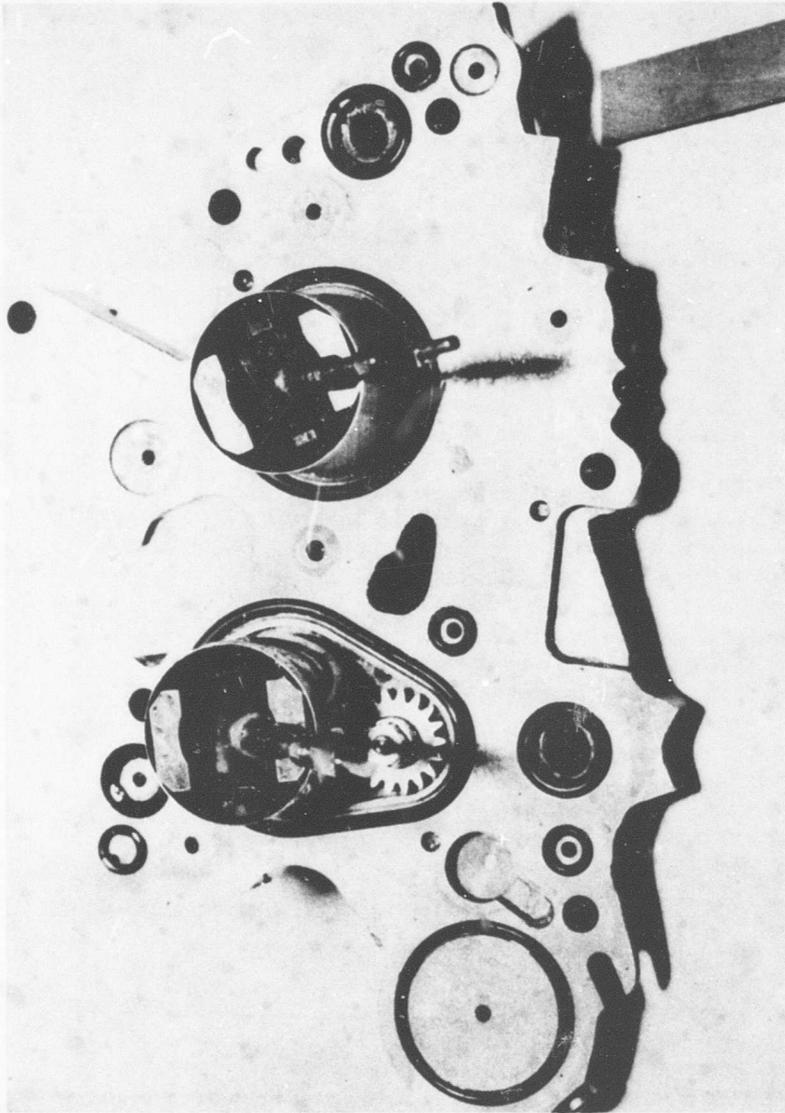
Figure 44. Fuel Control Pilot Valve and Spin Cup
Assembly Showing Emulsion in Spin Cups.

123
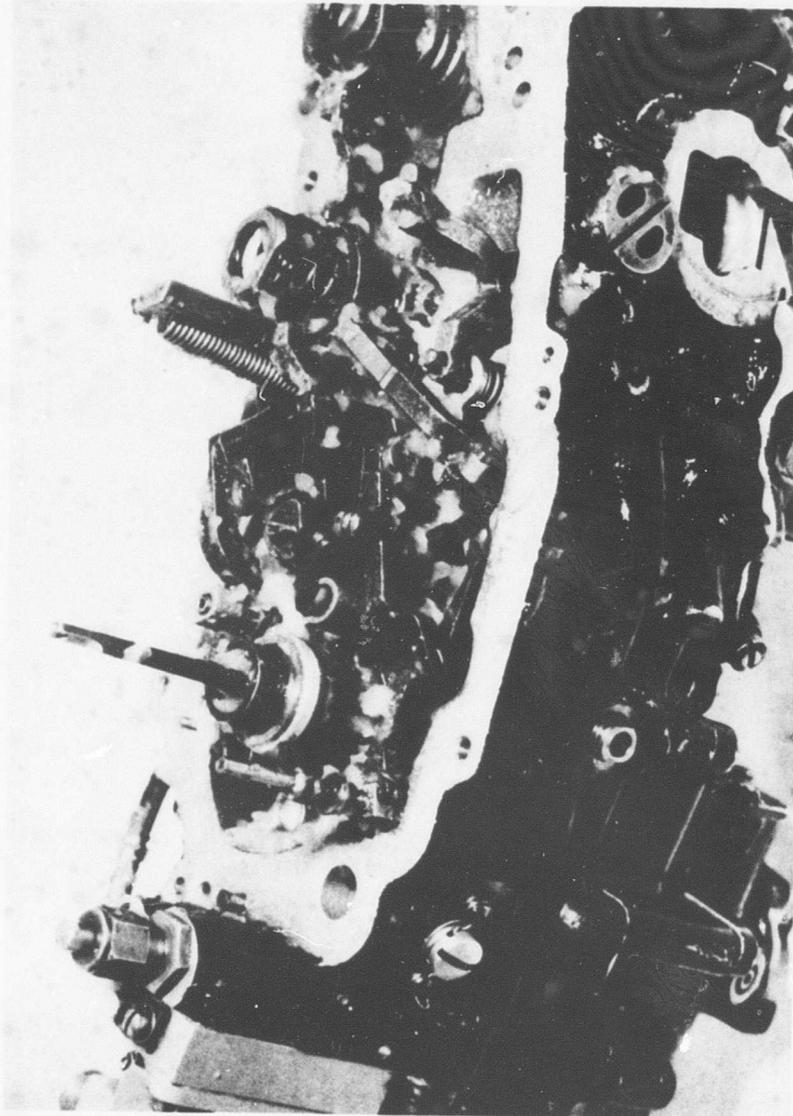
Figure 45.   JFC 31 - Fuel Control Computer Cavity
(After Being Blown Out With Air Gun).
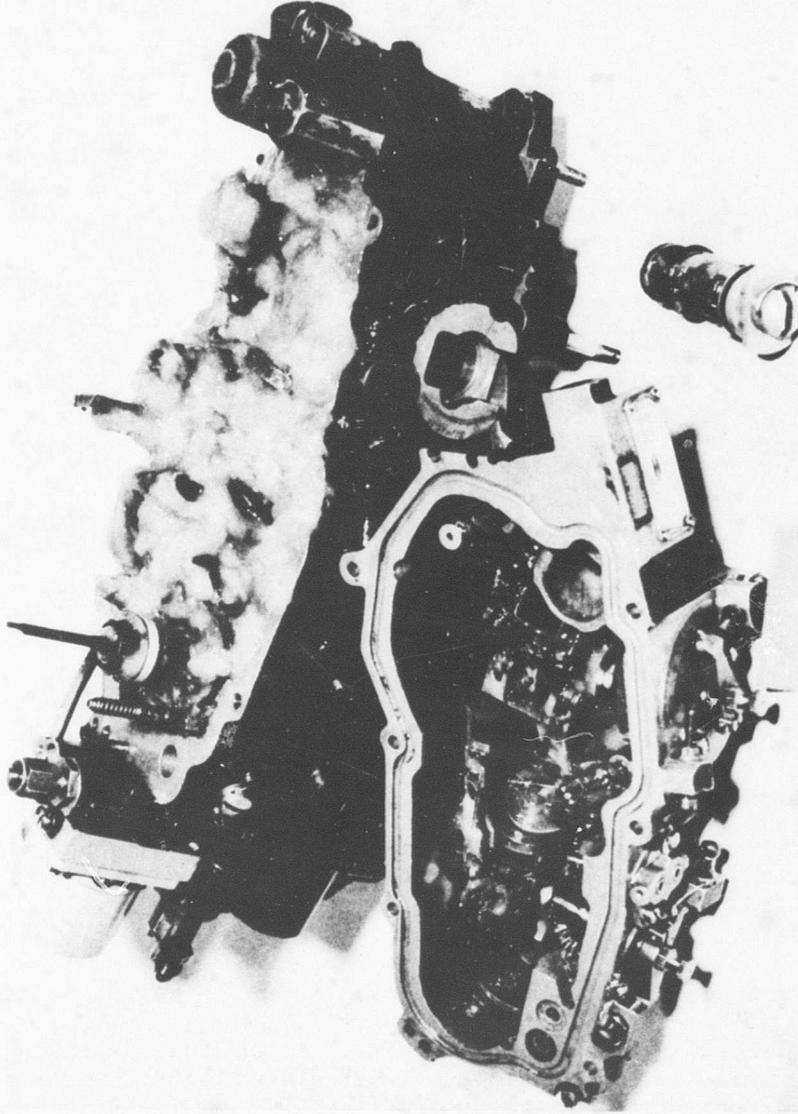
Figure 46. JFC 31 - Fuel Control Computer Cavity (After 100
Gallons of WSX-7063 Being Metered Through Control).

CONTAMINATION, PARTICLE SIZE AND YIELD STRESS METHODS

Investigation of Emulsion Droplet Size

Introduction

The stability of an emulsion, other parameters being the same, is determined by the droplet size of the disperse phase. Because droplet size of the same emulsion can vary from one batch to another, efforts were made to develop a technique for determining the droplet size of high-internal phase fuel emulsions. A microscopic technique appeared to be the approach that would best lend itself for use as a plant control device. Therefore, this approach was investigated first. The main difficulty associated with the use of the microscopic approach is that of discerning the two phases of these emulsions in the microscope. Because of the high concentration of the disperse phase, the boundary which allows the droplets to be distinguished approaches the thickness of the interfacial film. Using the Phase Contrast Microscope, it was possible to estimate the size of the droplets; however, the resolution was not too good. This indicates that the boundary between droplets approaches the dimensions of the wavelength of visible light ($\sim$6,000 Å).

Because of the poor resolution obtained with the phase contrast microscope, another microscopic approach was taken. This approach involved the use of ultraviolet Fluorescence Microscopy. Very simply, the approach involves the use of a material, which when added to the emulsion, will (1) concentrate at the disperse phase-continuous phase interface and (2) undergo fluorescence when irradiated with ultraviolet light. When the emulsion containing the fluorescent material is irradiated, the material at the interface fluoresces. The light due to the fluorescence produces an image of the interface which is observed in the microscope. In essence, the fluorescent material delineates the interface between the dispersed droplets and the continuous phase. This approach produces an image of the emulsion structure which allows for a more accurate determination of droplet size because of better resolution and clarity.

Experiment

Sodium fluorescein representing 0.1 percent by weight of the total emulsion (WSX-7065) was dissolved in the formamide, and a small batch of the emulsion was completed by the usual procedure. An aliquot was then spread on a microscope slide and protected by a cover glass, both of which were coated with silicone oil to prevent interaction with the glass surface. The microscope used in this study was a Zeiss Photomicroscope equipped to operate with ultraviolet accessories. The microphotographs of the samples were made under the following conditions:

- Magnification - 400X
- Film - Polaroid 3000 ASA
- Exposure time - 20 seconds

Results and Discussion

The photomicrographs (Figure 47) of the undisturbed emulsion (WSX-7063) show that the dispersed droplets are, indeed, distorted polyhedra. They also show that the dispersed droplets of the laboratory prepared WSX-7063 ranged in size from 1 to 2 microns.

The photograph shown in Figure 48 represents the emulsion in an area where some coalescence had taken place, and Figure 49 represents an edge where the disturbing effects of evaporation had caused almost complete merging of the disperse phase. Due to the fact that the visible light is all emitted from the continuous phase, the dark areas represent JP-4.

It is evident from this series of photomicrographs that even the undisturbed emulsion is not a uniform dispersion, and that there is reason to hope that a correlation between stability and some index of dispersion could be developed. If so, this technique could be worked out and made available as a plant control device.

Conclusions

WSX-7063 has a droplet size between 1 to 2 microns, and these droplets are polyhedric in shape. The emulsion in the undisturbed state is not completely homogeneous.

Development of a Contamination Control Method

The study of contamination control was advanced by modifying an ASTM method to fit aircraft emulsion fuels. First, a Lycoming engine nozzle which had plugged on WSX-7063 after a few shots through the thrust rheometer was cleaned out by a modified D 2429 procedure in which butyl carbitol was the flush fluid and the components were vibrated for 1 hour at 22 kilocycles. The resulting particulate collection consisted of many yellow-white fibers, plus sand-like particles, black specks, a few metal chips, and some orange-red particles resembling lead or iron oxide.

A series of samples of the WSX-7063 which had caused plugging of the Lycoming engine nozzle was subjected to modifications of D 2387 for gravimetric analysis of insolubles content. One hundred grams of the emulsion were broken in a Waring blender by the addition of 5 ml of (1) butyl carbitol, (2) acetone, and (3) isopropanol. It was found that solvent (1) gave 17.7 mg/gal of total particulates, of approximately the same character as that removed from the Lycoming engine nozzle. This level of contaminants is several times that allowed for JP-4 (4 mg/gal). Solvents (2) and (3) gave equally good breaks, but no fibers. This could have been due to an uneven distribution of contaminants in the drum of emulsion. To check this, the membrane filter containing the particulates using solvent (1) was washed with isopropanol; this removed essentially all of the fibers. The residue after this treatment was less than 4 mg/gal, indicating that the fibers were the main contaminant. It is well known that fibers are especially bad from the standpoint of nozzle plugging. The butyl carbitol method thus appears to have produced the correct particulate level in the fuel emulsion.

127
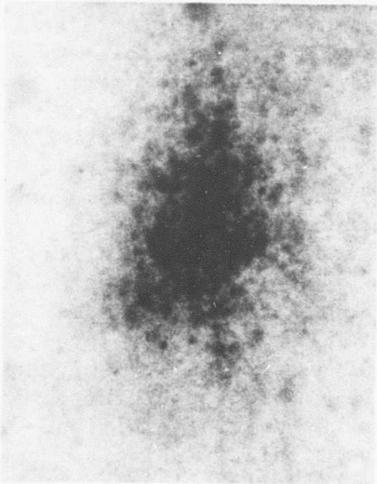
Figure 47. Ultraviolet Fluorescence Micrographs   Figure 48. Ultraviolet Fluorescence Micrographs of
of WSX-7063 - Main Part of Emulsion   WSX-7063 - Partial Coalescence
(400X Magnification).   (400X Magnification).
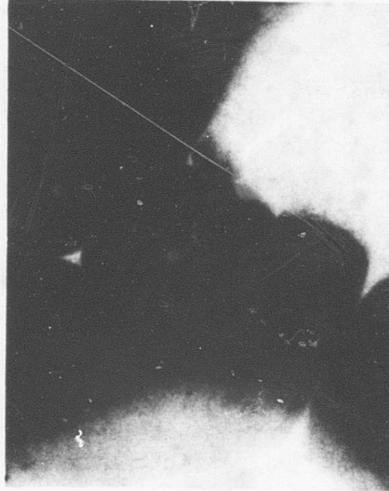
Figure 49. Ultraviolet Fluorescence Micrographs of
WSX-7063 - Coalescence Near an Edge
(400X Magnification).

128

On the basis of this study, the butyl carbitol modification of
ASTM test D 2387 is recommended as the procedure to follow for the determi-
nation of particulates in fuel emulsions.

Development of a Simplified Yield Stress Method

The development of a simplified yield stress method was advanced
by modifying an existing method to fit aircraft fuel emulsions. The method
which appeared to be the simplest and most easily adaptable was yield stress
method JAN-711, Method 200. This method consists of placing 5 ml of the
sample at the center of a piece of plate glass. A second piece of plate
glass is then lowered over the first piece containing the sample, and then
a weight (2,000 grams minus weight of plate glass) is added to the top plate
directly over the sample. The diameter to which the sample spreads is
measured, and the consistency of the sample is reported as such. This
method was tried unmodified with emulsions but did not work, as the data in
Table 41 show.

TABLE 41	
EFFECT OF YIELD STRESS ON DIAMETER OF SPREAD	
Yield Stress (dynes/cm^2)	Av Diameter of Spread (cm)
2100	7.05
1400	7.0

These data show that the test is not sensitive enough to distinguish the
emulsions on the basis of yield stress.

In this test the shear is high enough to level the viscosity of
these emulsions to a common value. Because of this, we decided to reduce
the shear by (1) reducing the weight acting on the emulsion between the
glass and (2) using a convex glass surface as opposed to the flat surface.
In addition, a can top was used to contain the emulsion. Table 42 shows the
equipment needed for the modified version of JAN-711 Method 200.

TABLE 42
LIST OF EQUIPMENT USED
Watch-Glass   14.0 cm in diameter   1.25 cm deep
Sample Holder   12.0 cm diameter   1.6 cm deep

In the proposed test, the sample holder is filled with the emulsion to the top and the surface is smoothed over. The water glass is held over the center of the sample with the convex surface just touching the surface of the emulsion. The glass is allowed to fall and remain in contact with the sample for 5 seconds and then is removed. The diameter of the wetted area of the glass surface is measured (make 8 marks on the edge of the wetted circle and average the 4 diameters).

Calculations

The total stress on the emulsion is the weight of the watch glass, and the area over which the stress is applied is the average diameter of the wetted surface. With this information, one obtains the following expression:

$$\frac{7.85 \times 10^4}{d^2} = \text{yield stress (dynes/cm}^2)$$

where

d = diameter in cm of the wetted area.

Results

The data obtained using the modified procedure are shown in Table 43 along with yield stress data obtained using the penetrometer.

TABLE 43			
YIELD STRESS DATA AS OBTAINED FROM THE MODIFIED TEST			
Emulsion	Penetrometer Yield Stress (dynes/cm^2)	Measured Diameter of Wetted Circle	Yield Stress (dynes/cm^2) from Modified Test
A	1425	7.3	1470
B	800	8.5	1087
C	1850	7.0	1560
D	3300	5.8	2320
E	6200	4.1	3880

The data in Table 43 are plotted in Figure 50. It would appear that the data obtained using the simple modified glass plate method can be related to the yield stress of fuel emulsions. More work is needed to assess the accuracy and reproducibility of this test method.
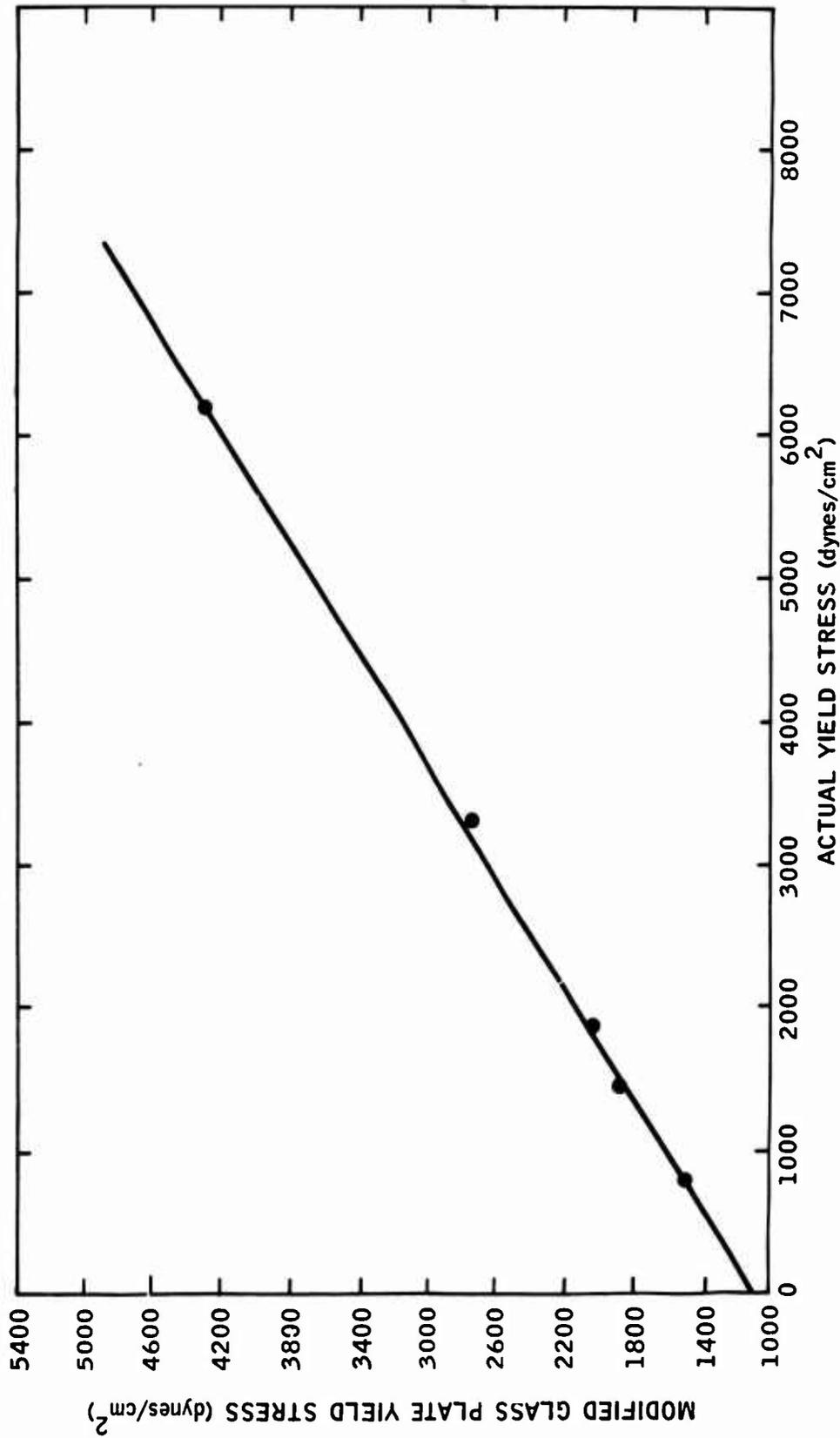
Figure 50. MODIFIED YIELD STRESS DATA VS. YIELD STRESS DATA FROM THE PENETROMETER

131

APPENDIX V

EXPERIMENTAL TEST PROCEDURES

1. **Viscosity** - Viscosity was determined by ASTM test D 1092. In this test the emulsion is extruded through capillaries of different diameter at a fixed flow rate.

2. **Modified Vapor Pressure** was determined by ASTM test D 323. The bomb used in this test was modified to hold three 1/2-inch steel balls which were to agitate the emulsion during shaking. In this test the bomb containing the sample is equilibrated at 100°F with intermittent shaking. This is continued until a constant pressure reading is achieved.

3. **Heat of Combustion** - The gross heat of combustion was determined by ASTM test D 2382. The net heat of combustion was then estimated using the procedure described in ASTM test D 2382.

4. **Vibration Stability** for screening purposes was determined using a standard machine. In this test, a 300-gram sample of the emulsion was contained in a capped jar and shaken at 6 cycles per second for 1/2 hour to 8 hours. The penetration of the emulsion before and after was measured.

5. **Corrosion Tests** - The metals were first cleaned with a mild acid solution and then thoroughly dried and measured to determine their surface area. The entire metal was then thoroughly rubbed with an eraser and then washed with toluene followed by a wash with isopropyl alcohol. The metals were then dried, weighed and placed inside a stainless steel nipple using metal tongs. The metal was stood up using a Teflon insert as a stand; it was then covered with the emulsion. The nipple was capped and stored at 130°F for one week. At the end of this period, the samples were cleaned with alcohol, dried and weighed. If there was corrosion, the metal was cleaned using emery cloth (fine) and steel wool and then was washed with alcohol to remove all products of corrosion. The metal was then weighed.

6. **Swelling of Elastomers** - O-rings were used for swelling tests. The O-rings were weighed and placed in a capped jar containing the emulsion. The jar was then stored at 130°F for one week. At the end of this period, the O-rings were removed, washed with isopropyl alcohol, blotted dry, and weighed. The swelling data were presented as percent weight increase.

7. **Four-Ball Wear** - The lubricity as measured by the four-ball wear test was determined by ASTM test D 2266. The test conditions used were 7.5 mg, 130°F, and 1,800 RPM for one hour.

8. **Ash Content** was determined by ASTM test D 482 without modification.

9. **Sulfur Content** was determined by ASTM test D 1266 without modification.

10. **Microbiological Test** - The three most common microbial contaminants of JP-4 fuel were used as test organisms in this study:

(Mold)	Cladosporium resinae	ATCC #11274
(Bacteria)	Pseudomonas aeruginosa	ATCC #1014S
(Bacteria)	Aerobacter aerogenes	ATCC #13048

The compositions of the mineral salts media used with each of these are shown below.

Czapek-Thom Medium (Mold)

$NaNO_3$	3.0 gms
KCl	0.5
$MgSO_4 \cdot 7H_2O$	0.5
$FeSO_4 \cdot 7H_2O$	0.01
K_2HPO_4	1.0 gm
Dist. H_2O	1000 ml

Modified P_1 Medium (Bacteria)

$(NH_4)_2HPO_4$	5.0 gms
K_2HPO_4	2.5
Na_2SO_4	0.5
Salts B	10.0 ml
Tap H_2O	1000 ml

Liquid Medium

The three test organisms were inoculated sep.rately as well as in a mixed culture into 100 ml serum bottles. The sterile serum bottles contained the JP-4 emulsion and mineral salts medium in two ratios: 95:5 and 5:95 emulsion to mineral salts medium. The emulsion was the sole source of carbon and energy present. The serum bottles containing the test organisms as well as controls were incubated at room temperature and 30°C for 30 days. Serum bottles were daily examined for growth, and pH was measured at the end of 30 days.

Solid Medium

Solid medium was prepared by the addition of 1.5 percent agar to the previously described liquid medium. Sterile petri plates were prepared containing the solid medium. The test organisms were streaked on the plate and the emulsion was added to sterile filter paper inserted in the top of the petri plate. The plates were inverted and incubated at room temperature and 30°C for 14 days. Plates were observed daily for growth indicating utilization of the emulsion.

11. **Burning Rate** - In this test, 6 grams of the sample were poured from a height of 1 foot into a flat pan (4 inches by 24 inches). The sample was then ignited and the time required to burn the 6-gram sample was measured.

12. **Propagation Rate** was determined by spreading the sample the length of an angle iron trough (3 inches by 36 inches). The sample was then ignited at one end and the time required for the flame to travel to the other end of the trough was measured.

1J. **Evaporation Loss** was determined using a thermal gravimetric balance.
The sample was contained in a holder having a surface area of 17.8 cm^2. For
dynamic evaporation loss, nitrogen was passed over the sample at a rate of
3.3 liters/minute and the change in weight was measured as a function of
time. (Sample size of 100 mg was used in this test.)

14. **Current Flow** was determined using two bronze electrodes having a
diameter of 0.130 inch. The electrodes, one having a length of 11 inches
and the other 6-3/4 inches, were separated by a distance of 0.750 inch.
They were connected to an ammeter and a 6-volt battery. For current flow,
the electrodes were immersed into the emulsion to a depth of 6 inches.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Government Research Laboratories Esso Research and Engineering Co. Linden, New Jersey	2b. GROUP

3. REPORT TITLE

INVESTIGATION AND ANALYSIS OF AIRCRAFT FUEL EMULSIONS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(First name, middle initial, last name)*

James Nixon, Alan Beerbower, Wladimir Philippoff,
Patricia A. Lorenz, and Thomas J. Wallace

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 1967	149	18

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
DA 44-177-AMC-387(T)	
b. PROJECT NO.	USAAVLABS Technical Report 67-62
1F121401A15003O2	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

This document is subject to special export controls, and each transmittal to foreign
governments or foreign nationals may be made only with prior approval of US Army
Aviation Materiel Laboratories, Fort Eustis, Virginia 23604.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U.S. Army Aviation Materiel Laboratories Fort Eustis, Virginia

13. ABSTRACT

This report summarizes work aimed at the formulation of JP-4 fuel emulsions which re-
duce the fire hazards associated with JP-4. Two fuel emulsions were formulated and
completely characterized during the course of this program. Both meet the stated
requirements for a safety fuel. They reduce the rate at which combustible vapors are
released; they have yield stresses in excess of what is required to retard flow through
a simulated .50-caliber bullet hole; they are stable over the temperature range of
-20°F to 130°F; and they are compatible with elastomers and metals of construction.

Studies were also carried out to develop techniques for determining contamination, drop
size, and a simple yield stress method for fuel emulsions. Techniques were developed
which appear to allow these determinations to be made. Further work is needed with
other emulsions to establish precision and reproducibility.

On the basis of the findings in this program, several recommendations have been made
with respect to improving emulsion stability, atomization in nozzles, and yield stress
retention. Further work is also needed to define the mechanism of emulsion breakdown
in nozzles and the relation between emulsion yield stress and breakdown in nozzles.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Rheology						
Fuel Emulsions						
Safe Fuels						
Modified Fuels						
Emulsions						

SUPPLEMENTARY

INFORMATION

AD-827 051 Esso Research and Engineering Co., Linden, N. J. Government Research Lab. Technical rept. Rept. no. USAAVLABS- TR-67-62 Nov 67 Contract DA-44-177- AMC-387(T)	No Foreign without approval of Army Aviation Materiel Labs., Fort Eustis, Va.	No limitation	USAAML notice, 14 May 69