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OPTIMIZATION OF NONAQUEOUS FUEL EMULSIONS

By

James Nixon
Wladimir Philippoff
Vincent J. Siminski

May 1969

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

CONTRACT DAAJ02-68-C-0013
GOVERNMENT RESEARCH LABORATORY
ESSO RESEARCH AND ENGINEERING COMPANY
LINDEN, NEW JERSEY

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DEPARTMENT OF THE ARMY
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FORT EUSTIS, VIRGINIA 23604

During FY 67, Esso Research and Engineering Company developed two 97 weight percent internal phase (JP-4) emulsions under contract to the U.S. Army. While these first-generation fuels met the Army's broadly stated requirements for an aviation safety fuel, they possessed unacceptable corrosion characteristics and were lacking in thermal and mechanical stability.

The effort reported herein had as its principal objective the optimization of these fuels to eliminate the obvious deficiencies. Also, work was directed toward further definition of the rheological properties of emulsified fuels and toward identification of problem areas, if any, associated with the utilization of these fuels in existing turbine engine combustor designs.

Significant achievements were realized in all major areas of effort. Three different compositions of one of the original fuels were formulated, and each can be considered to be potentially suitable for future aircraft use, with refinement. The rheological and propulsion efforts, while limited, did yield information of significant value with respect to the flow properties and combustion characteristics of emulsified fuels. The need for additional work in these areas is evident.

The U.S. Army Aviation Materiel Laboratories concurs in the contractor's conclusions and recommendations as they relate to technical data applicable to those emulsions developed under this contract. Comments relative to other emulsified fuels being considered for use by the Army, or relative to the course of future Army programs, are not confirmed or endorsed by the Government through the publication of this report.

Project 1F162203A529
Contract DAAJ02-68-C-0013
USAAVLABS Technical Report 69-26

May 1969

OPTIMIZATION OF NONAQUEOUS FUEL EMULSIONS

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Prepared by

Government Research Laboratory
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Linden, New Jersey

For

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SUMMARY

In a previous program [Contract DA 44-177-AMC-387 (T)], two first-generation nonaqueous JP-4 fuel emulsions were formulated. The objective of the current program was to optimize the formulations of these two nonaqueous fuel emulsions, WSX-7165 and WSX-7063, to improve their quality for possible use in gas turbine engines.

Because the overall objective of the emulsified fuel program is to develop a safe fuel, the strategy followed in this program was to develop the safest possible fuel and to determine in the rheology and combustion phases of the program the problems that would be encountered in the handling and combustion of such a fuel. After having optimized the formulations from the standpoint of safety, the fuels were then optimized with respect to combustion efficiency. The fuel emulsions which are expected to be the safest invariably had the lowest combustion efficiency. Data were obtained which indicate that modification of some existing fuel system hardware will probably be required to burn high-yield-stress fuel emulsions efficiently.

Several optimized fuel emulsions were formulated and characterized during this program. All of the recommended formulations meet the initial established contractual requirements. These fuel emulsions are stable under a variety of conditions from -65°F up to at least 140°F. The emulsions are compatible, in general, with the same elastomers and metals as WSX-7165 fuel emulsion. All the recommended optimized formulations contain a corrosion inhibitor which also makes them compatible with mild steel.

The recommended optimized fuel emulsions have thermal stability comparable to WSX-7165, as evidenced by stability at -65°F, 77°F, and 140°F for periods greater than 90 days. In addition, the rate of evaporation for these emulsions at 140°F and room temperature (77°F) is comparable to that for WSX-7165. However, the mechanical stability of these optimized emulsions is decidedly better than that for WSX-7165 fuel emulsion, as evidenced by stability to pumping and filtration. These emulsions do not break down when they are pumped by either a gear pump or a centrifugal pump even after they have been allowed to age for 30 days. WSX-7165 fuel emulsion under similar pumping conditions, particularly in the centrifugal pump, undergoes significant breakdown. It is thus concluded that the optimized formulations are more stable to mechanical forces than is WSX-7165 fuel emulsion.

In the combustion phase of the program, the effects of the emulsion parameters listed below on combustion efficiency and percentage of emulsion breakdown in the nozzle (degree of atomization) were investigated:

- Emulsion yield stress
- Emulsifier level
- Water
- Corrosion inhibitor

This study has indicated that only fuel emulsions having a yield stress of less than 1500 dynes/cm^2 have combustion properties comparable to those of JP-4. The breakdown characteristics of the fuel emulsion in the nozzle are determined predominately by the emulsifier level. These statements are congruent, since yield stress increases with increasing emulsifier level.

The addition of corrosion inhibitors to the fuel emulsion formulations has a significant effect on the breakdown characteristics of the fuel emulsion and, therefore, the combustion efficiency of the emulsion relative to JP-4 under the same conditions. Such emulsions, in general, required higher atomization pressures to induce adequate atomization and to achieve combustion efficiencies which begin to approach those for JP-4.

The combustion efficiency of fuel emulsions is improved by the use of an air-assist nozzle. The improvement in combustion efficiency caused by introducing air into the nozzle is not due to increasing the emulsion breakdown, which is unaffected, but is due to better mixing of the atomized fuel in the primary combustion zone.

Studies carried out in the rheology phase of this program have indicated that the emulsion is broken as it enters the nozzle and undergoes no further breakdown on exiting from the nozzle. The atomized fuel emulsions, in general, appeared to be atomized to the same extent as JP-4 at high atomization pressures (>125 psig). At lower atomization pressures (~60 psig), the fuel emulsions gave decidedly coarser sprays than did JP-4 under similar conditions.

In studies carried out using a capillary, the extent of emulsion breakdown did not vary significantly from one emulsion to another at atomization pressures greater than 125 psig. On the basis of these rheological studies, it is suggested that difficulties should not be expected in the combustion of the fuel emulsions investigated at high atomization pressures. Some difficulty can be expected, however, at low atomization pressures, where very little emulsion breakdown occurs. Therefore, additional work is required to define the magnitude of the problems at low atomization pressures and to determine what can be done to minimize or alleviate them.

It is concluded, on the basis of this program, that burning of high-yield-stress emulsions directly in turbine engines will require certain fuel system modifications. The hardware changes envisaged will have to involve systems which will aid the breakdown of the emulsion in or prior to the nozzle. This will be required for improved performance at low atomization pressures such as those involved during idling. Such an aid would have to effectively break down high-yield-stress, high emulsifier-containing emulsions (0.7% to 1%), i.e., the most stable fuel emulsions.

FOREWORD

This report summarizes the work carried out to optimize the formulations of two nonaqueous fuel emulsions, WSX-7165 and WSX-7063.

This work was initiated in October 1967 and completed in October 1968. The program was administered by the U.S. Army Aviation Materiel Laboratories, Fort Eustis, Virginia, with Mr. William J. Nolan and Captain George Bowling acting as coordinators. We are grateful to them both for their help and timely suggestions.

The work was carried out under the authority of DA Project 1F162203A529.

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I. INTRODUCTION

Under the previous contract on fuel emulsions (DA 44-177-AMC-387 (T)), two emulsions designated WSX-7063 and WSX-7165 were formulated and characterized. However, since these fuels represented first generation products, additional work was required to improve the quality of these fuels for possible use in gas turbine engines. Thus, the objective of this program was to vary the composition of WSX-7063 and WSX-7165 fuel emulsions and to evaluate the physical, combustion, and rheological properties of these emulsions in an effort to arrive at an optimum JP-4 fuel emulsion suitable for Army application. The emphasis in this program was on WSX-7165, since it represented our best fuel emulsion candidate.

Both WSX-7063 and WSX-7165 met the initial established requirements of a safe fuel emulsion. These emulsions, however, were developed using stability and JP-4 content as the main criteria of acceptance or rejection. That is, neither the flow behavior (rheological properties) nor the combustion performance of these fuels was directly considered as a variable in the formulation of these two fuel emulsions. Since the principal use envisaged for fuel emulsions by the Army is burning directly in gas turbine engines, it is obvious that the fuel emulsions should be optimized to achieve the optimum safety and combustion efficiency. For maximum safety, the fuel emulsion must possess a high yield stress and be exceedingly stable both thermally and mechanically. On the other hand, for maximum combustion efficiency and for flow behavior which can be handled by existing fuel system components, the reverse emulsion properties are desirable. We thus have an apparent paradox.

Therefore, the strategy followed in this program was to formulate the safest possible fuel emulsion and to investigate the rheological and combustion properties of these fuels to determine if fuel system modifications would be required to handle them. At the same time, fuel emulsions were formulated to achieve a combustion efficiency comparable to that of JP-4 with the maximum safety advantage possible with such a constraint.

II. STUDY OF THE VARIABLES AFFECTING THE PROPERTIES OF WSX-7165 FUEL EMULSION

EXPERIMENTAL PROCESS

During the optimization studies, the effect of adding water either at the beginning or at the end of emulsification on fuel emulsion properties was investigated. It was found that the addition of water at the beginning of emulsification had little or no beneficial effect on fuel emulsion properties. However, when water was added at the end of emulsification, it had a significant beneficial effect on the fuel emulsion properties. Because of this and our previous studies (Reference 9), the process of adding water at the end rather than at the beginning of emulsification was used.

During the course of this program, two experimental processes were investigated and are outlined in Table 1. One of these (Process I) involved adding all the emulsifiers and the corrosion inhibitor (where applicable) to the continuous phase. The other process (Process II) involved adding the Atlas IL-851 to the JP-4 and the other emulsifiers (including corrosion inhibitor where applicable) to the continuous phase. The latter process could be used with any of the emulsion formulations, whereas the former could be used only where the total emulsifier level was 0.60% or less. When all the emulsifiers were added to the continuous phase at an emulsifier level greater than 0.60%, the emulsion became extremely viscous and plastic-like and would not take up any more JP-4, even though only about one-third of the JP-4 fuel had been added.

For these studies, 2000-gram batches of the emulsions were prepared using a Hobart mixer equipped with a 7-inch-wide paddle and a 10-quart-capacity bowl. The mixer was operated on the number 2 speed range throughout the emulsification process. Figure 1 shows a sketch of the flow system used in the laboratory preparation of the fuel emulsions.

Screening Tests

For evaluating the effects of various emulsion parameters, 2000-gram batches of the emulsions were prepared and evaluated in the following screening tests:

- Yield stress and conductivity at 77°F on freshly made emulsion and after aging 1 week.
- Stability at -65°F and 140°F after 1 week.

TABLE 1
PROCESS CONDITIONS USED THROUGHOUT THE PROGRAM

Process I

- Add all emulsifiers to the continuous phase in the Hobart mixer.
- Start the emulsion ("seed" emulsion) in the Hobart mixer using a wire paddle.
- With the Hobart mixer on speed range No. 2, follow the scheduled addition of JP-4 in forming the "seed" emulsion as follows:
    - Start JP-4 addition at the rate of 10 cc/min and hold this rate for 1 minute.
    - Increase the JP-4 addition rate by increments of 10 cc/min and hold at each level for 1 minute until a rate of 40 cc/min is reached.
    - Hold the JP-4 addition rate at 40 cc/min for 20 minutes.
- Stop the JP-4 addition and switch from the wire paddle to the regular Hobart paddle.
- Continue the JP-4 addition at the rate of 40 cc/min until the emulsion is completed.
- Add water and mix for 3 additional minutes.

Process II

- Add water soluble emulsifiers to the continuous phase in the Hobart mixer (ENJ-5728 and corrosion inhibitors).
- Add the oil soluble emulsifiers to the JP-4 in the reservoir (Atlas IL-851 emulsifier).
- The remainder of the process is identical to Process I.

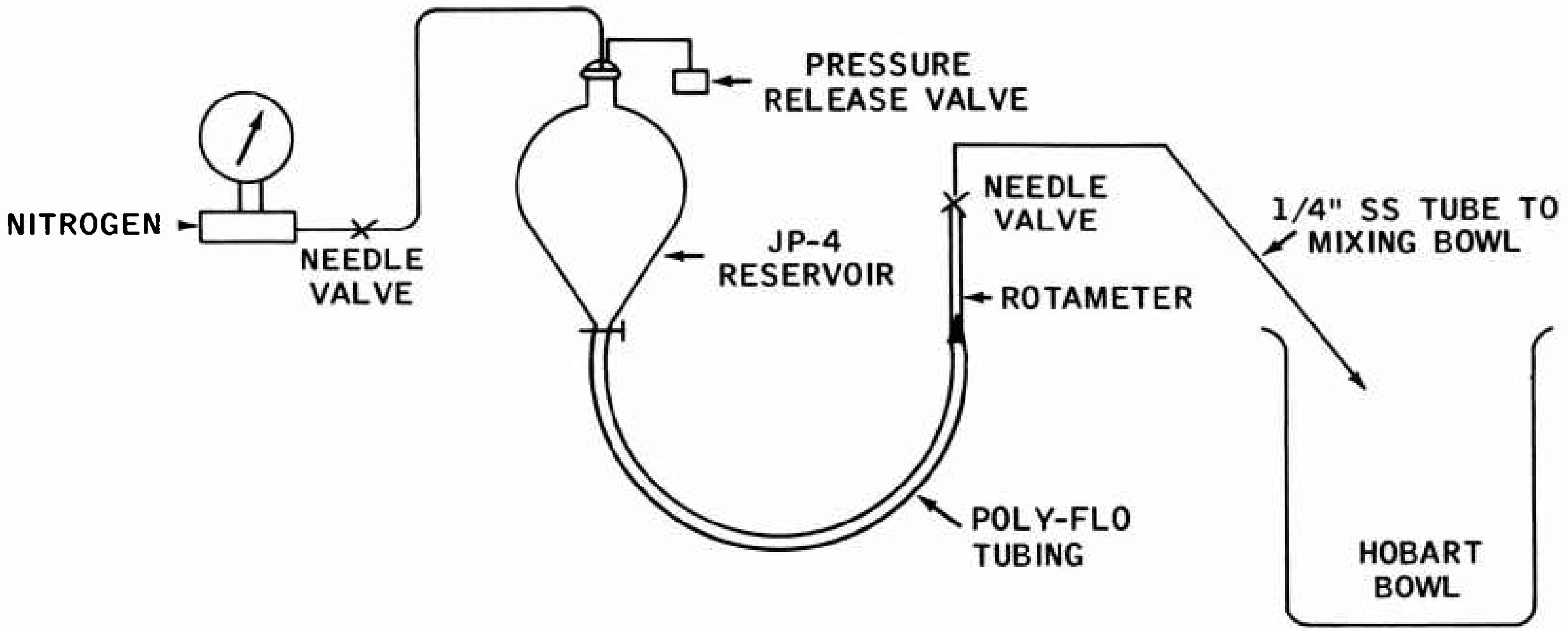

Figure 1. Sketch of Flow System for Emulsification of JP-4.

- Stability after 1 week of cycling between -65°F and 140°F.
- Conductivity and yield stress after storage at -65°F and 140°F for 1 week.
- Vibration stability at 6 cycles/sec at 77°F for 1/2 hour to 8 hours.
- Stability to centrifugation at 500 RCF after 8 hours.

Those emulsion formulations which passed the above screening tests, i.e., those which had an equilibrium yield stress greater than 1000 dynes/cm^2 and remained stable under the conditions cited, were investigated further.

Variables Investigated With Respect to WSX-7165

During the course of this program, in order to optimize fuel emulsion WSX-7165, the following variables were investigated:

- Composition of the continuous phase
- Disperse phase level
- Ratio of continuous phase to emulsifier
- Effect of water
- Effect of Atlas IL-851/ENJ-5728 ratio
- Effect of emulsifiers of same chemical type

To minimize the number of experiments required to investigate these variables, the designed experiments shown in Table 2 were utilized (two-level factorial).

TABLE 2
TWO-LEVEL FACTORIAL DESIGN USED ON OPTIMIZING WSX-7165

Variables	Levels	
	-%	+%
1. Composition of Continuous Phase	20% Urea in Formamide	0.0% Urea in Formamide
2. Concentration of JP-4	97.0	98
3. Continuous Phase to Emulsifier	2/1	5/1
4. Water Level	0	0.50 (added at end)
5. Atlas IL-851 to ENJ-5728	3/1	1/3

Process Reproducibility

As stated, two processes were used during the program (Table 1). Because Process I could be used only when the emulsifier level was 0.60% or less, Process II was used for formulations containing an emulsifier level greater than 0.60%. To assess the effect of these two process conditions on emulsion properties, three emulsion preparations were carried out, two via Process I and one via Process II. The properties of the emulsions prepared via these two processes are summarized in Table 3. These data show that the critical properties of the emulsions prepared via the two processes are essentially the same. Therefore, there is no significant effect of the emulsion processes on the properties of these emulsions; thus, process can be removed as a variable in these studies.

RESULTS AND DISCUSSION

Effect of Water

The WSX-7165 fuel emulsion was first investigated at an emulsifier level of 1.0% to assess the effect of the variables cited above on the properties of this emulsion. The data in Table 4 show the effect of urea, water, and the ratio of Atlas IL-851 to ENJ-5728 on the properties of 7165 emulsions at the 1% emulsifier level. To minimize contamination of emulsions with atmospheric water, the emulsification was carried out in a covered vessel using essentially dry JP-4 which was added in such a manner as to minimize the pickup of water from the atmosphere. That is, the JP-4 was charged to the vessel in the vicinity of the paddle of the mixer below the cover so that it came in contact only with the air space in the covered bowl of the Hobart mixer.

Our studies showed that if WSX-7165 fuel emulsion is prepared in the manner discussed, i.e., to minimize the pickup of atmospheric water, the emulsion prepared has poor -65°F stability and poor stability to vibration. This indicates the strong effect of even small quantities of water on the properties of WSX 7165 fuel emulsion.

The data in Table 4 show the strong effect of adding water to the finished emulsion. The water improved the overall stability of the emulsion, particularly at -65°F and with respect to vibration. If conductivity can be used to indicate the degree of dispersion, and we believe it is an indication of this, the substantial increase in emulsion conductivity on the addition of water is caused by a decrease in droplet size and an increase in packing efficiency of the dispersed droplets. The increased packing efficiency manifests itself by a decrease in emulsion yield stress on the addition of 0.5% water to the emulsions (compare columns 1 and 4, Table 4).

The decrease in stability for emulsion 3 (Table 4) at 140°F is due to the increased solubility of the emulsifiers in the continuous phase at 140°F caused by increasing the ratio of ENJ-5728 to Atlas IL-851. Thus, at 140°F most of the emulsifiers are extracted into the continuous phase which results in emulsion instability.

TABLE 3
REPRODUCIBILITY OF THE PROCESS CONDITIONS
USED THROUGHOUT OPTIMIZATION STUDIES

	Weight Percent		
	1	2	3*
20% Urea-Formamide	2.5	2.5	2.5
ENJ-5728	0.13	0.13	0.13
Atlas IL-851	0.37	0.37	0.37
JP-4	97.0	97.0	97.0
Distilled H_2O	-	-	-
Properties			
Yield Stress (dynes/cm^2)			
• Initial	2550	2300	2500
• After 1 Wk. at Room Temperature (R.T.)	960	700	810
• 1 Wk. at 140°F	680	620	590
• 1 Wk. at -65°F	Broken	Broken	Broken
Stability (wt. % separation)			
• Vibration - 1/2 Hr.	0.30	0.60	0.30
Conductivity (microamps)			
• Initial	73	73	80
• 1 Wk. at R.T.	98	100	120
• 1 Wk. at 140°F	780	850	1050
• 1 Wk. at -65°F	Broken	Broken	Broken

* Formulations 1 and 2 prepared via Process I.
Formulation 3 prepared via Process II.

TABLE 4
EFFECT OF UREA, WATER, AND RATIO OF ATLAS IL-851/ENJ-5728 ON 7165 EMULSION PROPERTIES (1% EMULSIFIER)

	Weight Percent			
	1	2	3	4
Formamide	-	2.0	-	-
20% Urea-Formamide	2.0	-	2.0	2.0
ENJ-5728	0.25	0.25	0.75	0.25
Atlas IL-851	0.75	0.75	0.25	0.75
JP-4	97.0	97.0	97.0	97.0
Distilled H_2O (by wt. emulsion)	-	-	0.50	0.50
Properties				
Yield Stress (dynes/cm^2)				
● Initial	2500	2500	2600	1925
● 1 Wk. at Room Tem Temperature (R.T.)	1400	925	1950	1650
● 1 Wk. at 140°F	680	Broken	Broken	1675
● 1 Wk. at -65°F	Broken	Broken	2700	1925
● 30 Days at R.T.	1450	--	1125	1525
● 90 Days at R.T.	1350	--	--	1700
Stability (wt. % separation)				
● Vibration				
- 1/2 Hr.	7.0	3.0	0.0	0.0
- 3 Hrs.	-	-	0.0	0.0
- 8 Hrs.	-	-	0.0	0.0
Conductivity (microamps)				
● Initial	40	73	175	105
● 1 Wk. at R.T.	35	75	280	238
● 1 Wk. at 140°F	650	Broken	Broken	1200
● 1 Wk. at -65°F	Broken	Broken	225	135
● 30 Days at R.T.	-	-	550	600
● 90 Days at R.T.	-	-	-	-

As indicated by the data in Table 4, water had a dramatic effect on emulsion stability, emulsion yield stress, yield stress decay with aging, and emulsion conductivity. Even the latter is somewhat unexpected since the formamide was much more conductive than was the added distilled water (Table 5). The yield stress decay for the emulsion containing added water is much less than that for the emulsion without added water. Water, because of its greater hydration of the emulsifier, probably causes a decrease in droplet sizes of the internal phase. This results in more efficient packing, a decrease in yield stress, and an increase in emulsion conductivity. The latter is due to a freeing of continuous phase from the lamellae between droplets brought about by decreasing droplet sizes. The added water also increases emulsion stability because of the stronger interfacial film and greater surface coverage due to stronger hydration. This is verified by the data shown in Table 6. The increased stability to vibration caused by the addition of water indicates increased interfacial film strength and greater surface coverage.

The effect of water on the decay of emulsion yield stress for a representative emulsion is shown in Figure 2. These data show that the addition of the water lowers the initial emulsion yield stress and raises slightly the equilibrium yield stress of the emulsion. The lowering of the initial emulsion yield stress by the addition of water is thought to be due primarily to the increased packing efficiency caused by decreasing droplet size. The following sections will discuss the effect of aging on emulsion yield stress and why this property is affected by the addition of water to these "nonaqueous" emulsions.

Effect of Aging on Emulsion Yield Stress

The tremendous internal strain that exists within high-internal-phase fuel emulsions manifests itself most dramatically in terms of the pronounced change in yield stress that these emulsions undergo on aging. Most of them undergo a sharp decrease in yield stress within 24 hours of preparation and a much slower decrease beyond that, provided the emulsions remain stable. Figure 2 shows the dramatic decrease in yield stress for two such high internal-phase emulsions.

Figure 3 shows what happens to the conductivity of these high-internal-phase fuel emulsions on aging. The conductivity of these emulsions increases with time gradually for about 4 days and then begins to increase at a much more rapid rate. One notes that the yield stress, on the other hand, undergoes its most dramatic decrease within the first day of preparation and changes much more slowly thereafter. This apparent paradox is rationalized in the following manner.

Three separate phenomena are taking place at various rates. The first, and probably fastest, is the disappearance of the smallest droplets. This proceeds by a well-known mechanism; small drops have an increased vapor pressure and hence "distill" into the larger ones. This undoubtedly

TABLE 5
EFFECT OF WATER ON 7165-TYPE EMULSION PROPERTIES

Storage (days)	Without Water*		With 0.5% Water	
	Yield Stress (dynes/cm^2)	Current Flow (microamps)	Yield Stress (dynes/cm^2)	Current Flow (microamps)
0	2500	40	1975	110
4	1600	40	1575	140
6	1400	35	1600	200
8	1450	50	1500	230
120	1350	--	1525	700
Stability (vol. % separation)				
● After 8 Hrs. Vibration	8.0		0.0	
● After 1 Wk. at -65°F	90.0		0.0	

Composition (by wt.)

JP-4 97.0%
Emulsifier 1.0%
Continuous Phase 2.0% (20% Urea-Formamide;
  Current Flow = 6000 Microamps)
Water (Current Flow = 200 Microamps)

* Added 0.5% Continuous Phase.

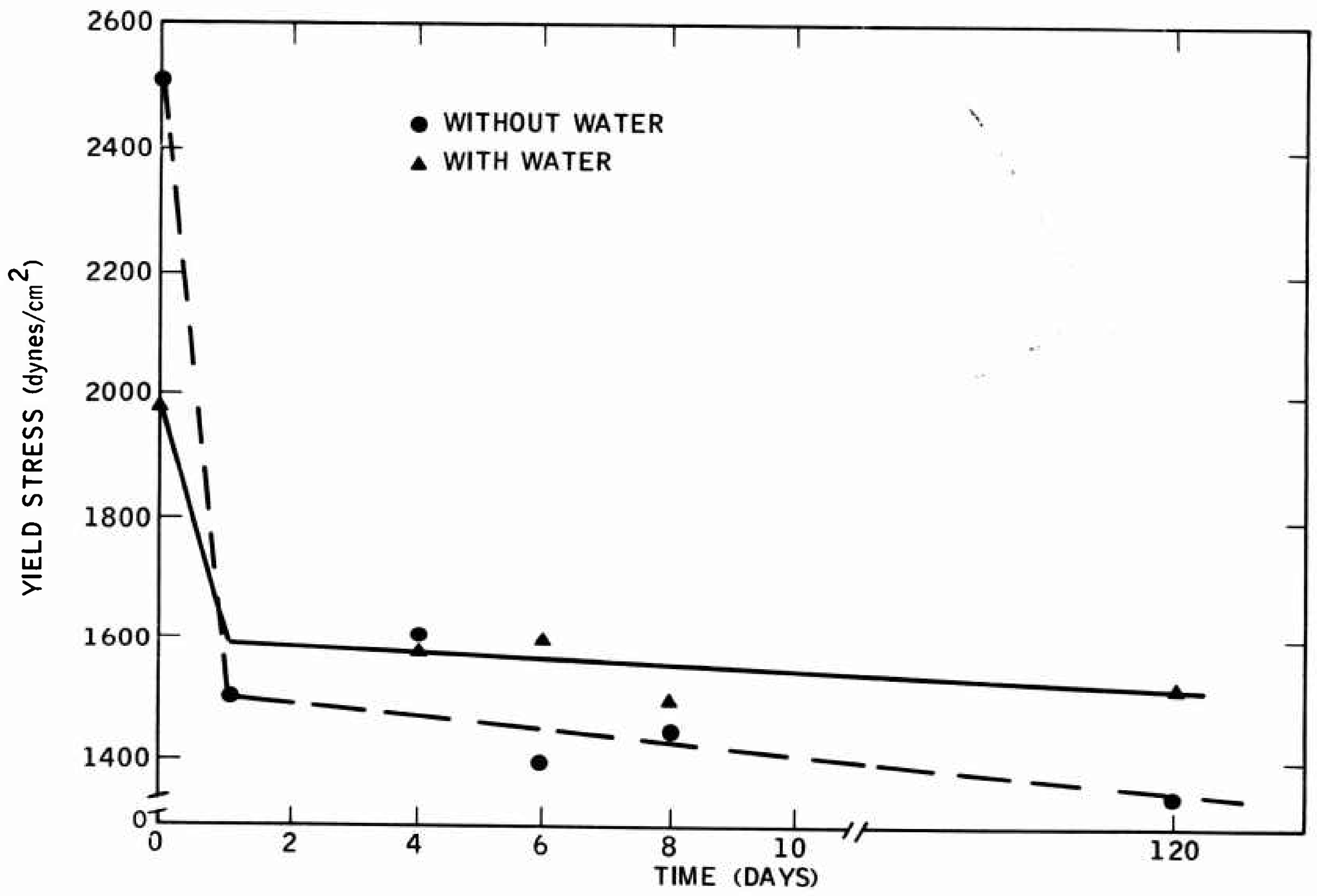

Figure 2. Effect of Emulsion Age on Emulsion Yield Stress.

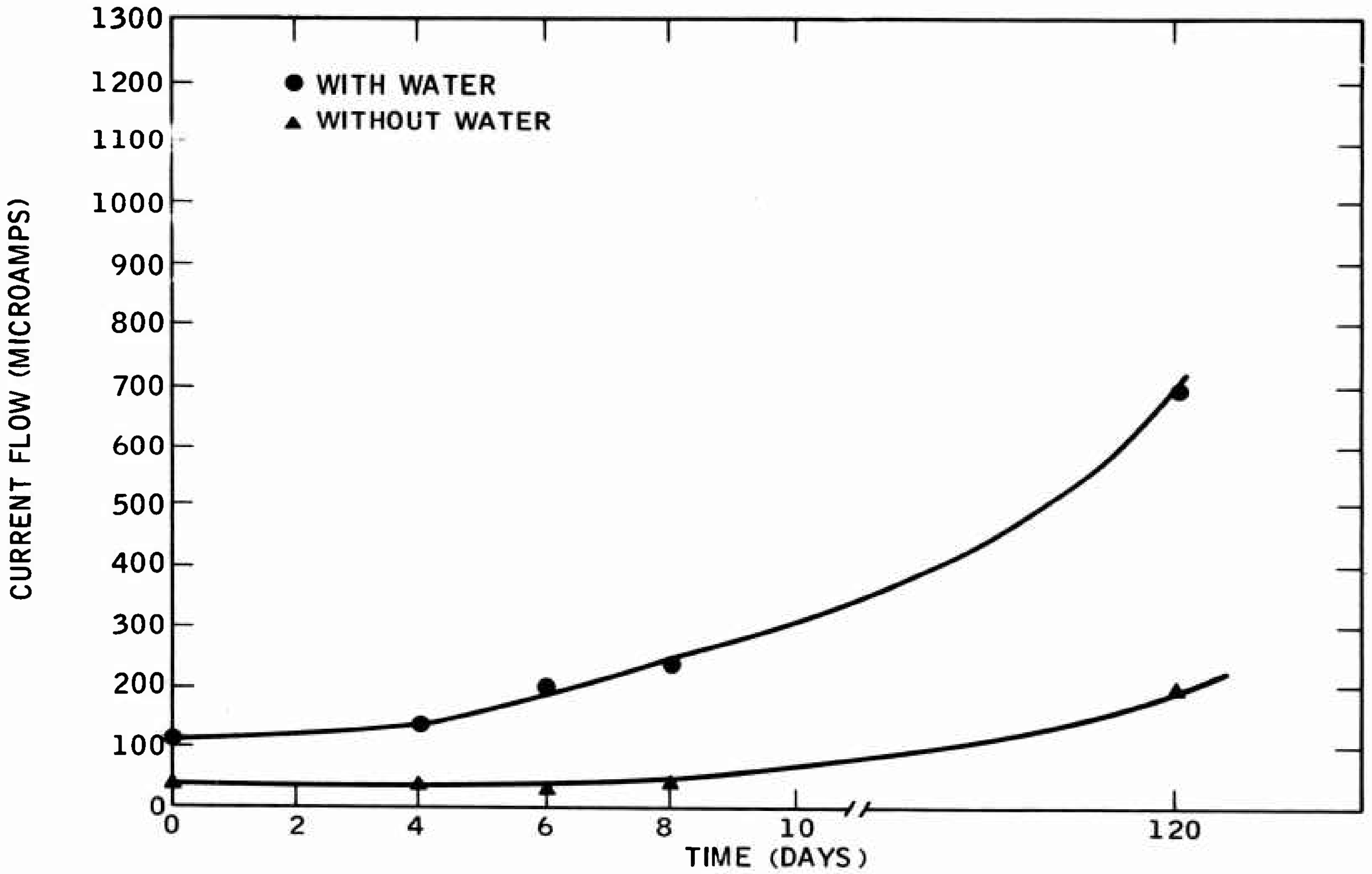

Figure 3. Effect of Emulsion Age on Conductivity of the Emulsion.

is the cause of the rapid loss of yield stress, as small drops have much more surface free energy than coarse ones. Since little free continuous phase is involved in this process, the conductivity is only slightly affected. The difference in extent of yield stress decay between the emulsion which contains water and the emulsion which does not is probably due to the former being more homogeneous than the latter. That is the former emulsion contains smaller particles, on the average, which are narrowly distributed about the smaller size. Therefore, since most droplets are of equivalent size, there is a reduced tendency of smaller droplets to "distill" into larger ones. Thus, there is a smaller yield stress decay for the emulsion containing water.

Second, the larger drops (which probably contain some excess emulsifier) tend to break up spontaneously (Reference 2). This would tend to increase the yield stress, but only to a trivial degree, as the surface generated by this means is minor compared to that lost by the first mechanism.

Third, the continuous phase from the faces of the polyhedra flows to the edges, as discussed above. This relatively slow process further decreases the yield stress--but in this case, reversibly. Shaking an aged emulsion of this sort is sufficient to restore much of its stiffness, a special case of rheopexy (ASTM D 2507). In addition, the continuous phase which accumulates in the form of triangular "wires" at the edges has much higher conductivity than that in the faces, where it is highly immobilized (condensed), probably resembling a solid. It is necessary to have some such mechanism to explain the increase in total conductivity, as this normally takes place only on homogenizing to reduced droplet size (Reference 6).

The significance of the third mechanism to the aging of high-internal-phase emulsion is that since the film separating droplets becomes thinner with aging, the barrier to coalescence is decreased. Thus, the change of emulsion conductivity with aging is one manifestation of emulsion instability. The unknowns here, however, remain film strength and surface coverage about the droplets. But other things being equal, those emulsions which show the greatest increase in conductivity on aging can be expected to be least stable. This is again consistent with the work of Holzner (Reference 6).

Effect of Urea

Table 4 also shows the effect of urea and the ratio of emulsifiers Atlas IL-851 to ENJ-5728 on the properties of 7165 emulsions. The data show quite definitively that the urea is necessary for high temperature emulsion stability. Using the data in Tables 4 and 6, it can thus be said that urea is necessary for low and high temperature stability. For stability of the emulsions at low temperatures, urea must be present with water. Urea also has the added effect of raising the equilibrium yield

TABLE 6

EFFECT OF UREA, RATIO OF IL-851 TO ENJ-5728 AND WATER ON 7165 EMULSION PROPERTIES (1% EMULSIFIER)

	Weight Percent				
	1	2	3	4	5
Formamide	1.5	-	-	1.5	-
20% Urea-Formamide	-	1.5	1.5	-	2.0
ENJ-5728	0.25	0.25	0.75	0.75	0.25
Atlas IL-851	0.75	0.75	0.25	0.25	0.75
JP-4	97.0	97.0	97.0	97.0	97.0
Distilled H_2O	0.50	0.50	0.50	0.50	-
Properties					
Yield Stress (dynes/cm^2)					
• Initial	2850	3300	2525	2000	2500
• After 1 Wk. at R.T.	1300	1400	1075	800	1400
• 1 Wk. at 140°F	Broken	1125	980	Broken	680
• 1 Wk. at -65°F	Broken	1850	1850	Broken	Broken
• 30 Days at R.T.	-	1450	960	-	1450
• 90 Days at R.T.	-	1605	940	-	1350
Stability (wt. % separation)					
• Vibration					
- 1/2 Hr.	1.8	0.85	0.0	0.0	17.0
- 3 Hrs.	-	0.85	0.0	0.0	-
- 8 Hrs.	-	0.85	0.0	0.0	-
Conductivity (microamps)					
• Initial	95	80	143	198	40
• 1 Wk. at R.T.	118	140	175	228	35
• 1 Wk. at 140°F	Broken	680	600	Broken	650
• 1 Wk. at -65°F	Broken	88	158	Broken	Broken
• 30 Days at R.T.	-	368	-	-	-
• 90 Days at R.T.	-	-	-	-	-

stress of the 7165 emulsion. The data in Table 6 further show that for acceptable stability to vibration and low temperatures (-65°F), the degree of dispersion as indicated by conductivity (as measured by current flow) must be greater than 90 microamps. The higher the conductivity of the emulsion, for the same continuous phase, the greater the degree of dispersion; i.e., the smaller the droplets of disperse phase and the more efficient the packing for high-internal-phase emulsions.

Effect of Ratio of Atlas IL-851 to ENJ-5728

Finally, Table 6 shows the effect of the ratio of emulsifiers Atlas IL-851 to ENJ-5728. The data show that decreasing this ratio increases the degree of dispersion as manifested by a significant increase in emulsion conductivity. The decrease in emulsion stability at 140°F caused by decreasing the ratio of emulsifier Atlas IL-851 to emulsifier ENJ-5728 is probably due to the significant increase in emulsifier solubility in the continuous phase at 140°F caused by having more of the water soluble ENJ-5728 present.

The effects of urea, water and the ratio of emulsifier Atlas IL-851 to emulsifier ENJ-5728 are further substantiated by the data shown in Table 6. These data were obtained on 7165 emulsions containing 1.5% of the continuous phase as compared to the 2% level for the emulsions shown in Table 4. The data shown in Table 5 also confirm that the urea is necessary for both low and high temperature stability regardless of the ratio of emulsifier Atlas IL 851 to emulsifier ENJ-5728. Further, the combination of urea and water is required for both acceptable high temperature and low temperature stability. The data also substantiate that increasing the ratio of Atlas IL-851 to ENJ 5728 improves the degree of the dispersion as manifested by higher emulsion conductivity; further, this is accomplished whether urea is present or not.

The data in Table 7 summarize the studies made on the effect of water, urea, and the ratio of Atlas emulsifier IL-851 to ENJ-5728 emulsifier on the properties of 7165 emulsions containing 0.50% emulsifier. These data basically confirm that the effect of water, urea, and the ratio of Atlas IL-851 to ENJ-5728 is the same whether the emulsifier level is 0.5% or 1.0%. The data in Table 7 show that water and urea are essential for emulsion stability at both 140°F and -65°F. The data here indicate that for acceptable stability to vibration, the emulsions must have a conductivity greater than about 90 microamps.

The obvious difference between the emulsions containing 0.50% emulsifier and those containing 1.0% emulsifier is in equilibrium yield stress. The data show that the equilibrium yield stress is highest for those emulsions containing 1.0% emulsifier. Another difference is the apparent difficulty in consistently producing emulsions containing 0.5% emulsifiers which are completely stable with respect to vibration stability.

TABLE 7
EFFECT OF WATER, UREA, AND RATIO OF ATLAS IL-851 TO ENJ-5728 ON 7165 EMULSION PROPERTIES (0.5% EMULSIFIER)

	Weight Percent				
	1	2	3	4	5
Formamide	-	-	-	2.5	2.0
20% Urea-Formamide	2.0	2.0	2.5	-	-
ENJ-5728	0.13	0.37	0.13	0.13	0.13
Atlas IL-581	0.37	0.13	0.37	0.37	0.37
JP-4	97.0	97.0	97.0	97.0	97.0
H_2O	0.50	0.50	-	-	0.50
Properties					
Yield Stress (dynes/cm^2)					
● Initial	3000	2150	2550	1400	1200
● After 1 Wk. at R.T.	975	900	960	660	Broken
● 1 Wk. at 140°F	1200	800	680	1050	Broken
● 1 Wk. at -65°F	1200	800	Broken	Broken	Broken
● 30 Days at R.T.	810	630	-	590	-
● 90 Days at R.T.	-	590	-	-	-
Stability (wt. % separation)					
● Vibration					
- 1/2 Hr.	Trace	0.0	0.30	0.0	0.0
- 3 Hrs.	Trace	0.0	-	0.0	-
- 8 Hrs.	0.50	0.0	2.0	Trace	Trace
Conductivity (microamps)					
● Initial	88	135	73	100	120
● 1 Wk. at R.T.	173	238	98	100	-
● 1 Wk. at 140°F	1400	1350	780	1150	-
● 1 Wk. at -65°F	145	175	Broken	Broken	-
● 30 Days at R.T.	600	730	-	148	-
● 90 Days at R.T.	-	-	-	-	-

Table 8 shows the effect of water level on the properties of 7165 emulsions containing 0.5% emulsifiers. About 0.65% water is the optimum level for maximum emulsion stability when the emulsifier level is 0.50%. The equilibrium yield stress of these emulsions is about 900 dynes/cm^2 after 30 days at room temperature. The initial yield stress of most of these emulsions is about 3000 dynes/cm^2. Thus, there is a tremendous yield stress decay for the 7165 emulsions containing only 0.5% emulsifier.

Effect of Internal Phase Level on Emulsion Stability

The effect of having an internal phase level greater than 97% by weight on the properties of 7165 emulsions was also investigated. The data in Table 7 show that emulsions containing more than 97% (JP-4) by weight can be prepared. As expected, however, as the concentration of the disperse phase is increased beyond 97%, emulsion stability decreases (Table 7). When the JP-content was about 97.4%, the stability of the emulsion appeared to be comparable to similar emulsions containing 97% JP-4. Thus, 97.0% JP-4 appears to approach very closely the upper limit for acceptable emulsion stability at an emulsifier level of 0.50%.

Optimum Fuel Emulsions Without Corrosion Inhibitors

On the basis of the data shown in Tables 4 through 9, it was obvious that optimum emulsions which meet the contractual requirements could be formulated at any emulsifier level ranging from 0.5% to 1.0%. Tables 10 and 11 show a series of such optimized emulsions for 0.50% and 0.75% emulsifier levels. The equilibrium yield stress of all these emulsions is about 1000 dynes/cm^2 at 140°F and room temperature. They all are stable with respect to low temperatures (-65°F) and vibrations. The conductivity of these emulsions, in general, is greater than 90 microamps, the minimum level that we believe is acceptable for stability to vibrations, pumping and low temperatures.

Effect of Water on Emulsion Corrosion Properties

The optimization studies discussed showed the beneficial aspect of added water on emulsion stability. It is intuitively obvious that other things being equal, water tends to increase the corrosiveness of the emulsions toward steel, and possibly other metals. Therefore, we investigated the effect of added water on the corrosiveness of WSX-7165. The WSX-7165 was prepared in the laboratory using the normal process conditions, and the results of these corrosion studies are summarized in Table 12.

TABLE 8

EFFECT OF WATER LEVEL ON PROPERTIES OF 7165 EMULSIONS (0.50% EMULSIFIER)

	Weight Percent		
	1	2	3
20% Urea-Formamide	2.0	1.85	1.5
ENJ-5728	0.25	0.25	0.25
Atlas IL-851	0.25	0.25	0.25
JP-4	97.0	97.0	97.0
Distilled H_2O	0.50	0.65	1.0
Properties			
Yield Stress (dynes/cm^2)			
• Initial	2700	3450	3850
• After 1 Wk. at R.T.	750	1000	1050
• 1 Wk. at 140°F	750	850	525
• 1 Wk. at -65°F	1500	1725	2100
• 30 Days at R.T.	Liq. Present	840	930
• 90 Days at R.T.	-	960	955
Stability (wt. % separation)			
• Vibration			
- 1/2 Hr.	0.0	0.0	0.0
- 3 Hrs.	0.0	0.0	0.0
- 8 Hrs.	Trace	0.0	0.0
Conductivity (microamps)			
• Initial	85	93	110
• 1 Wk. at R.T.	143	213	293
• 1 Wk. at 140°F	850	1230	1280
• 1 Wk. at -65°F	105	108	135
• 30 Days at R.T.	425	800	800
• 90 Days at R.T.	-	-	-

TABLE 9
EMULSIONS CONTAINING MORE THAN 97% JP-4 BY WEIGHT

	Weight Percent		
	1	2	3
Urea	0.26	0.35	.12
Formamide	1.49	1.40	1.03
JP-4	97.25	97.35	98.0
ENJ-5728	0.20	0.20	0.20
Atlas IL-851	0.30	0.30	0.30
H_2O	0.50	0.40	0.35
Properties			
Yield Stress (dynes/cm^2)			
● Initial	2400	2900	1825
● 1 Wk. at R.T.	1000	980	Liq. Present
● 1 Wk. at 140°F	850	930	Broken
● 1 Wk. at -65°F	1600	1700	1300
● 30 Days at R.T.	925	980	Broken
Stability (wt. % separation)			
● 1 Wk. at R.T.	0.0	0.0	0.50
● 1 Wk. at 140°F	0.0	0.0	25
● 1 Wk. at -65°F	0.0	0.0	0.0
● 8 Hrs. Vibration	0.0	0.0	0.65
Conductivity (microamps)			
● Initial	93	85	100
● 1 Wk. at R.T.	180	143	Liq. Present
● 30 Days at R.T.	550	485	Broken

TABLE 10
7165 EMULSIONS OPTIMIZED WITH 0.5% EMULSIFIERS

	Weight Percent		
	1	2	3
Urea	0.40	0.37	0.35
Formamide	1.60	1.48	1.40
JP-4	97.0	97.0	97.0
ENJ-5728	0.13	0.25	0.20
Atlas IL-851	0.37	0.25	0.30
H_2O	0.50	0.65	0.75
Properties			
Yield Stress (dynes/cm^2)			
• Initial	2150	3450	3300
• 1 Wk. at R.T.	975	1000	1000
• 1 Wk. at 140°F	1200	850	1050
• 1 Wk. at -65°F	1200	1725	2150
• 30 Days at R.T.	810	840	930
Stability (wt. % separation)			
• 1 Wk. at R.T.	0.0	0.0	0.0
• 1 Wk. at 140°F	0.0	0.0	0.0
• 1 Wk. at -65°F	0.0	0.0	0.0
• 8 Hrs. Vibration	0.50	0.0	0.0
Conductivity (microamps)			
• Initial	88	93	98
• 1 Wk. at R.T.	173	213	215
• 30 Days at R.T.	600	800	800

TABLE 11
7165 EMULSIONS OPTIMIZED WITH 0.75% EMULSIFIERS

	Weight Percent			
	1	2	3	4
Urea	0.20	0.19	0.19	0.18
Formamide	1.80	1.66	1.66	1.57
ENJ-5728	0.25	0.25	0.25	0.25
Atlas IL-851	0.50	0.50	0.50	0.50
JP-4	97.0	97.0	97.0	97.0
H_2O	0.25	0.40	0.40	0.50
Properties				
Yield Stress (dynes/cm^2)				
● Initial	2900	2900	2900	3300
● 1 Wk. at R.T.	1125	935	1135	1125
● 1 Wk. at -65°F	2175	1725	2185	1800
● 1 Wk. at 140°F	1090	1000	1090	1000
● 30 Days at R.T.	1150	1175	1350	970
Stability (wt. % separation)				
● 30 Days at R.T.	0.0	0.0	0.0	0.0
● 8 Hrs. Vibration	0.0	0.0	0.0	0.40
Conductivity (microamps)				
● Initial	148	195	150	138
● 1 Wk. at R.T.	145	218	148	133
● 30 Days at R.T.	245	485	295	290

TABLE 12
EFFECT OF WATER ON THE CORROSION PROPERTIES
OF 7165 FUEL EMULSIONS

		Weight Percent		
	7165**	1	2	3
Urea	0.40	0.37	0.30	0.40
Formamide	1.60	1.48	1.20	1.60
JP-4	97.0	97.35	97.0	97.0
ENJ-5728	0.25	0.25	0.25	0.25
Atlas IL-851	0.75	0.25	0.25	0.75
H_2O	0.0	0.30	1.0	0.50
Corrosion (mg/in.^{2})*				
• Mild Steel	0.5-2.5	12.2	15.4	11.0
• Aluminum	1.2	1.4	1.4	0.20
• Stainless	0.20-0.70	0.20	0.50	0.0

*1 Week at 140°F

**Laboratory Prepared

The data in Table 12 show that small quantities of water significantly increase the corrosiveness of 7165 emulsions toward mild steel; the behavior of the emulsion toward other metals is unaffected by water. Because it is virtually impossible to keep water out of the emulsions during the emulsion preparation in the plant or in handling, the emulsions can all be considered to be aqueous. It was thus obvious that even if water were not incorporated in the emulsions intentionally, the emulsion would still contain a fair amount of water. Therefore, it was decided that any optimized formulation of 7165 should contain a corrosion inhibitor to minimize or eliminate the corrosiveness of these emulsions toward mild steel. At the same time, this would permit the use of water in the formulation to enhance the stability of the emulsion. Therefore, the effort was shifted toward optimizing WSX-7165 emulsions which contained a corrosion inhibitor.

Investigation of Corrosion Inhibitors (Coupling Agents)

During this phase of the program, a large number of corrosion inhibitors were screened. The screening of the inhibitors initially involved simply adding 0.10% of the inhibitor to WSX-7165, to which was also added 0.50% water. These were simply mixed into the emulsion using a spatula. The emulsion containing a mild steel test sample was then stored at 140°F for 1 week. Those inhibitors which looked most promising ($\approx$5.0 mg/in^2 weight loss) in this test were evaluated further. Further evaluation consisted of incorporating the inhibitor into the emulsion prior to emulsification and evaluating the corrosiveness of the emulsion toward mild steel at 140°F for 1 week. Failure of the formulation to look promising in this test eliminated the inhibitor from further consideration.

The inhibitors investigated in this program are summarized in Table 13. Most of the inhibitors investigated were of the film-forming type. That is, they depended on adsorbing onto the metal surface to form a protective film to keep water from the surface. The effective inhibitors would therefore be expected to also be emulsifying agents. One would thus expect the effective inhibitors to alter the properties of the emulsion, either in a desirable or an undesirable manner. Many of the emulsifiers, when added to the emulsion for screening, broke the emulsions, whereas others actually increased the yield stress of the emulsion. Table 13 shows the relative effectiveness of the inhibitors investigated in terms of their ability to inhibit 7165 emulsions from the standpoint of corrosion of mild steel in the presence of 0.50% water.

Most Promising Corrosion Inhibitors

Of the materials screened as potential corrosion inhibitors for use in 7165 fuel emulsions, the materials listed below looked most promising:

- Santolene C
- Alkyl ammonium phosphate
- Trisaziridylmethylamine (TAMA)
- TAMA + B-DDSA (branched dodecenyl succinic anhydride)
- Lithium salt of B-DDSA (Li-B-DDSA)
- Hydrazine and ammonium salts of B-DDSA
- N,N'-disalicylidine-1,2-propanediamine

TABLE 13
CORROSION INHIBITORS EVALUATED IN THE PROGRAM

Name	Comments*
Vanlube 601	Ineffective
Alkaterge T (an Oxazoline)	Ineffective
Alkaterge T + H_3PO_4	Ineffective
Aziridine Phosphates	Moderately Effective
Polyethylene Glycol	Ineffective
C_{36} Dimer Acid	Moderately Effective
Branched Dodecenyl Succinic Anhydride (B-DDSA)	Moderately Effective
Linear Dodecenyl Succinic Anhydride (DDSA)	Ineffective
Ethomeen 18/25 (Ethoxylated Amine)	Ineffective
Ethomid HT/15 (Ethoxylated Amide)	Moderately Effective
Armac 18D (Aliphatic Amine Acetate)	Ineffective
Sindar G-4.40	Ineffective
Alkyl Ammonium Phosphate	Quite Effective
Organic Phosphate	Moderately Effective
Santolene C	Quite Effective
Lithium Salt of B-DDSA (Lithium Salt of Branched Dodecenyl Succinic Anhydride)	Very Effective
Lithium Salt of L-DDSA (Lithium Salt of Linear Dodecenyl Succinic Anhydride)	Moderately Effective
NaSUL EDS (Ethylene Diamine Sulfonate)	Moderately Effective
Alkaterge T + HOAc	Ineffective
Hydrazine Salt of B-DDSA (Hydrazine Salt of Branched Dodecenyl Succinic Anhydride)	Very Effective

TABLE 13 CONTINUED

Name	Comments*
Ammonium Salt of B-DDSA (Ammonium Salt of Branched Dodecenyl Succinic Anhydride)	Quite Effective
Tenamine 60 (N,N' Disalicylidine 1,2-Propanediamine)	Quite Effective
DuPont AFA-1	Moderately Effective
DuPont A-022	Ineffective
DuPont B-A023 (N,N'-Diisopropyl-Para-Phenylenediamine)	Moderately Effective
Tenamene 7 (Mixture of Substituted Phenyldiamines)	Moderately Effective
Trisaziridylmethylamine (TAMA)	Quite Effective

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* Comments refer to ability of inhibitor to control corrosion toward mild steel in initial screening tests.

Evaluation of Santolene C Inhibitor

The results obtained in the further evaluation of Santolene C are shown in Table 14. The material did indeed decrease the corrosiveness of the emulsion toward mild steel; however, the emulsion still significantly corroded mild steel. The presence of the Santolene C appears to have increased the initial yield stress and the equilibrium yield stress of the emulsion after 1 week at room temperature and 140°F. Other than these changes, the additive does not appear to have had any significant effect on the properties of the emulsion. Because of the moderate effect of Santolene C on the corrosiveness of the emulsion toward mild steel, it was not evaluated further.

Evaluation of Alkyl Phosphate Inhibitor

Table 15 summarizes the results obtained in the further evaluation of the alkyl ammonium phosphate inhibitor. This material was moderately effective as a corrosion inhibitor when the emulsifier level was 0.60%. However, when the emulsifier level was increased to 1.0%, the effectiveness of the alkyl ammonium phosphate as a corrosion inhibitor diminished. This effect is observed because the phosphate is an inhibitor of the film-forming type. That is, to be effective it must be adsorbed by the metal, and to do this the inhibitor must be in the interface. So, as the emulsifier level is increased, more of the inhibitor molecules are forced out of the interface by the emulsifier molecules. Therefore, at the higher emulsifier level, there are little or no corrosion inhibitors at the interface; thus, the effectiveness of the inhibitor decreases.

It is further observed from the data in Table 15 that the presence of the phosphate inhibitor increases the conductivity of the emulsion significantly. This indicates that the inhibitor molecules are acting effectively as emulsifiers and enhance the degree of dispersion. That is, the emulsion droplets in the emulsion containing the phosphate inhibitor are probably smaller on the whole than the droplets of the same emulsion prepared without the inhibitor. However, because of the moderate corrosion inhibition achieved with the use of the phosphate inhibitor, no further evaluations of this material were carried out.

Evaluation of Lithium Salt of B-DDSA Inhibitor

The results of the further evaluation of the lithium salt of branched dodecenyl succinic anhydride (Li-B-DDSA) as a corrosion inhibitor are summarized in Table 16. This material is a highly effective corrosion inhibitor in 7165 emulsions. For the emulsions containing 1% emulsifier and 0.50% water, the presence of 0.1% of the Li-B-DDSA inhibited completely the corrosiveness of the emulsion toward mild steel. Because of these results, the B-DDSA salts were investigated further as corrosion inhibitors, and emulsion formula 1, Table 16, was thus investigated in the rheology and combustion programs.

TABLE 14
EFFECT OF SANTOLENE C ON THE CORROSIVENESS OF 7165 EMULSIONS

	Weight Percent 1	Weight Percent 2
JP-4	97.0	97.0
Santolene C*	0.10	-
ENJ-5728	0.40	0.40
Atlas IL-851	0.60	0.60
Urea	0.40	0.40
Formamide	1.60	1.60
H_2O*	0.50	0.50
Properties		
Yield Stress (dynes/cm^2)		
• Initial	2800	2300
• 1 Wk. at R.T.	1875	1350
• 1 Wk. at -65°F	2900	2185
• 1 Wk. at 140°F	960	700
• 30 Days at R.T.	1750	1630
Stability (wt. % separation)		
• 30 Days at R.T.	0.0	0.0
• 8 Hrs. Vibration	0.0	0.0
Corrosion (mg/in.^{2})**		
• 1 Wk. at 140°F	3.5	12.0
Conductivity (microamps)		
• Initial	125	125
• 1 Wk. at R.T.	175	155
• 30 Days at R.T.	550	650

* Based on wt. of emulsion
** AISI 1010 steel

TABLE 15
EFFECTIVENESS OF A PHOSPHATE INHIBITOR ON THE CORROSIVENESS OF 7165 EMULSIONS

	Weight Percent			
	1	2	3	4
JP-4	97.0	97.0	97.0	97.0
Urea	0.28	0.28	0.28	0.40
Formamide	1.57	1.57	1.57	1.60
ENJ-5728	0.20	0.20	0.20	0.40
Atlas IL-851	0.40	0.40	0.40	0.60
Alkyl Ammonium Phosphate	0.00	0.10	0.05	0.10*
H_2O	0.55	0.45	0.50	0.50*
Properties				
Yield Stress (dynes/cm^2)				
● Initial	2500	3450	2700	3450
● 1 Wk. at R.T.	1150	1025	780	1850
● 1 Wk. at -65°F	2000	1950	1400	3400
● 1 Wk. at 140°F	1050	950	920	1050
● 30 Days at R.T.	940	1300	860	1725
Stability (wt. % separation)				
○ 30 Days at R.T.	0.0	0.0	0.0	0.0
○ 8 Hrs. Vibration	0.0	0.0	0.5	0.0
Corrosion (mg/in.^{2})**				
● 1 Wk. at 140°F	12.1	2.4	2.2	8.0
● 30 Days at R.T.	-	0.20	-	-
Conductivity (microamps)				
● Initial	140	295	205	375

* By wt. of emulsion

** AISI 1010 steel

TABLE 16
EFFECTIVENESS OF Li-B-DDSA AS A
CORROSION INHIBITOR IN 7165 EMULSIONS

	Weight Percent		
	1	2	3
JP-4	97.0	97.0	97.0
ENJ-5728	0.40	0.75	0.25
Atlas IL-851	0.60	0.25	0.75
Urea	0.40	0.40	0.40
Formamide	1.60	1.60	1.60
Li-B-DDSA	0.10*	0.10*	0.10*
H_2O	0.50*	0.50*	0.50*
Properties			
Yield Stress (dynes/cm^2)			
● Initial	3700	3400	3450
● 1 Wk. at R.T.	1725	1450	2225
● 30 Days at R.T.	1325	1135	2800
● 1 Wk. at 140°F	930	Broken	1475
● 1 Wk. at -65°F	3450	2650	2750
Stability (wt. % separation)			
● 8 Hrs. Vibration	0.0	0.0	6.3
● 30 Days at R.T.	0.0	0.0	0.0
Corrosion-Wt. Loss (mg/in.^{2})**			
● 1 Wk. at 140°F	0.0	0.0	0.10
● 30 Days at R.T.	0.0	0.0	0.0
Conductivity (microamps)			
● Initial	1200	1150	850

* By wt. of emulsion
** AISI 1010 steel

Evaluation of Nonmetallic Salts of B-DDSA Inhibitors

Table 17 shows the results of further evaluation of other nonmetallic salts of branched dodecenyl succinic anhydride, which included the hydrazine and ammonium salts. The hydrazine salt is quite effective in inhibiting the corrosiveness of the 7165 emulsions toward mild steel. These salts are apparently more effective when the emulsifier is less than 1%. The hydrazine salt of B-DDSA is more effective as a corrosion inhibitor for a given concentration than is the ammonium salt of B-DDSA. The ammonium salt of B-DDSA is most effective if the ENJ-5728 emulsifier is not present. Either these two materials, ENJ-5728 emulsifier and the ammonium salt of DDSA, compete for the interface when they are present together, or the mixed film formed is so expanded that its efficiency in protecting the metal surface is greatly minimized. Thus, when the ammonium salt of B-DDSA is alone in the film with the Atlas IL-851, the film is sufficiently condensed so as to be a rather effective barrier to corrosion.

Because the hydrazine salt of B-DDSA was found to be a more effective corrosion inhibitor than the corresponding ammonium salt, no further work was carried out using the ammonium salt of B-DDSA as a corrosion inhibitor. In the final formulation of optimized 7165 fuel emulsions, the B-DDSA salt of hydrazine was included as an inhibitor in several of the formulations.

Evaluation of Trisaziridylmethylamine Inhibitor

Table 18 shows the results of the studies carried out in the further evaluation of trisaziridylmethylamine (TAMA) as a corrosion inhibitor. Column 1, Table 18, shows that TAMA is a rather effective corrosion inhibitor, having almost inhibited completely the corrosion of mild steel by the emulsion. The emulsion containing TAMA was quite stable as evidenced by the performance data in the other tests. In an effort to reduce the level of bronze corrosion achieved with the emulsion containing TAMA, branched dodecenyl succinic anhydride was used in combination with TAMA (see columns 2 and 3, Table 18). The addition of the B-DDSA had no significant effect on the bronze corrosion of these emulsions. However, it does appear that the level of mild steel corrosion was reduced by the addition of 0.02% B-DDSA. Replacement of 0.02% of the .10% TAMA with B-DDSA caused a reduction of the mild steel corrosion without adversely affecting the overall stability of the emulsion. Replacement of 0.05% of the 0.10% TAMA with B-DDSA adversely affected both emulsion stability and corrosion properties. Because of the results achieved with the use of 0.08% TAMA in combination with 0.02% B-DDSA, this corrosion inhibitor combination was further evaluated in an effort to form an optimized formulation containing it as the corrosion inhibitor. This formulation is discussed further under Section VI, dealing with the complete characterization of the optimized 7165 formulations.

TABLE 17
EFFECTIVENESS OF HYDRAZINE AND AMMONIUM SALTS OF DDSA AS CORROSION INHIBITORS

	Weight Percent			
	1	2	3	4
JP-4	97.0	97.0	97.0	97.0
ENJ-5728	0.40	0.13	-	0.16
Atlas IL-851	0.60	0.32	0.50	0.40
Urea	0.40	0.20	0.40	0.20
Formamide	1.60	1.80	1.60	1.80
Hydrazine Salt of DDSA	0.10*	0.15*	-	-
Ammonium Salt of DDSA	-	-	0.15*	0.15*
H_2O	0.50*	0.50	0.50	0.50
Properties				
Yield Stress (dynes/cm^2)				
• Initial	5100	3120	3150	4050
• 1 Wk. at R.T.	1525	1300	1560	1450
• 30 Days at R.T.	2100	980	1350	1145
• 1 Wk. at 140°F	1135	1060	1110	680
• 1 Wk. at -65°F	2900	2800	3250	1950
Stability (wt. % separation)				
• 8 Hrs. Vibration	0.0	0.0	0.0	0.0
• 30 Days at R.T.	0.0	0.0	0.0	0.0
Corrosion-Wt. Loss (mg/in.^{2})**				
• 1 Wk. at 140°F	0.8	0.0	0.8	2.2
• 30 Days at R.T.	0.0	-	-	-
Conductivity (microamps)				
• Initial	500	305	395	245

* By wt. of emulsion
** AISI 1010 steel

TABLE 18
EFFECTIVENESS OF TAMA-DDSA AS CORROSION INHIBITOR

	Weight Percent		
	1	2	3
Urea	0.40	0.40	0.40
Formamide	1.60	1.60	1.60
JP-4	97.0	97.0	97.0
Atlas IL-851	0.60	0.60	0.60
ENJ-5728	0.40	0.40	0.40
TAMA*	0.10	0.05	0.08
DDSA*		0.05	0.02
H_2O	0.50	0.50	0.50
<u>Properties</u>			
<u>Yield Stress (dynes/cm^2)</u>			
• Initial	3120	2175	4100
• 1 Wk at R.T.	2100	Liq. on surface	2225
• 30 Days at R.T.	1400		1250
• 1 Wk. at 140°F	930	750	1400
• 1 Wk. at -65°F	3100	2225	3375
<u>Stability (wt. % separation)</u>			
• 30 Days at R.T.	0.0		
• 8 Hrs. Vibration	0.0	0.0	0.0
<u>Corrosion-Wt. Loss (mg/in.^{2})</u>			
• 1 Wk at 140°F With Steel**	0.50	6.3	0.13
• 1 Wk. at 140°F With Bronze	13.0		15.0
<u>Conductivity (microamps)</u>			
• Initial	385	295	265

* By wt. of emulsion

** AISI 1010 steel

Evaluation of N,N'-disalicylidine 1,2-propanediamine Inhibitor

Table 19 shows the results of the further evaluation of the final most promising corrosion inhibitor, N,N'-disalicylidine 1,2-propanediamine. At the 0.10% level, the N,N' -disalicylidine 1,2-propanediamine is quite effective as a corrosion inhibitor in 7165 emulsions. This is particularly true if the emulsifier level is maintained at 1%. At lower emulsifier levels, either more of the inhibitor is required for equivalent effectiveness when the emulsion contains a 0.5% water, or the water level of the emulsion must be reduced from 0.5% to 0.2%. The data in Table 19 also indicate that the addition of the inhibitor also increases the thermal stability of these emulsions.

All the potential inhibitors discussed so far were soluble in the continuous phase of the emulsions. However, the N,N'-disalicylidine 1,2-propanediamine is not very soluble in the continuous phase. Thus, the dependence of the effectiveness of the N,N'-disalicylidine 1,2-propanediamine on the level of emulsifier is probably due to its being insoluble in the continuous phase. This inhibitor is dispersed into droplets in the continuous phase by the emulsifiers. Therefore, at lower emulsifier levels the N,N'-disalicylidine 1,2-propanediamine is not as effectively dispersed as when higher emulsifier levels are used. If it is once again assumed that the corrosion inhibitor works by an adsorption mechanism, the greater the degree of dispersion for a given emulsifier level, the greater the surface coverage of the metal by the inhibitor. Anything that would thus tend to reduce surface coverage, such as a decrease in the dispersibility of the inhibitor as caused by reducing the emulsifier level, reduces the effectiveness of the corrosion inhibitor. Stated another way, at reduced emulsifier levels, either less water can be tolerated or more inhibitor is required to handle a given water level. The data in column 3, Table 19, show that reducing the water level from 0.5% to 0.2% essentially eliminates corrosion by the emulsion when the emulsion contains 0.1% of the N,N'-disalicylidine 1,2-propanediamine. The data in column 4, Table 19, show that the same emulsion, however, is quite corrosive if the emulsion does not contain the inhibitor. Therefore, N,N'-disalicylidine 1,2-propanediamine at the 0.1% level is an effective corrosion inhibitor either in the presence of 0.5% water or less when the emulsion contains 1% emulsifier or in the presence of 0.2% water or less when the emulsion contains 0.5% emulsifier.

Because of the effectiveness of N,N'-disalicylidine 1,2-propanediamine as a corrosion inhibitor in 7165 emulsions and because of its advantageous effect on emulsion stability (Table 19), 7165 emulsion formulations were optimized to contain it as a corrosion inhibitor. These will be discussed further in Section VI, which deals with the characterization of the optimized 7165 formulations.

TABLE 19
EFFECT OF EMULSIFIER AND WATER LEVELS ON CORROSION INHIBITOR EFFECTIVENESS

	Weight Percent			
	1	2	3	4
JP-4	97.0	97.0	97.0	97.0
ENJ-5728	0.40	0.20	0.20	0.20
Atlas IL-851	0.60	0.30	0.30	0.30
Urea	0.40	0.40	0.48	0.35
Formamide	1.60	1.60	1.92	1.40
N,N'-Disalicylidine 1,2-Propanediamine	0.10*	0.10*	0.10	-
H_2O	0.50*	0.50	0.20*	0.20
Properties				
Yield Stress (dynes/cm^2)				
• Initial	2900	2350	2825	2475
• 1 Wk. at R.T.	2185	1150	1145	860
• 30 Days at R.T.	1900	-	-	640
• 1 Wk. at 140°F	1145	530	640	Partially Broken
• 1 Wk. at -65°F	3050	1605	1560	1350
Stability (wt. % separation)				
• 8 Hrs. Vibration	0.0	1.0	0.0	0.1
• 30 Days R.T.	0.0	-	-	0.0
Corrosion-Wt. Loss (mg/in.^{2})**				
• 1 Wk. at 140°F	0.80	3.0	0.30	11.3
• 30 Days at R.T.	0.0	-	-	-
Conductivity (microamps)				
• Initial	185	185	155	105

* By wt. of emulsion

** AISI 1010 steel

Side Benefits of the Corrosion Inhibitors

On the basis of the more detailed evaluations of the most promising materials as corrosion inhibitors, the materials listed below were incorporated in optimized formulations for complete evaluation:

- N,N'-disalicylidine 1,2-propanediamine
- Hydrazine salt of B-DDSA
- TAMA + B-DDSA

The detailed characterization of the emulsions formulated using these inhibitors is discussed in Section VI.

In general, the corrosion inhibitor behaved as an ionic emulsifier and thereby enhanced the mechanical stability of the emulsion because of reduced droplet size and increased strength of the interfacial film about the droplets. The presence of the ionic material in the interfacial film along with the nonionic emulsifier makes for greater surface coverage and a stronger interfacial film. This is caused by the attractions between the ionic molecules (corrosion inhibitor) and the polar nonionic molecules (emulsifier) being greater than the attractions between polar nonionic molecules. These effects were manifested in the emulsion by higher emulsion conductivity, greater stability to vibration, and increased stability toward pumping.

The other beneficial effect caused by the incorporation of the ionic corrosion inhibitor into the 7165 emulsion is the greatly reduced pressure drop required to pump the emulsion through metal pipes. This is due to the adsorption of the ionic corrosion inhibitor onto the metal surface, which not only protects the metal against corrosion but also changes the surface from a high-energy surface that is wettable by the emulsion to a low-energy surface that is not wettable by the emulsion. Because the emulsion containing the corrosion inhibitor no longer wets the surface, the emulsion flows as a plug which is "lubricated" by a thin film of the continuous phase. This is then manifested by a substantially reduced pressure drop being required to pump the emulsion through metal pipes (see Section VI).

Screening of Other Emulsifiers for Use in 7165 Fuel Emulsions

Other emulsifiers similar chemically to those in WSX-7165 were also evaluated in this program. Since the HLB of the emulsifier package in WSX-7165 is estimated to be about 13.2, emulsifier packages having this HLB were evaluated as well as ones that could directly replace the Atlas IL-851, a part of the current emulsifier package. The emulsifiers evaluated in this program are shown in Table 20 along with comments as to how they differ from the emulsifier package currently being used in WSX-7165 fuel emulsion.

TABLE 20
OTHER EMULSIFIERS OF CHEMICAL TYPE SIMILAR TO THOSE IN 7165 FUEL EMULSION

Name	HLB	Mol. Wt.	Comments*
IL-851	13.0	2500	Emulsifier Used in WSX-7165
IL 870	13.0	2700	No Low Molecular Weight Polyol Esters
IL 871	13.0	2500	Different Distribution of Ethylene Oxide
IL 872	13.2	2700	Contains Some Abietic Acid Moities
IL 873	13.2	2700	Contains Some Branched Chained Hydrophobe
IL 874	13.2	2000	Higher Percentage of Low Molecular Weight Esters
IL 875	13.0	11,000	High Percentage of Hexitol Rather than Hexitan Esters

* All comments relative to IL-851 emulsifier

To evaluate the emulsifiers listed in Table 20, Process II (Table 1) was used in every case and all the emulsifiers were evaluated at the 1% level. To investigate the effect of water on emulsions containing the emulsifiers under investigation, the batch of emulsion was divided in half. To one half, water was added; the other half was evaluated as the case without water. In this wav the effects observed were due entirely to water and not to process variations.

Tables 21 through 24 show the results of the evaluation of the six emulsifiers listed in Table 20. These data show that it is possible to formulate 7165 fuel emulsions using each of the emulsifiers alone,with the exception of emulsifiers IL-870 and 875. Therefore, no further studies were carried out using emulsifiers IL-870 and 875. Tables 21 through 24 show that of the emulsifiers investigated, only emulsifiers IL-871 and IL-872 when used alone formed emulsions which were stable without the use of water under all the conditions at which the emulsions were tested. Only emulsifier IL-871 produced an emulsion in the absence of added water which had a sufficient degree of dispersion as evidenced by the high emulsion conductivity (115 microamps) to insure acceptable stability to vibration and pumping. A minimum emulsion conductivitv of 90 microamps appears to be necessary for acceptable emulsion mechanical stability as measured via vibration and pumping tests. As stated, we believe that emulsion conductivity is a measure of the degree of dispersion for emulsions having the same continuous phase.

Since emulsifier IL-871 is of the same chemical type as emulsifier IL-851, the data indicate the strong influence of molecular weight on the effectiveness of these materials as emulsifiers. The calculated molecular weights of IL-871 and IL-851 are the same, but they differ with respect to the distribution of ethylene oxide per emulsifier molecule.

Tables 21 and 22 show that the addition of water to any of the emulsions containing the alternate emulsifiers invariably made the emulsion stable under all conditions at which the emulsions were tested. Thus, the beneficial effect of water on the properties of these "nonaqueous" emulsions can be considered a general phenomenon. That is, the addition of water to otherwise nonaqueous emulsion systems will enhance their overall stability when the water is added to the finished emulsion.

Emulsifiers IL-872, 873, 874, and 875 (Tables 21 and 22) when used alone, either in the presence of added water or in the absence of added water, do not produce emulsions which have acceptable dispersibility, as evidenced by the emulsion conductivities being less than 90 microamps. Because of the good yield stress retention and thermal stability of these emulsions containing emulsifiers IL-872, 873, 874, and 875, these emulsifiers were evaluated in combination with ENJ-5728 emulsifier. The results of these studies are summarized in Tables 23 and 24. Table 23 shows that when the ENJ-5728 emulsifier is used in combination with emulsifier IL-872 in the presence of water (0.5%), an emulsion is produced which has a high degree of dispersion, as evidenced by the emulsion conductivity (125 microamps).

TABLE 21
7165-TYPE EMULSIONS FORMULATED WITH ALTERNATE EMULSIFIERS

	Weight Percent				
	1	2	3	4	5
JP-4	97.0	97.0	97.0	97.0	97.0
Urea	0.40	0.40	0.40	0.40	0.40
Formamide	1.6	1.6	1.6	1.6	1.6
Emulsifier IL-870 (HLB 13)*	-	-	-	-	1.0
Emulsifier IL-871 (HLB 13)*	1.0	1.0	-	-	-
Emulsifier IL-872 (HLB 13.2)*	-	-	1.0	1.0	-
H_2O (Per Wt. of Emulsion)	-	0.50	-	0.50	0.50
Properties					
Yield Stress (dynes/cm^2)					
● Initial	1650	1900	2250	2225	No
● 1 Wk. at R.T.	1300	1605	1875	2175	Emulsion
● 1 Wk. at 140°F	1145	980	1390	1420	Possible
● 1 Wk. at -65°F	1920	1725	1500	2200	
Conductivity (microamps)					
Initial	115	175	55	87	-

* IL-872 Mol. Wt. = 2700; IL-870 Mol. Wt. = 2700;
IL-871 Mol. Wt. = 2500

TABLE 22
7165-TYPE EMULSIONS FORMULATED WITH ALTERNATE EMULSIFIERS

	Weight Percent				
	1	2	3	4	5
JP-4	97.0	97.0	97.0	97.0	97.0
Urea	0.40	0.40	0.40	0.40	0.40
Formamide	1.60	1.60	1.60	1.60	1.60
Emulsifier IL-873 (HLB 13.2)*	1.00	1.00	-	-	-
Emulsifier IL-874 (HLB 13.2)*	-	-	1.00	1.00	-
Emulsifier IL-875 (HLB 13)*	-	-	-	-	1.0
H_2O (Per Wt. of Emulsion)*	-	0.50	-	0.50	0.5
Properties					
Yield Stress (dynes/cm^2)					
• Initial	3125	2850	1850	2175	No
• 1 Wk. at R.T.	2600	2175	1035	1350	Emulsion
• 1 Wk. at 140°F	1235	1650	680	930	Possible
• 1 Wk. at -65°F	Broken	4050	Broken	2175	
Conductivity (microamps)					
Initial	48	73	43	74	-

* IL-873 Mol. Wt. = 2700

IL-874 Mol. Wt. = 2000

TABLE 23

EFFECT OF ENJ-5728 ON 7165-TYPE EMULSIONS FORMULATED WITH ALTERNATE EMULSIFIERS

	Weight Percent			
	1	2	3	4
JP-4	97.0	97.0	97.0	97.0
ENJ-5728	0.40	0.40	-	-
Atlas IL-872 (HLB 13.2)	0.60	0.60	1.0	1.0
Urea	0.40	0.40	0.40	0.40
Formamide	1.60	1.60	1.60	1.60
H_2O*	-	0.50	-	0.50
<u>Properties</u>				
<u>Yield Stress (dynes/cm^2)</u>				
• Initial	2825	2900	2250	2225
• 1 Wk. at R.T.	1800	2225	1875	2175
• 1 Wk. at -65°F	Broken	2150	1500	2200
• 1 Wk. at 140°F	950	1125	1390	1420
• 30 Days at R.T.	1300	1605	-	-
<u>Conductivity (microamps)</u>				
• Initial	75	125	55	87

* Based on Wt. of Emulsion

IL-872 (Mol. Wt. = 2700)

TABLE 24
EFFECT OF ENJ-5728 ON 7165-TYPE EMULSIONS FORMULATED WITH ALTERNATE EMULSIFIERS

	Weight Percent			
	1	2	3	4
JP-4	97.0	97.0	97.0	97.0
Urea	0.40	0.40	0.40	0.40
Formamide	1.60	1.60	1.60	1.60
Emulsifier IL-873 (HLB 13.2)	1.0	1.0	0.60	0.60
ENJ-5728	-	-	0.40	0.40
H_2O	-	0.50	-	0.50
<u>Properties</u>				
<u>Yield Stress (dynes/cm^2)</u>				
• Initial	3125	2850	3120	3800
• 1 Wk. at R.T.	2600	2175	1920	2175
• 1 Wk. at -65°F	Broken	4050	2900	2675
• 1 Wk. at 140°F	1235	1650	1200	1450
• 30 Days at R.T.	-	-	1950	1725
<u>Conductivity (microamps)</u>				
• Initial	45	75	115	155

This is not the case when ENJ-5728 is not included in the emulsion (column 4, Table 23). On this basis, it can be concluded that emulsifier IL-872 can be substituted in a 7165 emulsion when the emulsion contains water and the ENJ-5728 emulsifier.

The results in Table 24 show the effect of using ENJ-5728 emulsifier in combination with emulsifier IL-873. The emulsion formulated with this combination is highly stable under all the conditions tested; the emulsion also has a high degree of dispersion, as evidenced by the emulsion conductivity (115 microamps), even in the absence of added water. By using water in conjunction with the emulsifier combination, ENJ-5728 and emulsifier IL-873, an emulsion is formed which has excellent overall stability, as evidenced by the excellent yield stress retention of the emulsion at room temperature and 140°F. The emulsion also has a high degree of dispersion and thus should have good mechanical stability, as indicated by the high emulsion conductivity (155 microamps). On the basis of these results, it can be concluded that emulsifier IL-873 represents a good alternate to emulsifier IL-851 and can be used in combination with emulsifier ENJ-5728 in the presence of water.

On the basis of the evaluations of alternate emulsifiers, two emulsifiers, IL-872 and IL-873, can be used as alternates to IL-851 in 7165-type emulsions. These are to be used in combination with emulsifier ENJ-5728 plus added water. Such formulations will have the maximum degree of dispersion and therefore the maximum overall emulsion stability, both thermal and mechanical.

CONCLUSIONS

The study shows that urea is necessary for good high-temperature stability and high equilibrium yield stress. Water in combination with urea makes for good low-temperature emulsion stability and good mechanical stability as measured by pumping and vibrational tests.

A high ratio of emulsifier IL-851 to emulsifier ENJ-5728 favors better high-temperature stability but poorer mechanical stability. Optimum thermal stability (high and low temperature) and mechanical stability are achieved by the use of high ratios of IL-851 emulsifier to ENJ-5728 emulsifier in combination with water.

Small quantities of water increase significantly the corrosiveness of nonaqueous emulsions with respect to mild steel. Several inhibitors, however, were uncovered which inhibit this corrosiveness and which impart several beneficial properties to the emulsion (improved mechanical stability and a lowering of the pressure drop required to pump the emulsions through metal pipes).

Work is still needed, however, to develop a better understanding of the mechanism of corrosion in fuel emulsions. Such an understanding is necessary in order to systematically control the corrosiveness of these emulsions toward metals and to determine what happens to the corrosiveness of the emulsions with age.

Two emulsifiers, IL-872 and IL-873, were uncovered which can be used as alternates for emulsifier IL-851 in 7165-type fuel emulsions. These emulisifiers are similar chemically to IL-851 and are to be used in combination with ENJ-5728 and preferably with added water (0.50%). Emulsions prepared using the alternate emulsifiers possessed good thermal stability (high and low temperature) and good mechanical stability.

III. OPTIMIZATION STUDIES ON WSX-7063 FUEL EMULSION

INTRODUCTION

Because WSX-7165 had been considered our best fuel emulsion, most of the effort of this program was devoted to its optimization. Thus, only a limited amount of time was devoted to the optimization of WSX-7063. Nevertheless, the effects of the variables listed below on the properties of WSX-7063 fuel emulsion were investigated:

- Ratio of continuous phase to emulsifier
- Water
- Urea

The effect of disperse phase level was not investigated further with WSX-7063 because it is known from our previous studies and from the literature that emulsion stability, in general, decreases with increasing continuous phase level. Our previous studies indicate that this effect is exponential at disperse phase levels greater than the 97 weight percent. As it turned out, the effects of the variables listed above are directionally similar to those found with 7165-type emulsions.

RESULTS AND DISCUSSION

The data in Table 25 show the effects of water and the ratio of continuous phase to emulsifier on the properties of WSX-7063. For acceptable low-temperature stability, the ratio of continuous phase to emulsifier must be at least two. This emulsion property seems to be more dependent on ratio of continuous phase to emulsifier than on water. The effect of added water on WSX-7063 appears to be only to raise the yield stress of the emulsion. Since the emulsions containing water shown in Table 25 were prepared with the continuous phase to emulsifier being less than two, this effect apparently outweighs the effect of added water on the properties of WSX-7063 emulsion. Therefore, to see the effect of water, much larger water levels may have been required when the emulsifier level was 1% or greater.

Data in Table 26 show the effect of urea and water on the properties of 7063-type emulsions. The presence of urea increases the yield stress of the emulsions under just about all conditions and decreases the degree of the dispersion of the emulsion, as evidenced by the lower emulsion conductivity. This effect is manifested by lower mechanical stability, as evidenced by the results in the vibration test (Table 26). The effect of water on the properties of 7063-type emulsions as indicated by columns 2 and 3, Table 26, is small. Directionally, however, it does appear that water also enhances the mechanical stability of the 7063-type emulsions when they contain 0.75% emulsifier.

TABLE 25
EFFECT OF WATER AND EMULSIFIER LEVEL ON THE PROPERTIES OF 7063-TYPE EMULSIONS

	Weight Percent				
	1	2	3	4	5
Formamide	2.0	1.5	1.75	2.25	1.5
Span 80	0.28	0.28	0.21	0.21	0.42
Tween 80	0.72	0.72	0.54	0.54	1.08
JP-4	97.0	97.0	97.0	97.0	97.0
H_2O	-	0.50	0.50	-	-
Properties					
Yield Stress (dynes/cm^2)					
● Initial, R.T.	1560	2300	2200	1725	3400
● After 1 Wk. at R.T.	1125	1300	1080	1050	2200
● 1 Wk. at 140°F	780	910	850	580	1250
● 1 Wk. at -65°F	1385	2150	1435	1125	Broken
● 30 Days at R.T.	950	1125	1150	900	1400
● 90 Days at R.T.	-	955	800	-	-
Stability					
● Vibration (wt. % separation)					
- 1/2 Hr.	0.0	0.0	0.0	0.0	0.0
- 1 Hr.	0.0	5.4	0.0	0.0	5.0
- 4 Hrs.	0.0	-	0.0	Trace	-
- 8 Hrs.	0.0	-	Trace	Trace	-
Conductivity (microamps)					
● Initial	135	135	155	125	105
● 1 Wk. at R.T.	145	145	195	135	-
● 1 Wk. at 140°F	150	2950	4850	2050	-
● 1 Wk. at -65°F	145	135	175	135	-
● 30 Days at R.T.	255	345	525	205	-
● 90 Days at R.T.	-	850	1350	-	-

TABLE 26
EFFECT OF WATER AND UREA ON THE PROPERTIES OF 7063 AT REDUCED EMULSIFIER LEVEL (HLB 12)

	Weight Percent		
	1	2	3
Formamide	-	2.25	1.75
20% Urea-Formamide	1.75	-	-
Span 80	0.21	0.21	0.21
Tween 80	0.54	0.54	0.54
JP-4	97.0	97.0	97.0
H_2O	0.50	-	0.50
Properties			
Yield Stress (dynes/cm^2)			
● Initial, R.T.	1950	1725	1600
● After 1 Week at R.T.	1050	1050	1200
● 1 Wk. at 140°F	1325	580	930
● 1 Wk. at -65°F	1900	1125	1550
● 30 Days at R.T.	1450	900	1300
● 90 Days at R.T.	1400	-	1200
Stability			
● Vibration (wt. % separation)			
- 1/2 Hr.	0.0	0.0	0.0
- 1 Hr.	Trace	0.0	0.0
- 3 Hrs.	Trace	Trace	0.0
- 4 Hrs.	Trace	Trace	0.0
Conductivity (microamps)			
● Initial	95	125	155
● 1 Wk. at R.T.	165	135	195
● 1 Wk. at 140°F	1350	2050	4050
● 1 Wk. at -65°F	108	135	165
● 30 Days at R.T.	450	205	450
● 90 Days at R.T.	1150	-	1250

The data in Table 27 show the effect of urea and water on 7063-type emulsions when the emulsifier level is 1%. The addition of urea to these emulsions generally increases the yield stress of the emulsions and decreases the degree to which the disperse phase is dispersed, as evidenced by lower emulsion conductivity. This manifests itself in terms of poorer vibration stability for the 7063-type emulsions containing urea than for those which do not contain urea. As was found for the 7063-type emulsions that did not contain urea and which contained 1% emulsifier, water tends to decrease the vibrational stability of these emulsions.

CONCLUSIONS

On the basis of these studies, it is concluded that the optimized formulation of 7063 emulsion would consist of the following formulation:

	Wt. Percent
JP-4	97.0
Formamide	2.0
Emulsifier (Span 80 and Tween 80 blended to HLB 12)	1.0

No further studies were carried out on this formulation because the emulsifiers (Span 80 and Tween 80) are much more expensive than those used in the 7165-type formulations. In addition, previous studies showed that the 7063 formulations are inherently less stable than are the 7165 formulations, and our optimization studies failed to show that this could be reversed (Reference 9).

The studies on 7063 showed that urea, while it increased the equilibrium yield stress, also decreased the mechanical stability of the emulsion, whether water was present or not. Further, the ratio of continuous phase to emulsifier at the 97% internal phase level appears to be more important than whether these emulsions (7063) contain water. A ratio of at least 2:1 appeared to be necessary for acceptable overall emulsion stability.

TABLE 27
EFFECT OF WATER AND UREA ON THE PROPERTIES OF 7063-TYPE EMULSIONS (HLB 12)

	Weight Percent				
	1	2	3	4	5
Formamide	-	-	-	-	2.0
20% Urea-Formamide	2.0	1.75	1.5	1.5	-
Span 80	0.28	0.28	0.28	0.28	0.28
Tween 80	0.72	0.72	0.72	0.72	0.72
JP-4	97.0	97.0	97.0	97.0	97.0
H_2O	-	0.25	0.50	0.50	-
Properties					
Yield Stress (dynes/cm^2)					
• Initial, R.T.	2050	1750	1755	2500	1500
• After 1 Wk. at R.T.	2300	1200	1375	1450	1125
• 1 Wk. at 140°F	760	1000	1125	1350	780
• 1 Wk. at -65°F	1050	1725	1950	2185	1385
• 30 Days at R.T.	1200	1450	1450	1435	950
• 90 Days at R.T.	1400	930	1700	2175	-
Stability					
• Vibration (wt. % separation)					
- 1/2 Hr.	0.0	0.0	-	-	0.0
- 1 Hr.	0.1	Trace	0.1	7.1	0.0
- 3 Hrs.	-	Trace	-	-	0.0
- 4 Hrs.	1.7	0.57	4.0	-	0.0
Conductivity (mciroamps)					
• Initial	75	85	95	115	135
• 1 Wk. at R.T.	98	75	95	145	145
• 1 Wk. at 140°F	650	8500	900	1150	2150
• 1 Wk. at -65°F	65	78	78	95	145
• 30 Days at R.T.	155	250	300	375	255
• 90 Days at R.T.	385	550	650	850	-

IV. COMBUSTION STUDIES

INTRODUCTION

After comparing the physical appearance of liquid JP-4 with that of emulsified JP-4 and their extremely different burning intensities during aircraft crash tests, an observer might raise the following questions. What is the combustion efficiency of the emulsion? Does it present any handling or storage problems? Is it fully compatible with present-day fuel control and management systems?

The objective of this part of the optimization program is to evaluate the effect of various emulsion properties on the combustion behavior of these emulsified fuels. This part of the report will therefore deal only with those aspects of the problem associated with the combustion of these fuels. The safety characteristics, fuel system compatibility, and storage behavior of various types of emulsified JP-4 are reported elsewhere (References 4,5,7,9,10 and 11).

A safe fuel emulsion is one which combines the greatest margin of safety with the highest combustion efficiency. Both of these criteria depend upon the ease with which the fuel emulsions can be broken or separated into their original phases. Although these criteria are seemingly contradictory, it must be remembered that the magnitudes of the shearing forces which cause the phase separation during an aircraft crash as compared to the shearing of the emulsion in a pressure-atomizing spray nozzle are quite different. Since the shearing force of a pressure-atomizing nozzle typical of the type used in operational engines is much higher than that usually obtained during the rupture of a fuel tank, it seem possible to formulate a high-yield-stress emulsion which can be broken, almost completely, by a spray nozzle but which remains relatively unbroken during a tank rupture.

The fuel emulsions selected for evaluation in both the combustion and rheology tasks are shown in Table 28. These emulsions all contain 97% internal phase (JP-4) and varying percentages of emulsifying agents, corrosion inhibitors, and continuous phase. As a result of these variations, the yield stress and the conductivity of the fuel emulsions were varied from 875 to 2100 dynes/cm^2 (after 30 days' storage) and 110 to 750 microamps, respectively. Thus, the emulsions evaluated in the combustion and rheology effort differed quite widely; therefore, the information generated should be generally applicable to the class of fuel emulsions containing 0.5% or less water.

Since relatively little is known about the rheological and combustion behavior of emulsions, in an optimization study of this type, it becomes necessary to prepare and test many different fuel formulations. Therefore, it is necessary to evaluate the rheological and combustion characteristics of each new fuel formulation in an inexpensive laboratory screening test device. It would be prohibitively expensive to evaluate the combustion efficiency of each candidate fuel in a full-size static rig. Another objection to full-scale evaluation is that partial breakdown of the fuel emulsion can occur in the fuel control system. Because of this, the rheological history of the fuel becomes uncertain by the time it is injected into the combustion chamber. Since the amount of fuel emulsion breakdown is dependent upon the fuel composition, nozzle size, pump speed, etc., the combustion efficiency results would be insensitive to small changes in fuel emulsion properties brought about by changes in emulsion composition. For these reasons, a laboratory-size combustion device resembling a typical straight-through-flow can combustor was used to study the effect of changes in fuel emulsion composition on combustion efficiency. The fuel system was designed such that no breakdown occurred until the emulsion was sheared in the swirl-type pressure-atomizing spray nozzle prior to atomization in the combustion chamber. With this technique, the only variables are the fuel emulsion formulation (constant 97% JP-4 internal phase concentration) and the shear which is controlled by the ΔP across the nozzle and nozzle size. Small changes in the combustion efficiency of different formulations, relative to neat JP-4, are thus reflected by the percentage of emulsion breakdown which controls the atomization and the mass flow characteristics of the fuel emulsion.

EXPERIMENTAL PROCESS

Combustor Design

In order to obtain realistic combustion data on emulsified fuels without testing them in a full-scale combustion system, a 2-inch tubular combustor (Figure 4) was designed and built for the laboratory studies. The 2-inch-diameter can, having an L/D of 2.5, is made of stainless (304) steel and is designed such that the total air mass flow is 214 pounds/hour. The primary and secondary air holes are sized to produce air inlet velocities of 15 to 40 ft/sec in the primary zone and about 150 ft/sec in the secondary zone.

The airflow is kept constant over the entire air/fuel range. The mixture ratio is changed by altering the fuel tank pressure. Ignition of the combustible mixture is initiated by a 10 kv spark which is located just above the face and about 60° off the axis of the nozzle. The pressure-atomizing swirl-type fuel nozzle is a domestic oil-burner type. The bulk of the results presented in this report were obtained with a 0.85 GPH nozzle which was equipped with a 75-micron Monel screen filter. The fuel spray angle was varied by using the appropriate angle nozzle. All these nozzles had the same flow capacity. A cross-sectional drawing of the nozzle is shown in Figure 5.

The combustor's air supply was derived from a diesel-driven compressor which had a capacity of 600 CFM at 125 psi. The air was filtered and dried prior to injection into the combustor. Figure 6 shows a schematic diagram of the air-fuel system. A 15-kw air heater was located

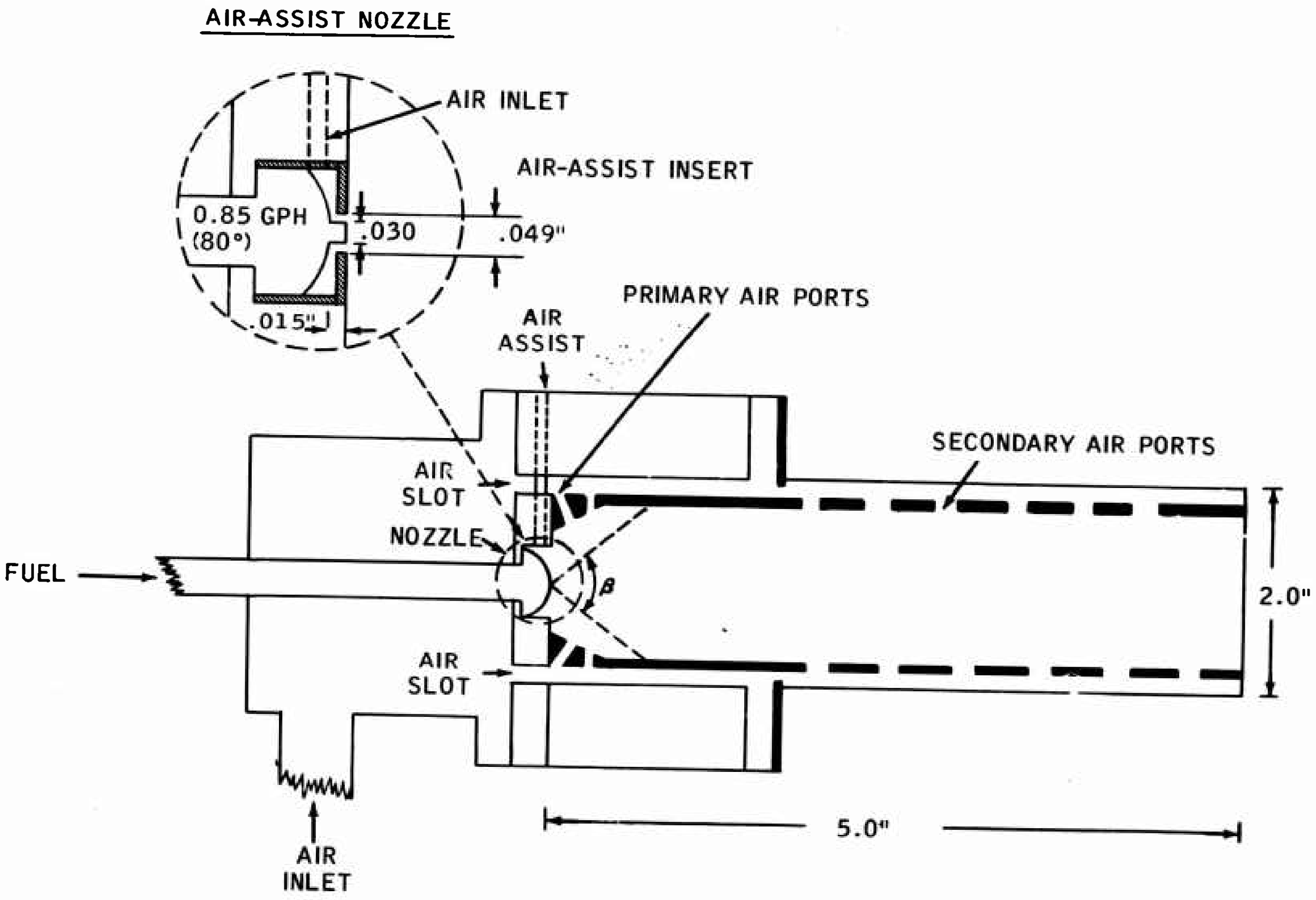
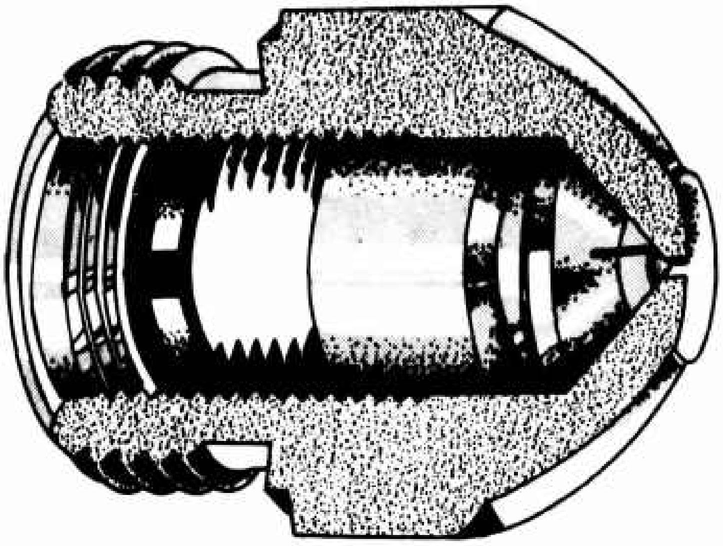


Figure 4. Laboratory-Size Can-Type Combustor.



NOZZLE DIMENSIONS

CAPACITY (GPH)	ORIFICE DIAMETER (IN.)		SLOT DIMENSION (IN.)
0.85	.010	.030" LONG	.008 X .008
1.75	.016		.008 X .008
2.50	.018		.008 X .008

Figure 5. Pressure Atomizing Swirl Nozzle.

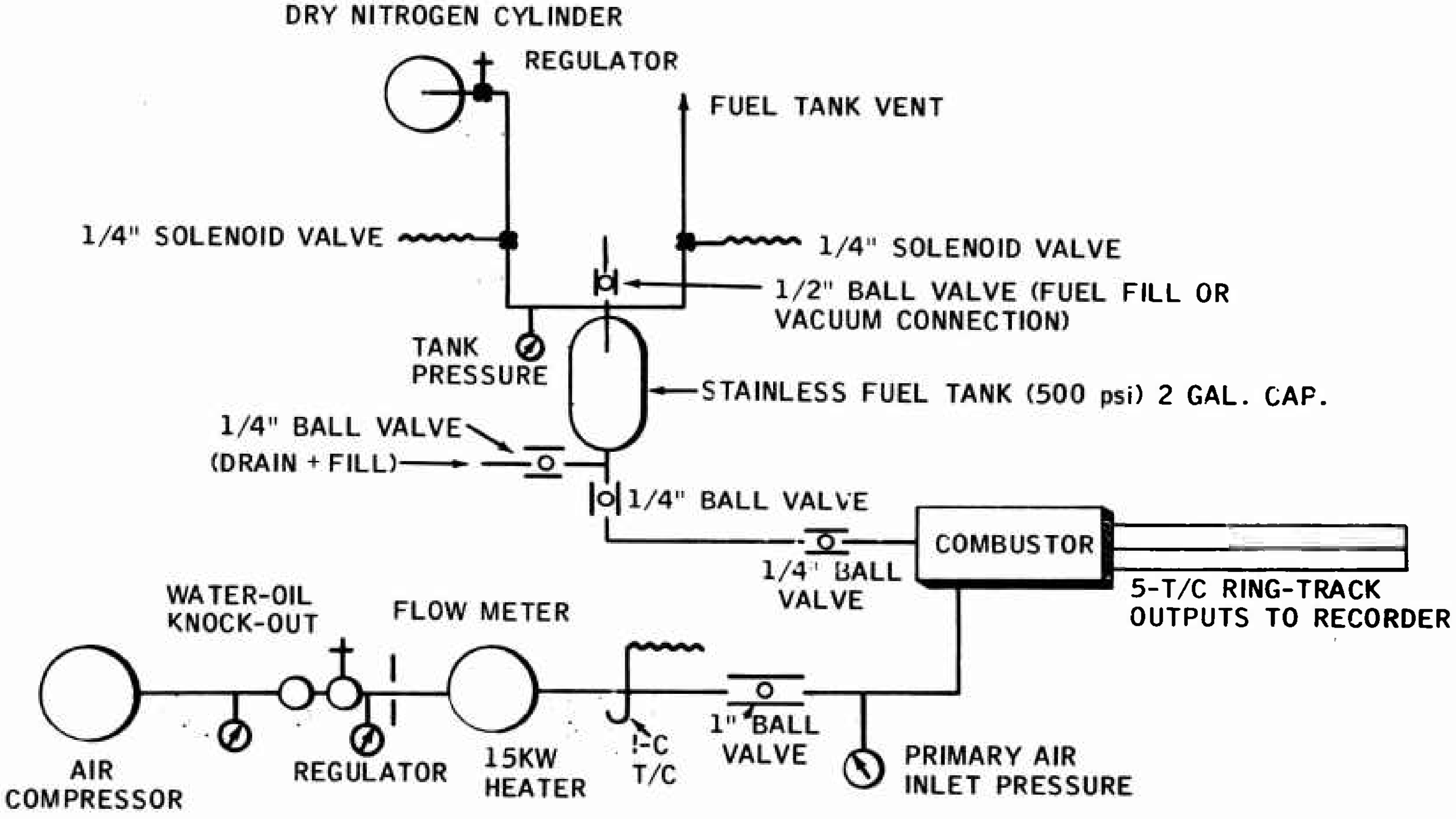


Figure 6. Plumbing Schematic of Air/Fuel Systems.

in the main air supply just upstream of the injector. The air mass flow was controlled by a throttling valve upstream of a high-volume-flow rotometer. Pressures were observed on bourdon-type gauges; the air, fuel, and exhaust temperatures were recorded on a 12-channel scanning strip-chart recorder.

Fuel System

The entire fuel system was made of type 304 stainless steel. The 2-gallon-capacity tank had a maximum working pressure of 500 psi. The fuel flow was controlled by stainless steel ball valves which had Teflon seats and seals. All valves were remotely operated either by electric solenoids or pneumatic actuators. The fuel was forced out of the bottom of the tank by a dry nitrogen pressure head over a range of 0-500 psi. One-quarter-inch O.D. tubing carried the fuel to the spray nozzle. Great care was taken in the design of the fuel system to insure against breakdown of the fuel prior to its arrival at the spray nozzle. The emulsified fuel was loaded into the tank by partially evacuating the tank from the top with a low-capacity vacuum pump. The fuel was then sucked out of its glass container through the bottom of the tank with a polyethylene tube. The ΔP between the tank and atmosphere was kept at about 5 psi in order to minimize the shearing forces in the fuel transfer system. After the fuel tank was filled, a fuel sample was taken at the entrance to the spray nozzle by "breaking into" the one-quarter inch line. A slight head pressure was applied to the tank, and a 50-gram sample was collected in a glass beaker. If any phase separation had occurred during the transfer process, it would have been observed in the sample. No separation was ever observed during the transfer process. It was desirable to have all emulsion breakdown occur in the nozzle. Therefore, in all tests, only the effectiveness of the nozzle to break the emulsion down is thus being evaluated.

The fuel mass flows were calibrated by the time-weight method. Emulsion breakdown, induced by the shearing forces of the nozzle, was determined by collecting the emulsion spray in a glass beaker and weighing the liquid and solid phases. Each calibration point was performed in triplicate, and the average values were recorded over a 0-500-psi pressure range.

Air-Assist Fuel Nozzle

During the course of combustor design optimization it was found for one particular configuration that poor mixing in the primary zone could be greatly improved by the use of an air-assist spray nozzle. The air mass flow through the nozzle annuli was about 1 percent of the total. Observation of the atomized spray pattern with and without the air-assist indicated that a substantial increase in mixing and atomization was obtained. During a combustion test, it was observed that a dramatic increase in combustion efficiency (15%) was obtained with WSX-7165-4 emulsion. The insert shown in Figure 4 illustrates the assembled air-assist nozzle. Emulsion breakdown studies performed with this nozzle showed that the air-assist had no effect on the percentage of emulsion breakdown. A subsequent change in the design of the primary combustion zone alleviated the mixing problem; as a result, no further work was done with the air-assist nozzle. The data presented in this report were obtained with a pressure-atomizing nozzle.

Fuel Properties

During this program, six different emulsified fuels were evaluated with respect to breakdown characteristics and combustion efficiency relative to neat JP-4. Table 28 summarizes the composition and pertinent properties of these fuel emulsions. The measured yield stress values (performed with a cone penetrometer) which most closely correspond to the state of the emulsions at the time of testing appear in the row labeled "Yield Stress (1 mo.)". Since the yield stress of the emulsion changes with age, it is most important to determine the stress prior to testing. All of the emulsions were prepared in the laboratory in 1-gallon batches and then stored in glass containers until ready for testing. JP-4 taken from the same source was used in all of the emulsions. This same JP-4 was also used in the combustion tests to compare its performance to that of the fuel emulsions.

TABLE 28
EMULSION FORMULATIONS EVALUATED IN
THE RHEOLOGY AND COMBUSTION PROGRAMS

	Emulsion Formulations (Wt Percent)					
	7165	7165-A1	7165-A2	7165-A3	7165-4	7063
JP-4	97.00	97.00	97.00	97.00	97.00	97.00
ENJ-5728	0.25	0.40	0.40	0.20	0.20	-
Atlas-IL851	0.75	0.60	0.60	0.30	0.50	-
Urea	0.40	0.40	0.40	1.75	2.00	-
Formamide	1.60	1.60	1.60			1.50
Hydrazine Salt*	-	-	0.10	-	0.10	-
DDSA-Li*	-	0.10	-	-	-	-
H_2O*	0.50	0.50	0.50	0.75**	0.50	-
SPAN-80	-	-	-	-	-	1.50
TWEEN-80						
	100.50	100.60	100.60	100.00	100.30	100.00
Yield Stress (fr.)	2700	3200	3120	3250	2800	2900
Yield Stress (1 wk.)	1500	1920	1725	1800	1525	2200
Yield Stress (1 mo.)	1450	1875	2100	875	1325	1525
Current (μA)	110	195	205	750	295	110

* By wt. of emulsion.

** Percent of emulsion.

Temperature Measurements

All of the flame and combustor can skin temperature measurements were made with 1/16-inch-diameter, thin-walled, stainless steel sheath chromel-alumel thermocouples. The temperatures were recorded on a 12-channel, scanning, strip-chart recorder. The flame tube outside wall temperature was monitored at two locations in the secondary zone. Profiles of the exhaust gas temperatures were obtained with a 5-thermocouple ring which held the equally spaced thermocouples at 1/4-inch radial increments from the exhaust center line. The thermocouple ring was mounted on an optical bar which was parallel to the longitudinal axis of the flame. A small, low-RPM electric motor and cable arrangement permitted the ring to scan the entire length of the visible exhaust flame, which was about 8 inches long.

RESULTS AND DISCUSSION

In the past, other researchers have looked at the combustion characteristics of emulsified fuels (Reference 11) in a variety of configurations and under different test conditions. But as far as is known, the present work is the first concentrated effort to determine the combustion properties of a wide range of emulsified fuel formulations, and their atomization and breakdown behavior, all in the same system operating at constant test conditions. With this approach, the only variable in the system is the rheological property of the fuels. As will be shown later, this method produces changes in the combustion efficiency data which are indicative of the emulsion's formulation and rheological properties.

After many flow tests with various emulsions and different capacity pressure-atomizing nozzles, a 0.85 gallon per hour (GPH) capacity nozzle was selected for use in all of the combustion and mass flow tests. This choice was dictated by the fact that only in this nozzle were all of the fuel emulsions broken down to a relatively high degree. In addition, this nozzle permitted the proper mass flow rate to be attained over practical ranges of fuel tank pressures and air/fuel ratios. The curves shown in Figures 7 and 8 summarize the mass flow measurements as a function of nozzle ΔP. Figure 9 illustrates the effect of emulsion yield stress on the breakdown characteristics of the fuel emulsions. Of special interest in Figure 10 are the curves for 7165-A2 and 7165-4; these particular emulsions contain a small percentage of a hydrazine salt corrosion inhibitor. Comparison of both formulae in Table 28 also shows that the emulsifier concentration of 7165-A2 is 1% compared to 0.7% for the 7165-4 system. The high yield stress of the 7165-A2 system as a result of the increased emulsifier level has an adverse effect on the breakdown characteristics of the emulsion. The mass flow curve of 7165-A2 is also observed to be higher relative to the other emulsions, as a result of the presence of the corrosion inhibitor. The magnitude of this effect, which is attributed to the corrosion inhibitor, is most obvious in the curve for 7165-4, which has the same concentration of corrosion inhibitor but a reduced emulsifier level. As a result, the atomization of the 7165-4 emulsion in nozzles having orifice diameters of .016 inch and .018 inch was not possible. The emulsion

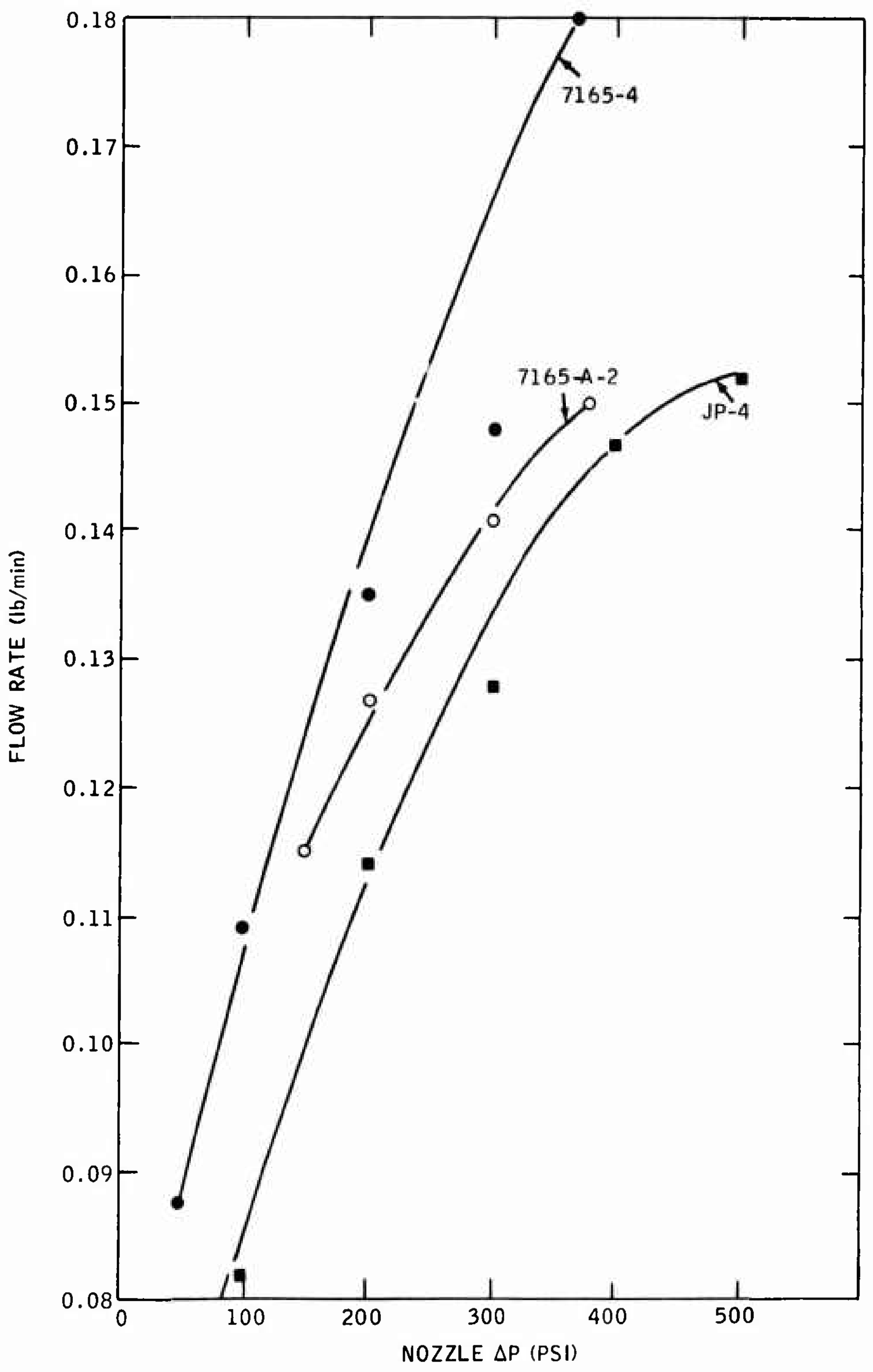


Figure 7. Emulsion Flow Rate Through a Nozzle (0.85 GPH Capacity at 80°F) Vs. Pressure Drop (The Nozzle Contained a 75 μ Filter Screen).

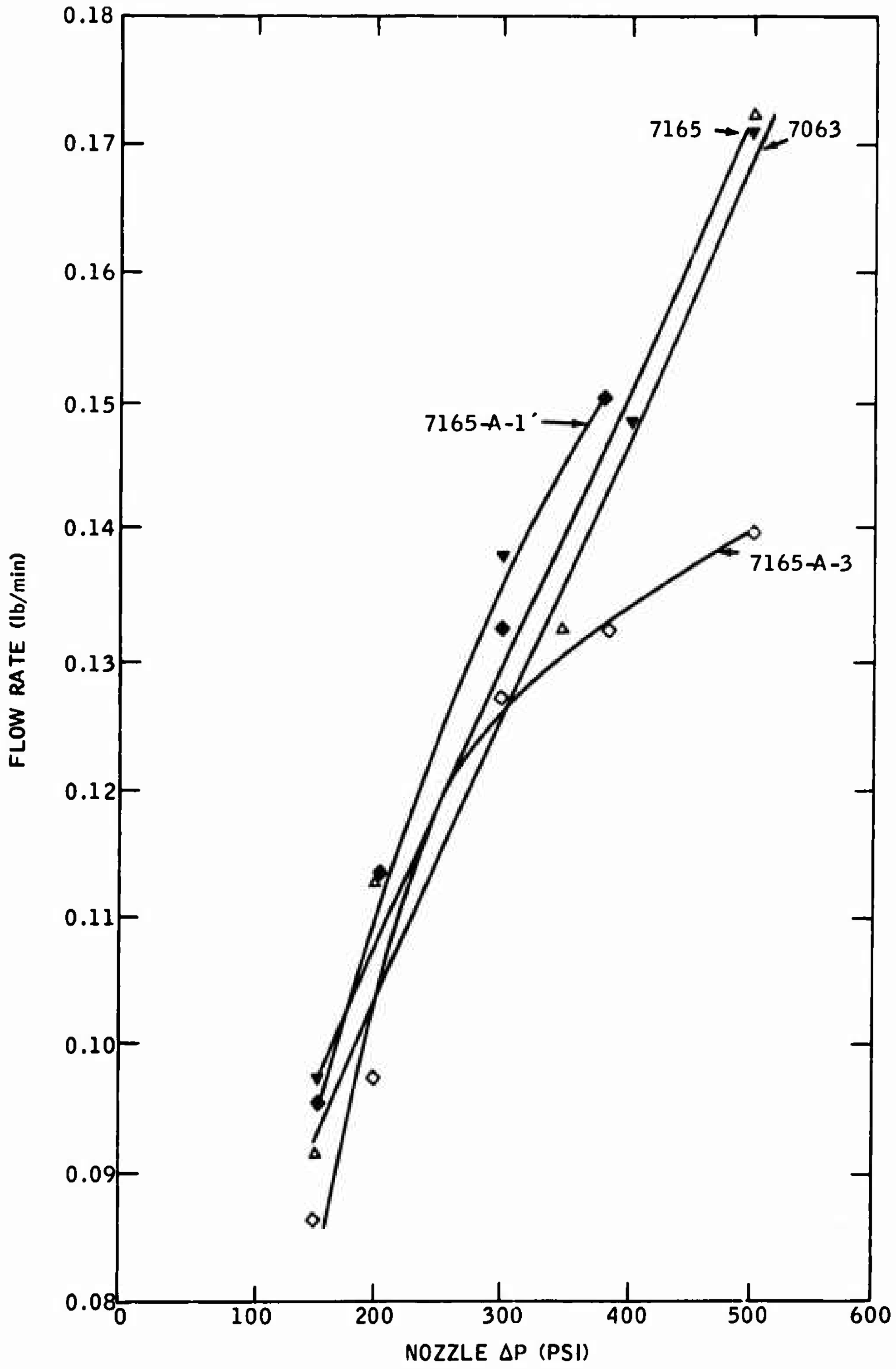


Figure 8. Emulsion Flow Rate Through a Nozzle (0.85 GPH Capacity at 80°F) Vs. Pressure Drop (The Nozzle Contained a 75 μ Filter Screen).

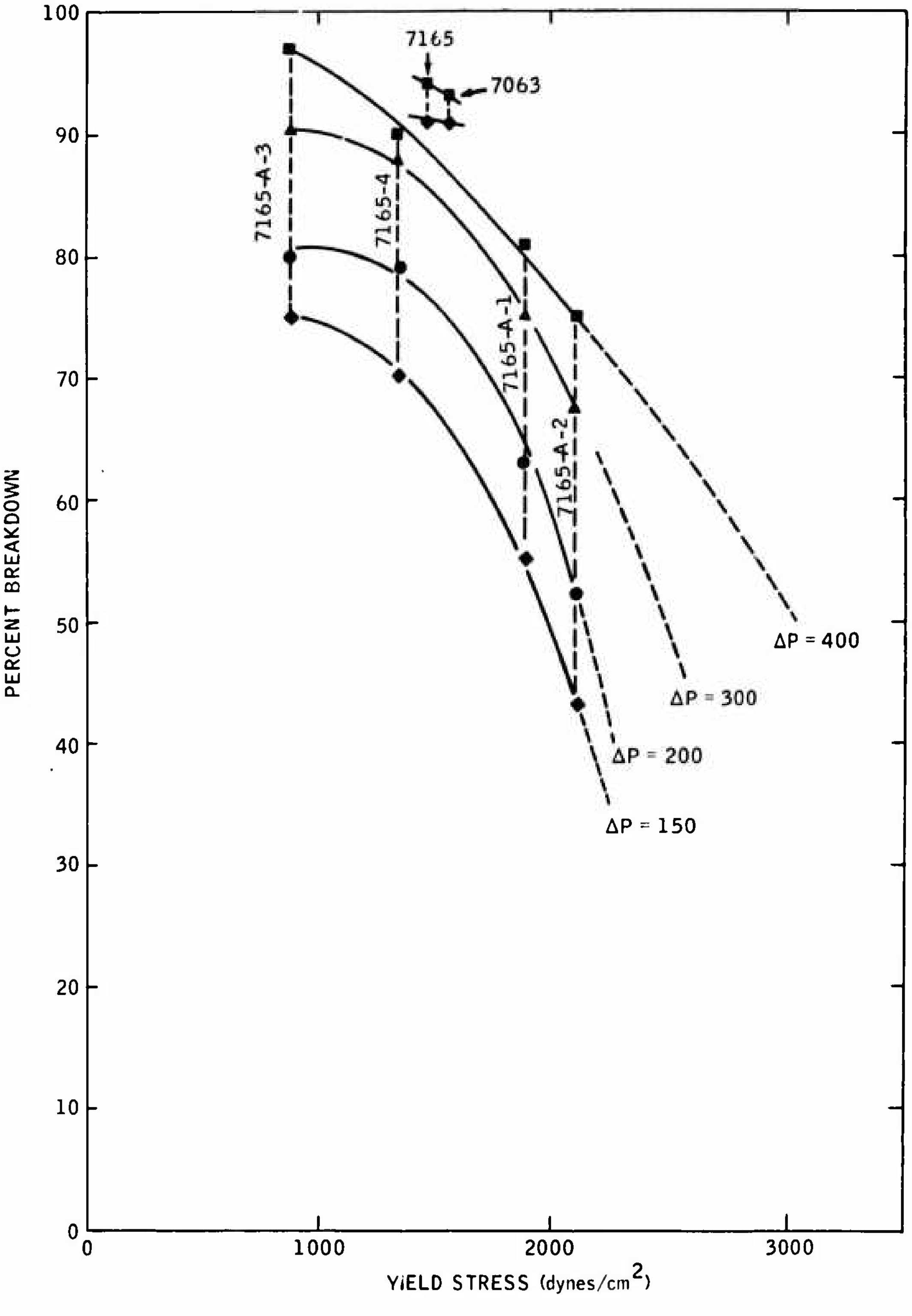


Figure 9. Phase Separation of Emulsions Through Nozzle (0.85 GPH Capacity) Vs. Emulsion Yield Stress.

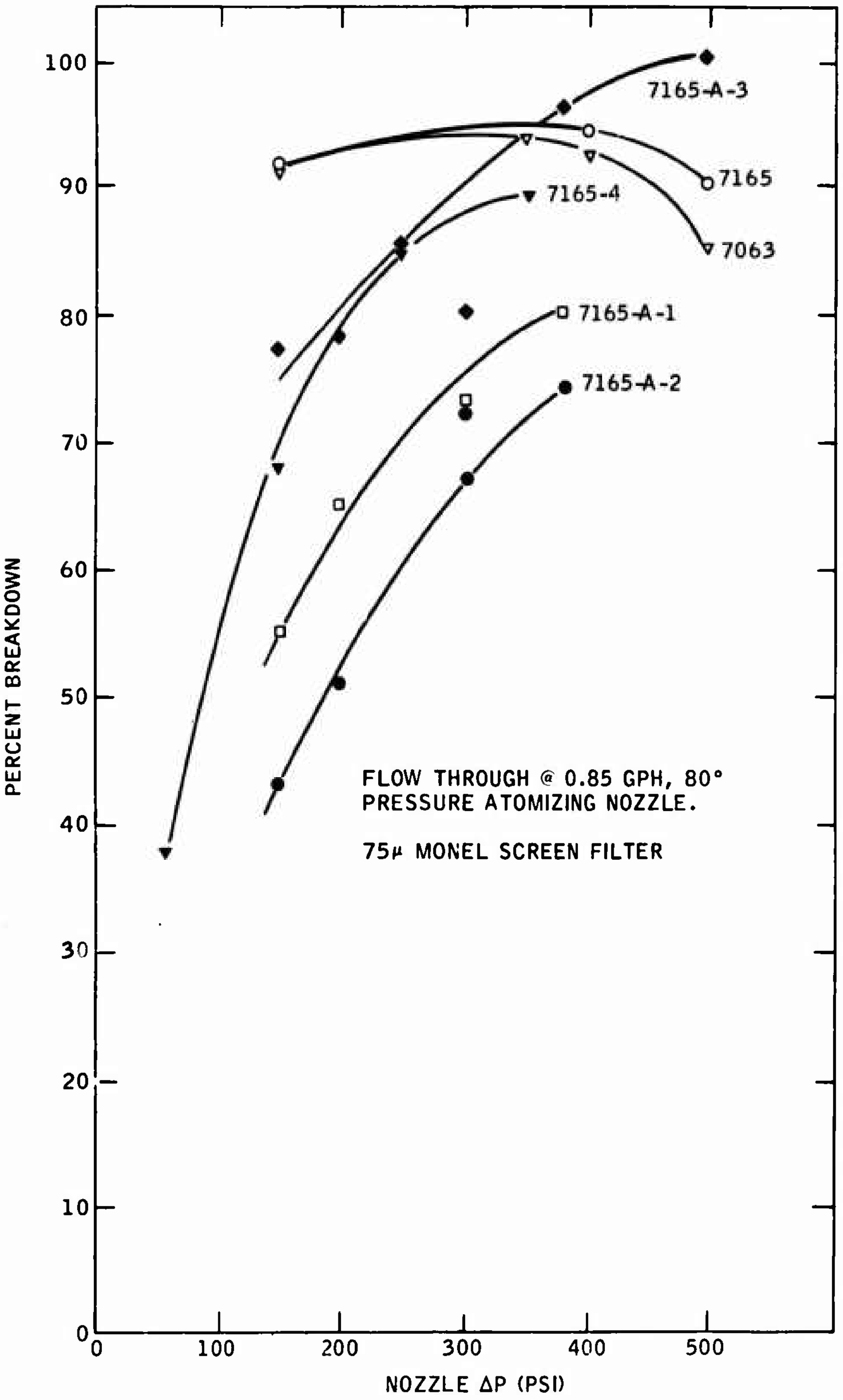


Figure 10. Effect of Atomization Pressure on Breakdown of Emulsion.

was observed to be slightly broken, but the effluent was a straight, unbroken rod for a nozzle ΔP of 30-100 psi. However, this emulsion was efficiently broken in a nozzle having a .010 inch orifice over a ΔP range of 100-400 psi. From these data, it is evident that the interfacial film which exists between adjacent fuel droplets has been substantially strengthened. Plug-flow and "slippage" of the 7165-4 emulsion in the swirl chamber* of the .016 inch and .018 inch orifice nozzles result in less turbulence being imparted to the fuel and in nonatomization at low-nozzle pressures. A cross section of the nozzle and pertinent dimensions are illustrated in Figure 5.

The emulsion breakdown data for four of the emulsions are plotted in Figure 9. Emulsions having yield values greater than 1500 dynes/cm^2 (after a 1-month relaxation period) are, as would be expected, more difficult to break down. This is in agreement with our initial premise; i.e., other things being equal, a high-yield-stress fuel emulsion is a safer fuel.

The combustion efficiencies (Figure 11) of six emulsions relative to pure JP-4 were determined by comparing their gas temperatures at the exit plane of the combustor. Exit temperatures varied from 1200° to 2000°F depending on the air/fuel ratio. In order to assure ourselves that the combustor was operating properly with JP-4, a complete temperature profile of the exhaust stream was obtained over an air/fuel ratio range of 10-20. The temperature was observed to peak at a mixture ratio of about 15, and no hot spots were measured in the stream. The combustion efficiencies of the emulsions were then obtained with the same fuel nozzle and air-to-fuel mass flows which corresponded to the conditions which existed during the pure JP-4 runs. Since the airflow velocity and mass flow remained constant throughout the entire test sequence, the mixing within the primary zone of the combustor was dependent upon the rheological properties of each fuel. All of the emulsions burned with an orange-red flame over the entire air/fuel ratio range examined. The pure JP-4 exhaust flames exhibited their characteristic blue-white color in the lean mixture region and a yellow white color in rich mixtures. The mass flows for the emulsions did not take into account the fact that 3 weight percent of the fuel was not JP-4. It was therefore expected that the air/fuel mixture ratio-exit temperature curves would be slightly shifted toward the lean side relative to that for pure JP-4.

With an 80 degree spray angle nozzle all of the emulsions except 7165-A2 exhibited relatively high combustion efficiencies. However, when the spray angle was changed to 45 degrees, all of the emulsions except the 7165 and 7063 types exhibited higher exhaust temperatures due to improper mixing patterns in the primary zone. The flames increased in length, and large fuel droplets appeared intermittently. The data presented in Table 29 illustrate the effects of spray angle on combustion

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* The rifle slots in all of the nozzles discussed had the same dimensions (0.256 x 10^{-3} in.^{2} cross sectional area).

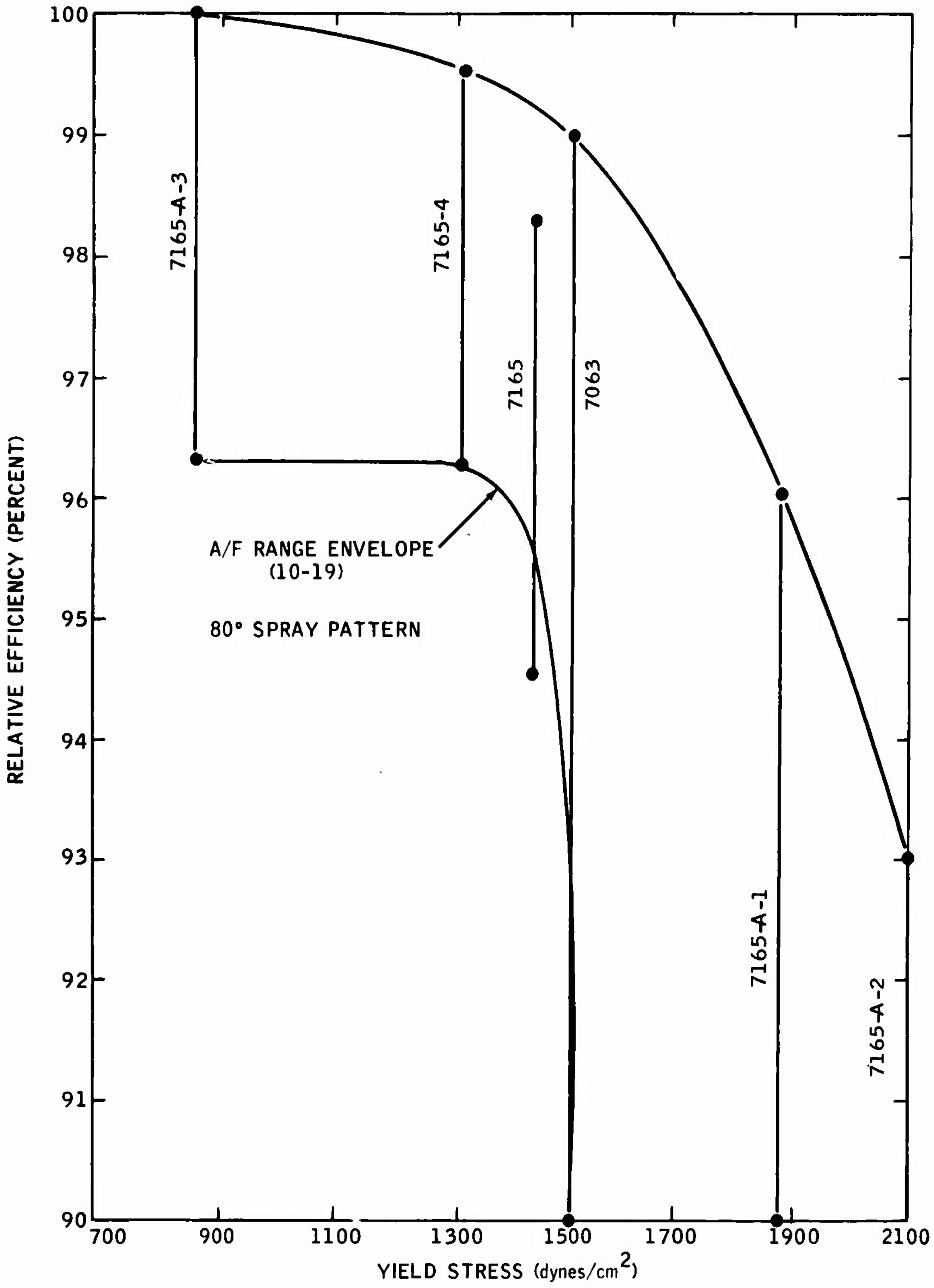


Figure 11. Relative Emulsion Combustion Efficiency Vs. Emulsion Yield Stress.

temperatures for all of the emulsions. Since the combustor was designed for an 80-degree spray angle, proper mixing in the primary zone was not achieved for all other angles. The temperature ratios given in Table 29 illustrate the trend that is to be expected when small spray angles are used.

TABLE 29
EFFECT OF SPRAY ANGLE ON
MAXIMUM CENTER-LINE EXHAUST TEMPERATURE

	Spray Angles			
Emulsions	45°	60°	70°	80°
7165	0.985	0.99	0.97	0.983
7063	0.99	0.96	0.98	0.99
7165-A1	1.05(1)	0.985	0.95	0.96
7165-A2	1.02(1)	0.95	0.975	0.93
7165-A3	1.005(1)	0.945	0.935	1.00
7165-4	1.06(1)	0.975	1.025*	0.955

* The exhaust flames were noticeably longer and of higher visible intensity.

CONCLUSIONS

It has been demonstrated that a wide variety of emulsified fuel formulations can be evaluated in a laboratory-scale can-type combustor equipped with a domestic oil burner pressure-atomizing nozzle. Emulsions possessing yield stress values of less than 1500 dynes/cm^2 burn as efficiently as pure JP-4 over the same air/fuel mixture range and fuel nozzle pressure range. Combustion is slow, as evidenced by high exhaust gas temperatures and the presence of burning fuel droplets, with fuel emulsions having a yield stress of >1500 dynes/cm^2.

More work needs to be done to determine the effect of nozzle spray angle on combustion efficiency, since in the present work the primary zone mixing patterns are greatly altered by varying the spray angle between 45 and 80 degrees. A trend toward longer combustion chambers has been observed for complete combustion of fuels being atomized by nozzles with narrow spray angles.

Two emulsion formulations, 7165 and 7063, which have respective yield stress values of 1450 and 1525 dynes/cm^2 exhibit very little dependence on nozzle pressure for attaining breakdown, once the yield stress of the emulsion has been reached. Over a ΔP range of 100-400 psi, the extent of breakdown is greater than 90%. The addition of corrosion inhibitors to the emulsions must be done with care, since it has been observed that the rheological and combustion properties of such fuels can be significantly changed as a result of strengthening the interfacial film. about the JP-4 droplets.

V. RHEOLOGICAL STUDIES

INTRODUCTION

The previous rheological studies on fuel emulsions (Reference 9) involved the atomization and flow behavior of WSX-7165 and WSX-7063 fuel emulsions from a capillary and engine nozzles. The purpose of the current study was to investigate the rheological behavior of optimized formulations of 7165 and 7063 and to compare their rheological behavior to that of JP-4 and emulsions WSX-7165 and WSX-7063. The specific objectives of this program were:

1. Determine where the emulsions break down--at the entrance, the inside, or the exit of the nozzle.
2. Determine the effect of aging the emulsions on their behavior in the nozzle.
3. Determine the effect of emulsion yield stress on their behavior in the nozzle.
4. Determine the relative drop size of the atomized fuel emulsions and JP-4.

EXPERIMENTAL PROCESS

Rheometer

The experimental setup used in this phase of the program is shown in Figure 12. The rheometer was designed to operate with small experimental quantities of the emulsion, 1 gallon or less. The so-called thrust part of the rheometer setup was eliminated and the capillary was rigidly mounted, since it was shown by our previous work (Reference 9) that the emulsions are not elastic under the conditions that were to be investigated in this program. The capillary was also enclosed in a Plexiglas box to minimize the fire hazards associated in working with finely atomized fuel sprays.

The jet emerging from the capillary was illuminated from the back with a flash unit which had a flash duration of 1/2 microsecond. The camera was rigidly mounted in front of the jet on a track which allowed the camera to be shifted along the length of the jet by more than a foot without changing the optics of the camera (Figure 12).

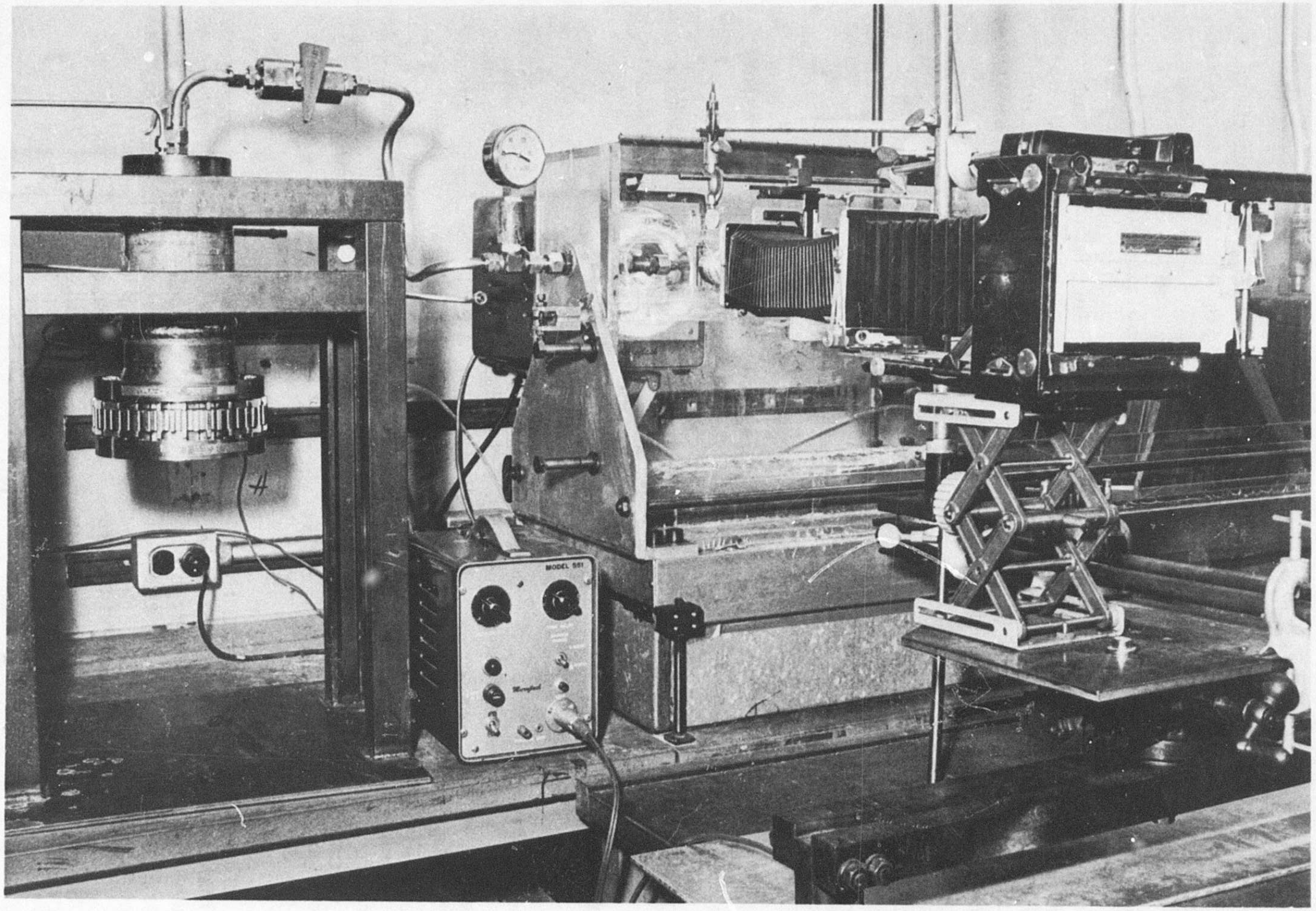


Figure 12. The Rheology Experimental Setup.

The initial pictures were made using an 11-millimeter focal length lens; however, it was found that whereas the pictures were quite good, the field of vision was too small (50X magnification). Therefore, in order to scan the length of the jet to observe its breakup, too many photographs would have been necessary. It was thus concluded that it would be best to use a 50-millimeter lens which produced an 11X magnification. This lens was therefore used throughout this program.

All investigations in this program were carried out using two special capillaries. The diameter of these capillaries was equivalent to the openings in the nozzle used in a standard turbine engine. All the openings in the nozzle measured 0.0115 inch in diameter and 0.033 inch in length. The capillaries were made from a hypodermic needle, which had a diameter of 0.0115 inch. One was cut down to a length of 0.033 inch to simulate a single opening of the nozzle. A second one was cut down to about 0.049 inch.

Nozzle Spray Droplet Size

The droplet size of the atomized fuel was determined by taking pictures of the spray atomized from the capillaries using the rheometer setup already described and shown in Figure 12. For droplet size analysis, the fuel was atomized at a pressure of 125 psig, and pictures of the spray were taken at a distance of 7.5 cm (3 inches) from the tip of the capillary. The breakup of all the fuels was rather complete at this distance.

Using the setup described, it was possible to measure particles no smaller than 15 microns. The particles were measured and counted by projecting the picture of the atomized spray onto a screen. The results are thus presented in terms of the percentage of those particles counted having the indicated size.

RESULTS AND DISCUSSION

The emulsions investigated in this phase of the program are shown in Table 30 along with the properties of the particular batches of these emulsions which were evaluated with respect to their rheology. It can be seen that these emulsions have widely different equilibrium yield stresses (800-1525 dynes/cm^2) and conductivities, as indicated by current flow (125 to 1250 microamps). These emulsions were thus selected for evaluation in this phase of the program because they are widely different. Therefore, the results of the evaluation should be quite general and applicable to other emulsions of this general type.

TABLE 30
EMULSIONS EVALUATED IN THE RHEOLOGY PHASE OF THE PROGRAM

	Weight Percent				
	7165	7165-A1	7165-A2	7165-A3	7063
JP-4	97.0	97.0	97.0	97.0	97.0
ENJ-5728	0.25	0.40	0.40	0.20	-
Atlas IL-851	0.75	0.60	0.60	0.30	-
Urea	0.40	0.40	0.40	1.75	1.5
Formamide	1.60	1.60	1.60		
Hydrazine Salt*	-	-	0.10	-	-
Li-DDSA*	-	0.10	-	-	-
H_2O*	0.50	0.50	0.50	0.75	-
Span 80	-	-	-	-	1.5
Tween 80					
	100.50	100.6	100.6	100.0	100.0
Properties					
Initial Yield Stress	3125	4500	3125	2500	2900
1 Wk. Yield Stress	1375	2250	1175	1300	2200
1 Mo. Yield Stress	1450	1350	800	980	1525
Initial Current (Microamps)	110	1150	175	85	105
Current (Microamps) After 1 Wk.	238	1250	285	175	125

* Based on wt. of emulsion

Throughput Versus Pressure

Using the experimental setup described, the atomization behavior of the five emulsions shown in Table 30 was investigated. Our initial investigations involved the evaluation of the relationship between throughput and pressure drop for these emulsions when atomized from capillaries. The results of these studies are summarized in Tables 31 and 32 along with the percentage of emulsion breakdown on atomizing the fuel emulsions at different pressures. Throughput versus pressure data for the emulsions are plotted in Figures 13 and 14, which show the square-root dependence of throughput on the pressure drop; the slope of the lines in Figures 13 and 14 is the required one-half.

These data are consistent with the results obtained previously (Reference 9) using a much larger capillary; the previous data are shown in the dotted curve in Figure 13. The deviation from the $P \sim M^2$ curve (linearity) was not observed in the current studies because even at the lowest shear rate levels (low pressures) investigated, the viscosity of the emulsion under these conditions is still small relative to the atomization pressure. This is due to the significant emulsion breakdown (76%) which occurred in the capillary used in the current study even at the low pressures. Therefore, the viscosity of the emulsion in the capillaries even at low pressures is more nearly that of JP-4 than it would be if the larger capillary were used (Reference 9).

Figures 13 and 14 (Tables 31 and 32) therefore show that the flow behavior of all the emulsions in the two capillaries under the conditions investigated is identical to that of JP-4. The reason for this is that under all the conditions investigated for both capillaries, the emulsions were broken down significantly (Tables 31 and 32).

Figures 15 and 16 (data in Tables 31 and 32) show the effect of atomization pressure on the breakdown of the emulsions in the two capillaries. At high atomization pressures (125 psig), the emulsions are broken down in excess of 50%. Further, if the length to diameter (L/D) of the capillary is 3:1 (Figure 15), the breakdown of the emulsions even at low pressures (60 psig) is greater than 50%. Even though 50% breakdown of the emulsion occurred at the low pressure (60 psig) using one of the capillaries (L/D=3), the degree of atomization of the emulsion was very poor (Figure 12). Only at an atomization pressure of about 125 psig are the fuel emulsions atomized to a degree approaching that of JP-4 (Figure 17). Because of this, difficulties in burning the emulsion at low atomization pressures are to be expected. This is consistent with what was concluded in the combustion phase of this program.

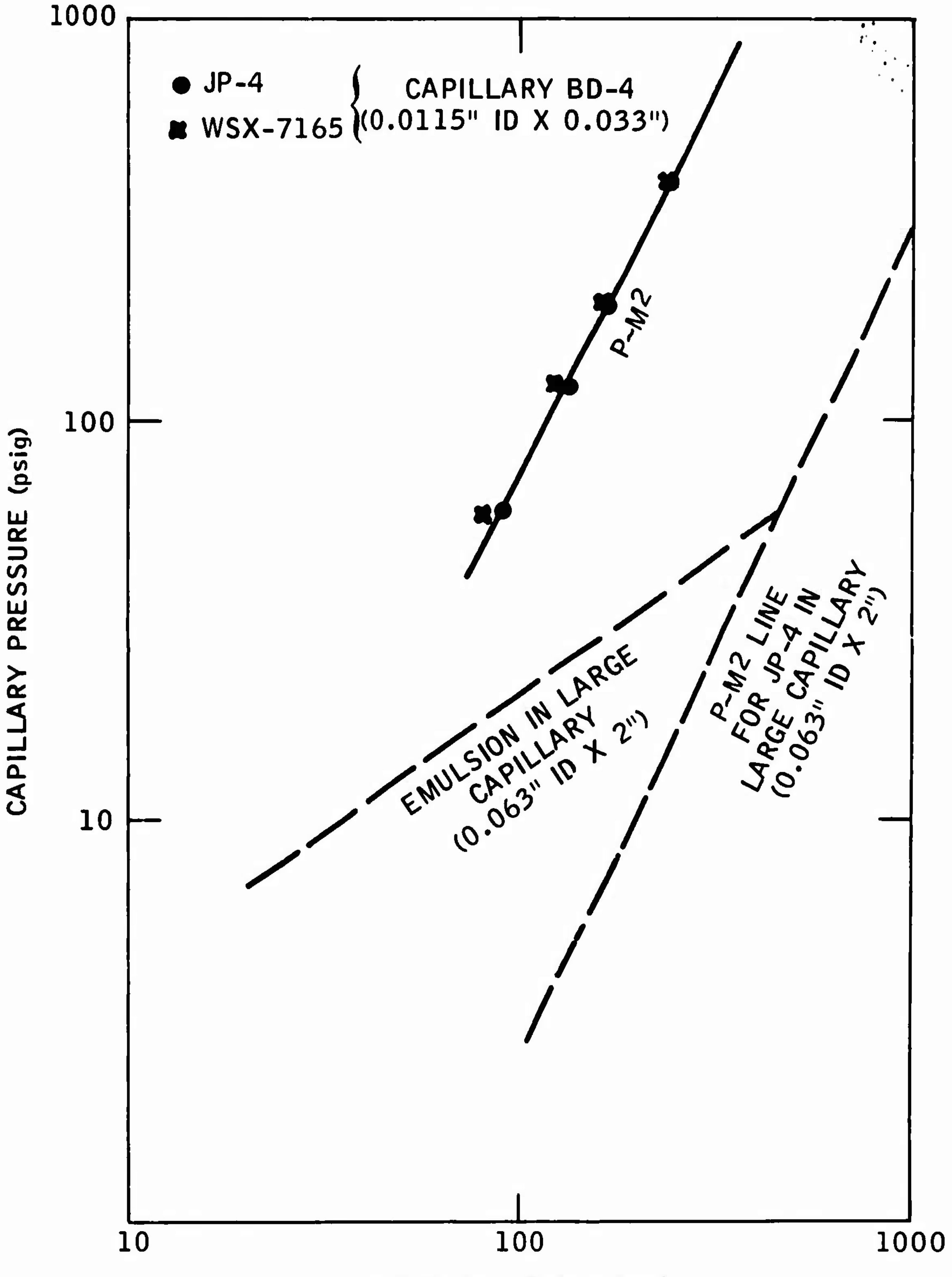


Figure 13. Relationship Between Throughput and Pressure Drop in a Capillary for JP-4 and WSX-7165 Emulsion.

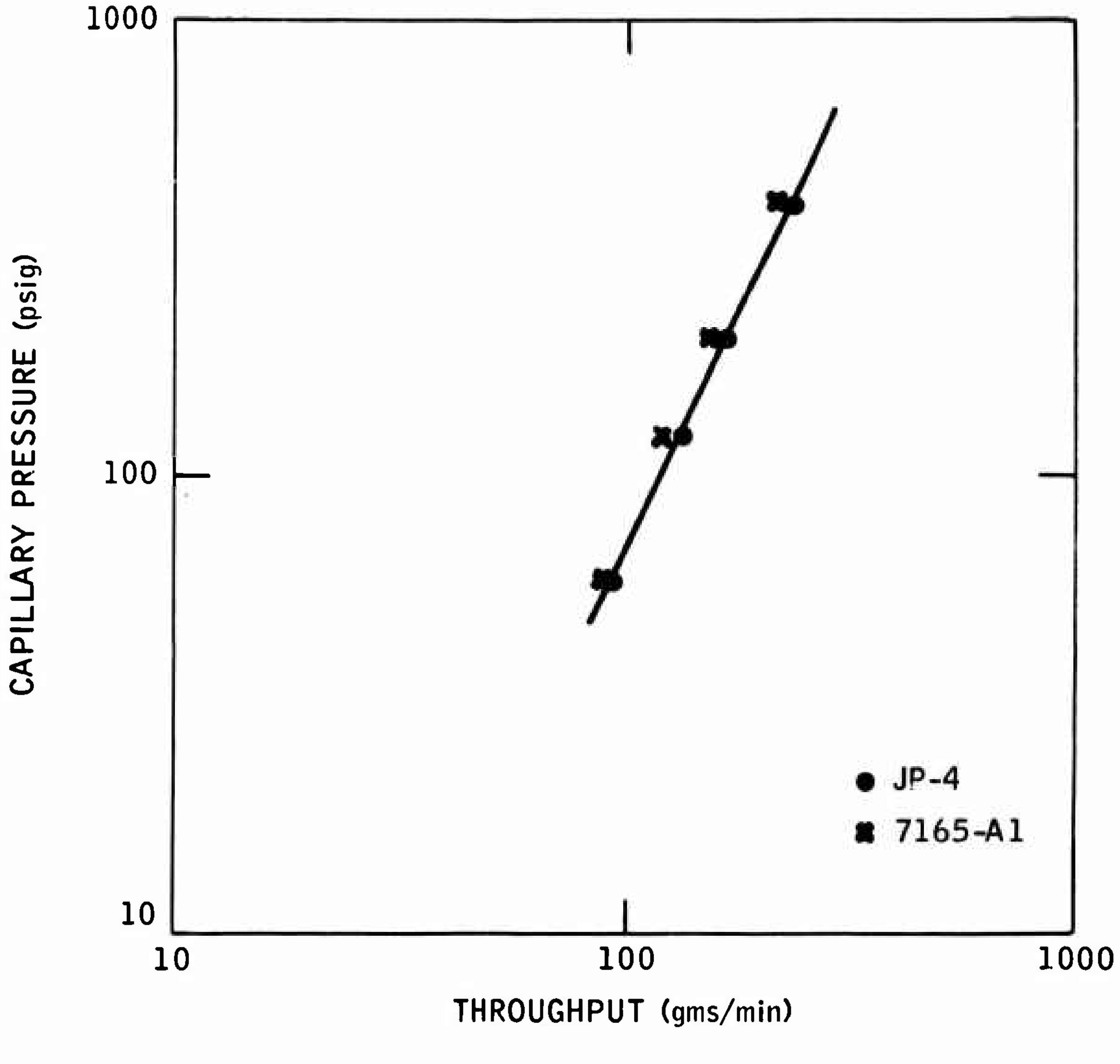


Figure 14. Relationship Between Throughput and Pressure Drop in a Capillary for JP-4 and 7165-A1 Emulsion.

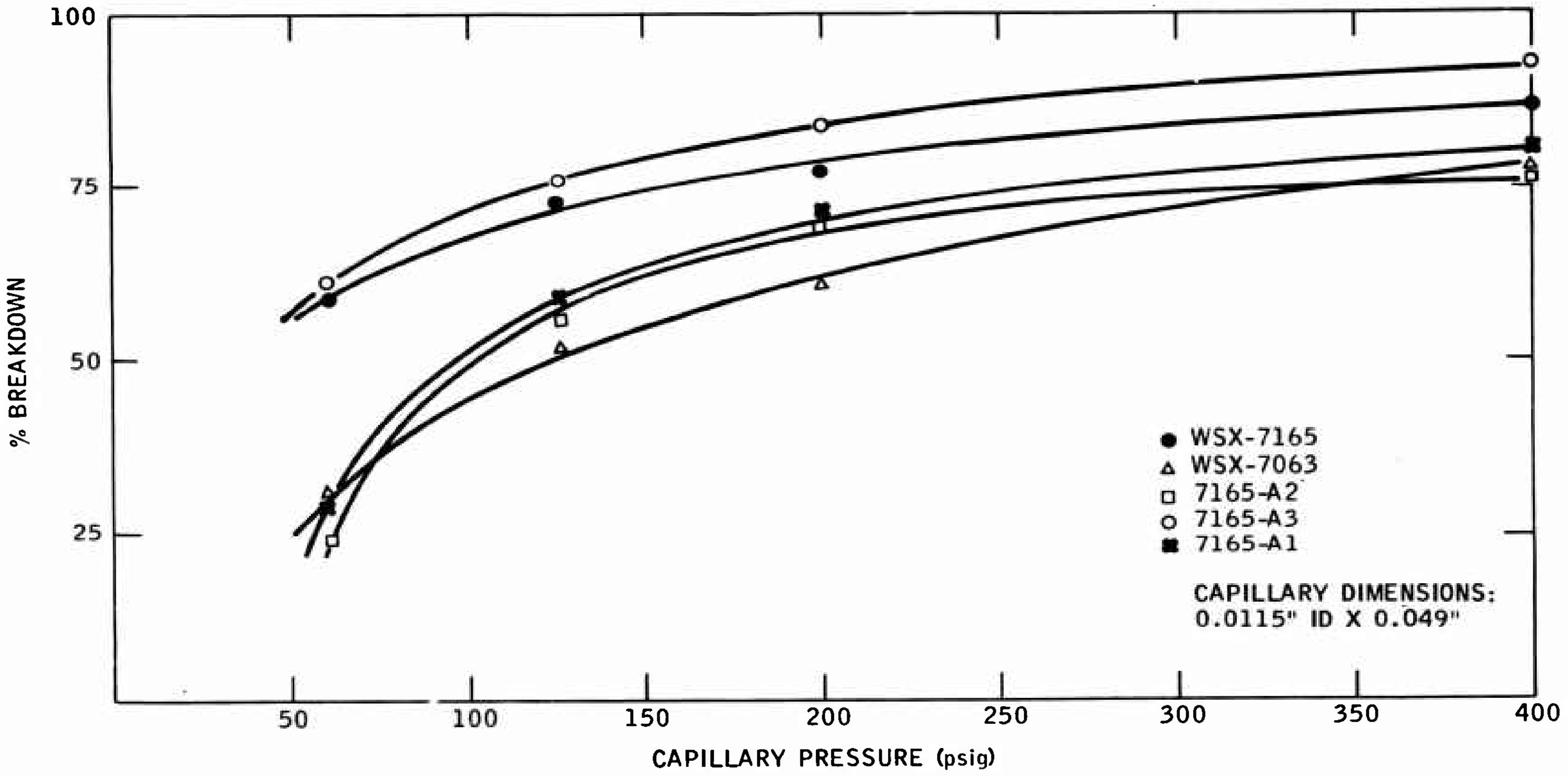


Figure 15. Effect of Atomization Pressure on Emulsion Breakdown in a Capillary.

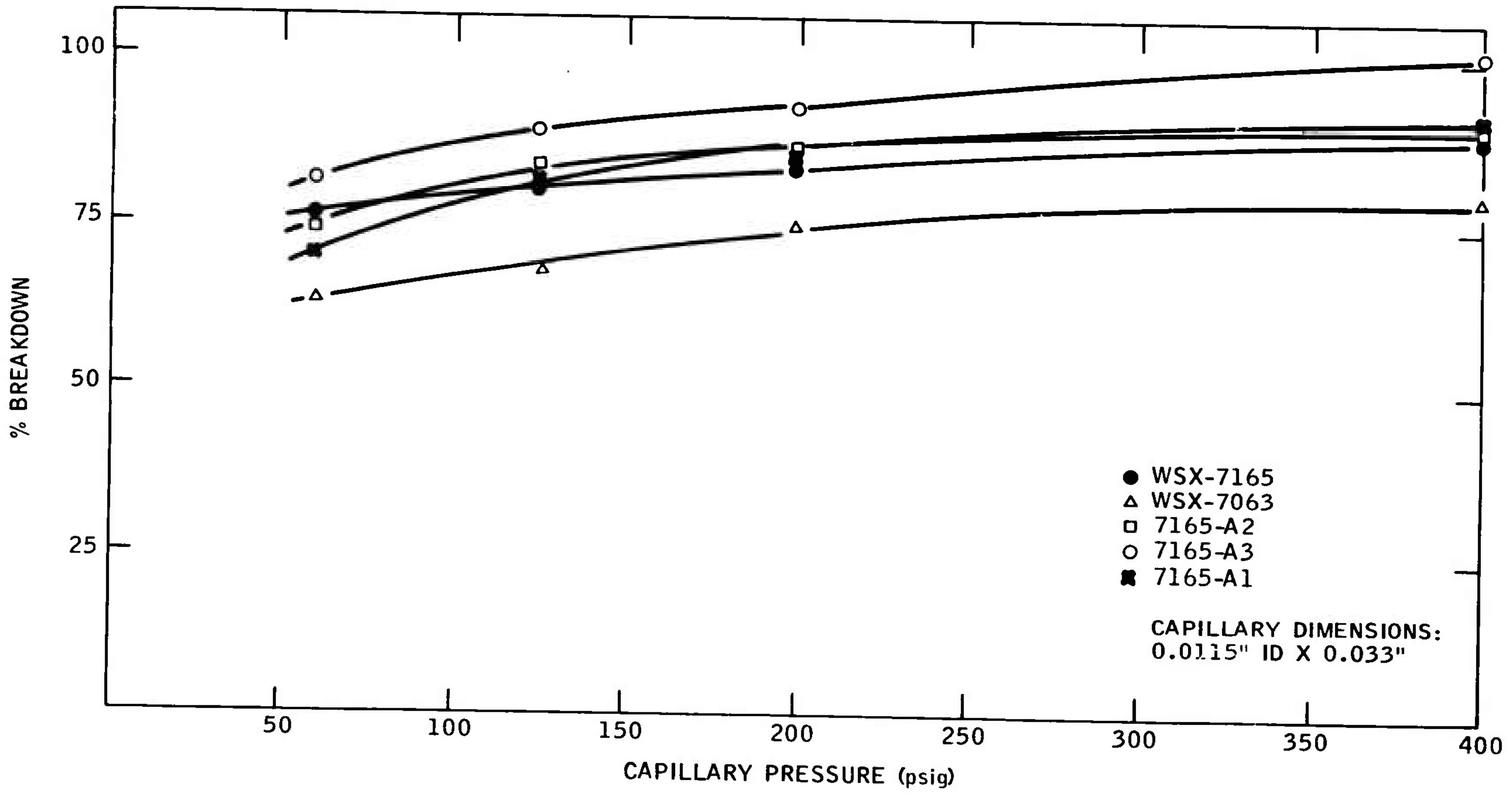
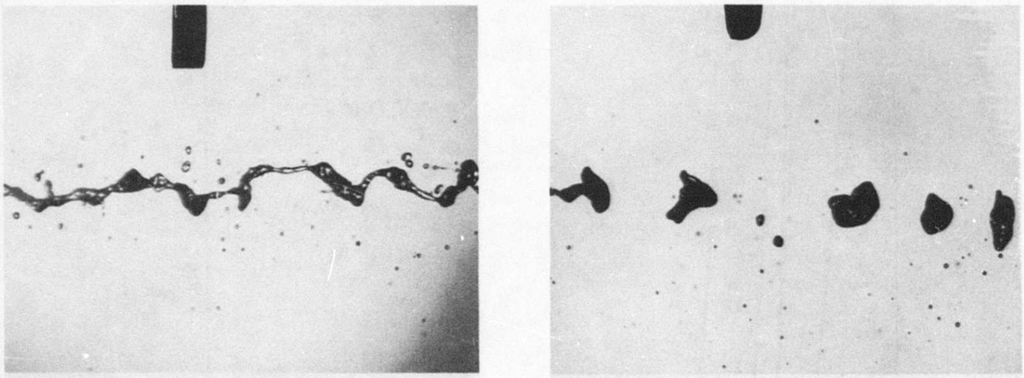
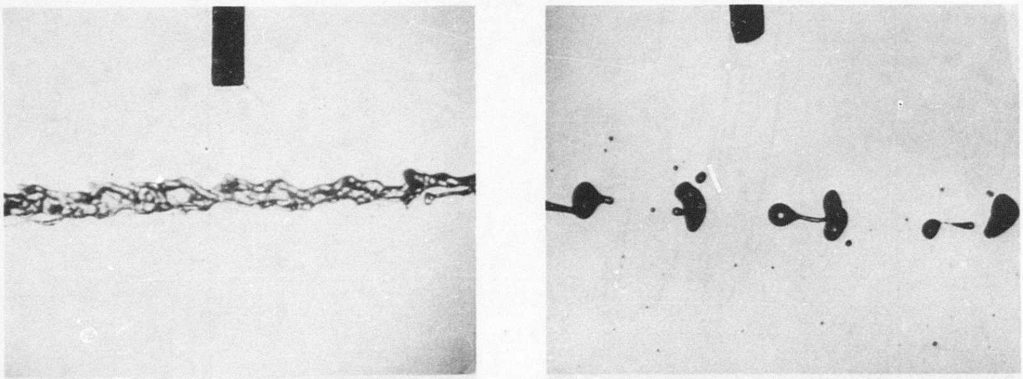


Figure 16. Effect of Atomization Pressure on Emulsion Breakdown in a Capillary.



JP-4 (60 psig) 40 mm FROM CAPILLARY

JP-4 (125 psig) 75 mm FROM CAPILLARY



EMULSION (60 psig) 40 mm FROM CAPILLARY

EMULSION (125 psig) 75 mm FROM CAPILLARY

Figure 17. Breakup of JP-4 and Fuel Emulsion From a Capillary at 60 and 125 psig (All Photographs are 11X Magnification).

TABLE 31
THROUGHPUT AND BREAKDOWN DATA FOR 7165 EMULSIONS ATOMIZED FROM A CAPILLARY*

Fuel	Atomization Pressure (psig)	Throughput (gms/min)	Percent Breakdown
JP-4	60	93.6	-
	125	133.6	-
	200	169.6	-
	400	233.0	-
WSX-7165	60	84.2	75.5
	125	127.8	79.0
	200	161.4	82.5
	400	232.2	87.6
WSX-7063	60	89.6	63.4
	125	122.6	67.7
	200	156.4	74.4
	400	220.4	78.9
7165-A3	60	88.2	81.4
	125	126.6	87.7
	200	160.6	91.7
	400	231.2	100
7165-A1	60	89.9	69.9
	125	125.4	80.2
	200	156.2	83.5
	400	218.2	87.6
7165-A2	60	74.4	75.1
	125	91.2	82.0
	200	155.4	84.7
	400	177.8	88.1

* Capillary Dimensions: 0.0115" ID x 0.033"

TABLE 32
THROUGHPUT AND BREAKDOWN DATA FOR 7165 EMULSIONS ATOMIZED FROM A CAPILLARY*

Fuel	Atomization Pressure (psig)	Throughput (gms/min)	Percent Breakdown
JP-4	60	73.7	-
	125	106.0	-
	200	137.2	-
	400	199.4	-
WSX-7165	60	64.4	57.8
	125	111.0	72.3
	200	140.0	76.7
	400	200.2	85.9
WSX-7063	60	47.5	31.2
	125	101.8	51.4
	200	143.0	60.4
	400	197.8	77.8
7165-A2	60	45.7	24.3
	125	97.7	54.6
	200	140.8	68.9
	400	196.6	75.5
7165-A3	60	65.1	57.9
	125	111.2	76.5
	200	139.8	83.5
	400	199.4	92.3
7165-A1	60	40.4	30.4
	125	98.8	57.4
	200	143.2	70.1
	400	201.4	79.2

* Capillary Dimensions: 0.0115" ID x 0.049"

Figures 15 and 16 also show that the amount of emulsion breakdown in the nozzle is dependent on the total emulsifier level for the emulsions investigated. The emulsion containing only 0.5% emulsifier (7165-A3) showed the most breakdown at all atomization pressures, while the emulsion containing 1.5% emulsifiers (WSX-7063) showed the least breakdown (see Figure 15). The emulsions (WSX-7165, 7165-A2, and 7165-A1) containing 1.0%-1.1% emulsifiers broke down somewhere between the other emulsions. Figure 16, which is a plot of the breakdown data for the emulsions in the capillary having an L/D of 40, further shows the effect of the inhibitors. The emulsion containing 0.5% emulsifiers (7165-A3) still gives the most breakdown, followed by WSX-7165, which contains 1.0% emulsifiers; neither of these emulsions contains a corrosion inhibitor. Emulsions 7165-A1 and 7165-A2, which contain 0.1% inhibitor and 1% emulsifiers, broke down to a somewhat lesser extent than the WSX-7165, which does not contain the inhibitor. This suggests that the inhibitors behave as emulsifiers and increase the resistance of the emulsion to breakdown. The effect of the inhibitors is even more dramatic at low atomization pressures, where the emulsions containing the inhibitor are as resistant to breakdown as WSX-7063, which contains 1.5% emulsifiers. The WSX-7063, however, once again is the most resistant to breakup at the higher atomization pressures.

As was found in the combustion phase of the program, for 7165 emulsions, emulsifier level is the parameter which has the dominant effect on the emulsion breakdown in a capillary. On this basis, it can be expected that the emulsions containing the highest emulsifier level will be the most difficult to atomize. Stated another way, the emulsions containing the highest emulsifier level will undergo the lowest degree of atomization for a given atomization pressure. In addition, the presence of corrosion inhibitors makes the emulsions more difficult to atomize. This too is consistent with what was observed in the combustion phase of this program (Section IV).

Effect of Capillary Length to Diameter on Emulsion Breakdown

To aid in our understanding of the mechanism of emulsion breakdown in a capillary, studies were carried out to evaluate the effect of capillary length to diameter on the breakdown of the emulsions shown in Table 30. The need for carrying out such a study was also dictated by the fact that the nozzles used by other engine manufacturers have length-to-diameter ratios which are larger (>3:1) than the nozzle used in this program.

In comparing Figures 15 and 16, it is observed that for the capillary having the greater length-to-diameter ratio, higher capillary pressures are required to achieve a given percentage of breakdown. This is to be expected, since the viscous effects are greater, the longer the capillary; therefore, less energy is available for breaking the emulsion.

A more informative approach to assessing the effect of capillary length to diameter on emulsion breakdown is to plot emulsion breakdown versus throughput; see Figures 18, 19 and 20. Figure 18 shows that at high throughputs (>120 gm/min), the breakdown of emulsion WSX-7165 is essentially the same for both capillaries. This indicates that emulsion breakdown occurs at the entrance to the capillary, and that no additional breakdown occurs either in the capillary or at the exit of the capillary.

The data points in Figure 18 at low throughputs, however, suggest that the breakdown of emulsion WSX-7165 is somewhat less for the capillary having the greater length-to-diameter ratio (L/D-40:1). That this is a general effect is further borne out by Figures 20A and 20, which show similar effects for emulsions 7165-A3 and WSX-7063. The data (Tables 31 and 32) for the other two emulsions are similar. At low throughputs, the shear stresses in the capillary (L/D-40) are such that the small amount of broken emulsion is probably re-emulsified in the capillary. This is consistent with the results obtained in the program on Demulsification and Coalescence of Emulsions (Contract DAAJ02-68-C-0011). As might be expected from such a mechanism, this effect is most pronounced for the emulsion (WSX-7063) having the highest emulsifier level (see Figure 20). At high throughputs, however, all the emulsions break down to about the same extent in both capillaries. That is, capillary length-to-diameter ratio has no effect on the breakdown of these fuel emulsions at high throughputs. At high throughputs, however, the amount of emulsion breakdown at the entrance to the capillary is so great that it is impossible to induce any significant re-emulsification inside the capillary.

These data suggest that low-pressure atomization in nozzles could be improved by using nozzles having openings with a smaller length-to-diameter ratio (L/D <3). Further, the presence of a corrosion inhibitor and higher emulsifier levels can be expected to accentuate the problems associated with the low-pressure atomization of fuel emulsions.

Attempts to Isolate "Free" JP-4 of Broken Emulsions

Attempts were made to isolate the "free" JP-4 of the broken atomized emulsion in an effort to gain further insight into the mechanism of emulsion breakdown in a capillary and to confirm what we extracted from the studies involving the effect of capillary length to diameter on emulsion breakdown in capillaries. The experimental procedures used in the attempts to isolate the JP-4 from the broken emulsion involved the use of several water-soluble dyes:

- Methyl red
- Fluorescein
- Vegetable dyes

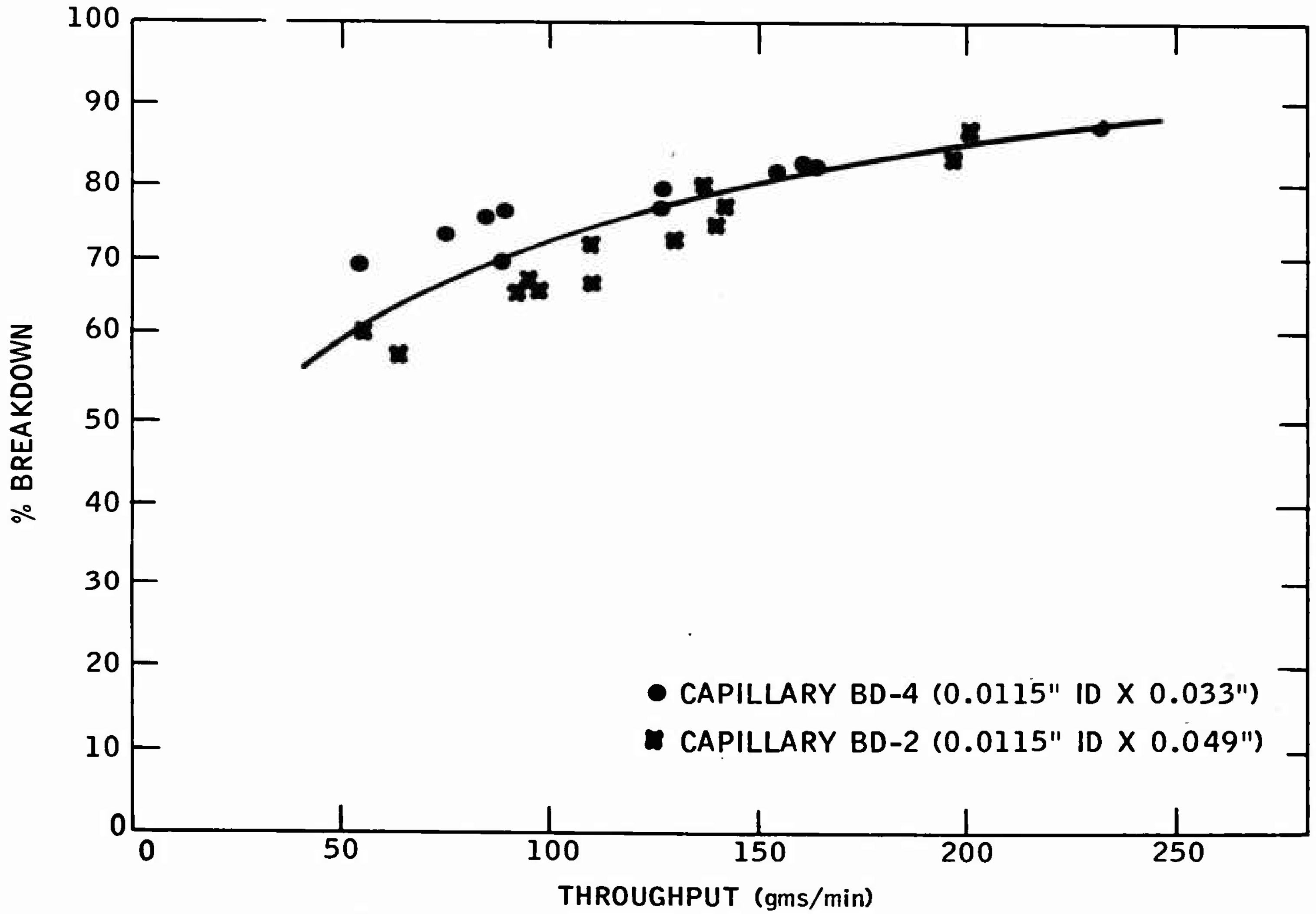


Figure 18. Effect of Capillary Length to Diameter on Breakdown of WSX-7165.

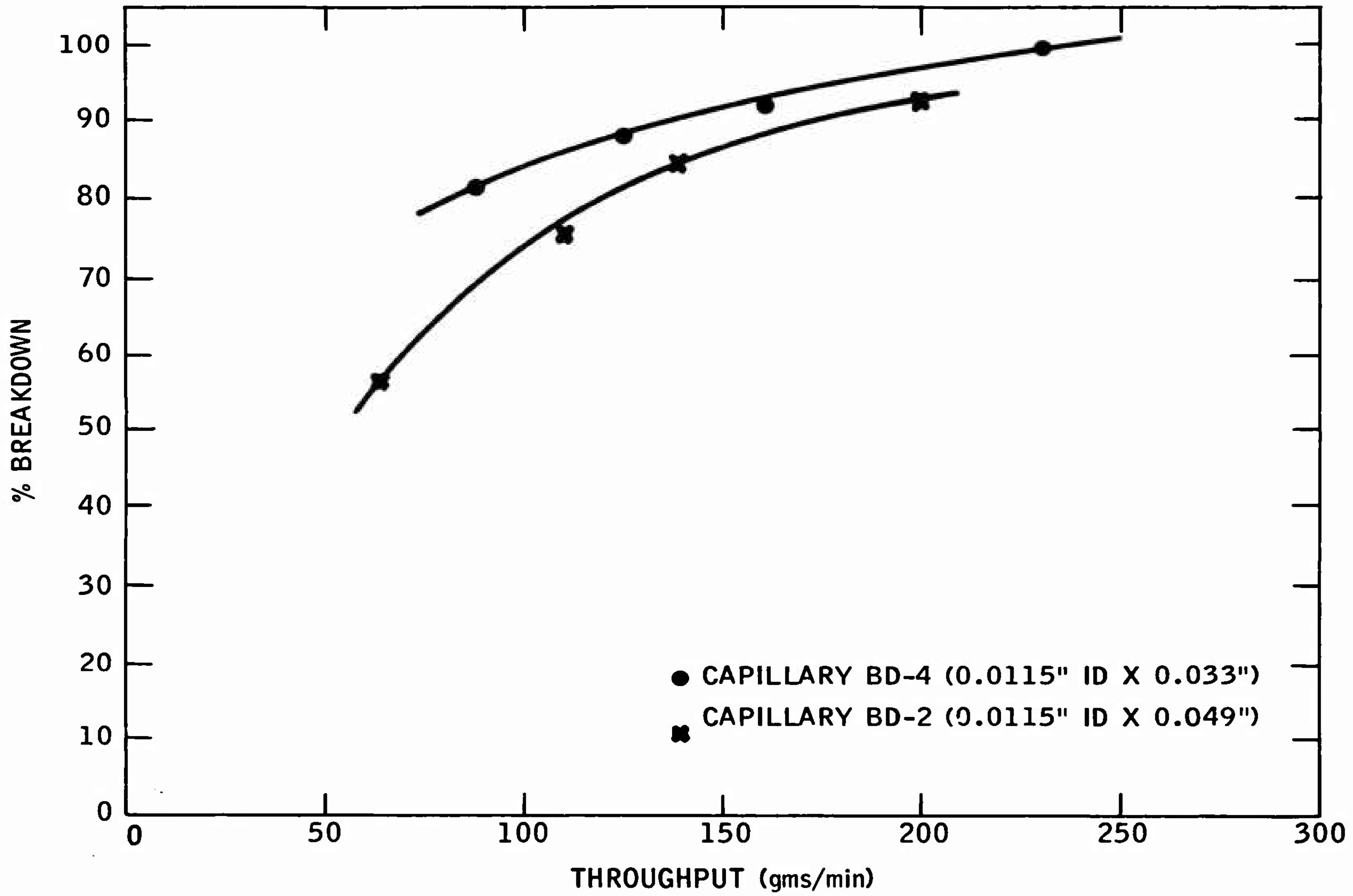


Figure 19. Effect of Capillary Length to Diameter on Breakdown of Emulsion 7165-A3.

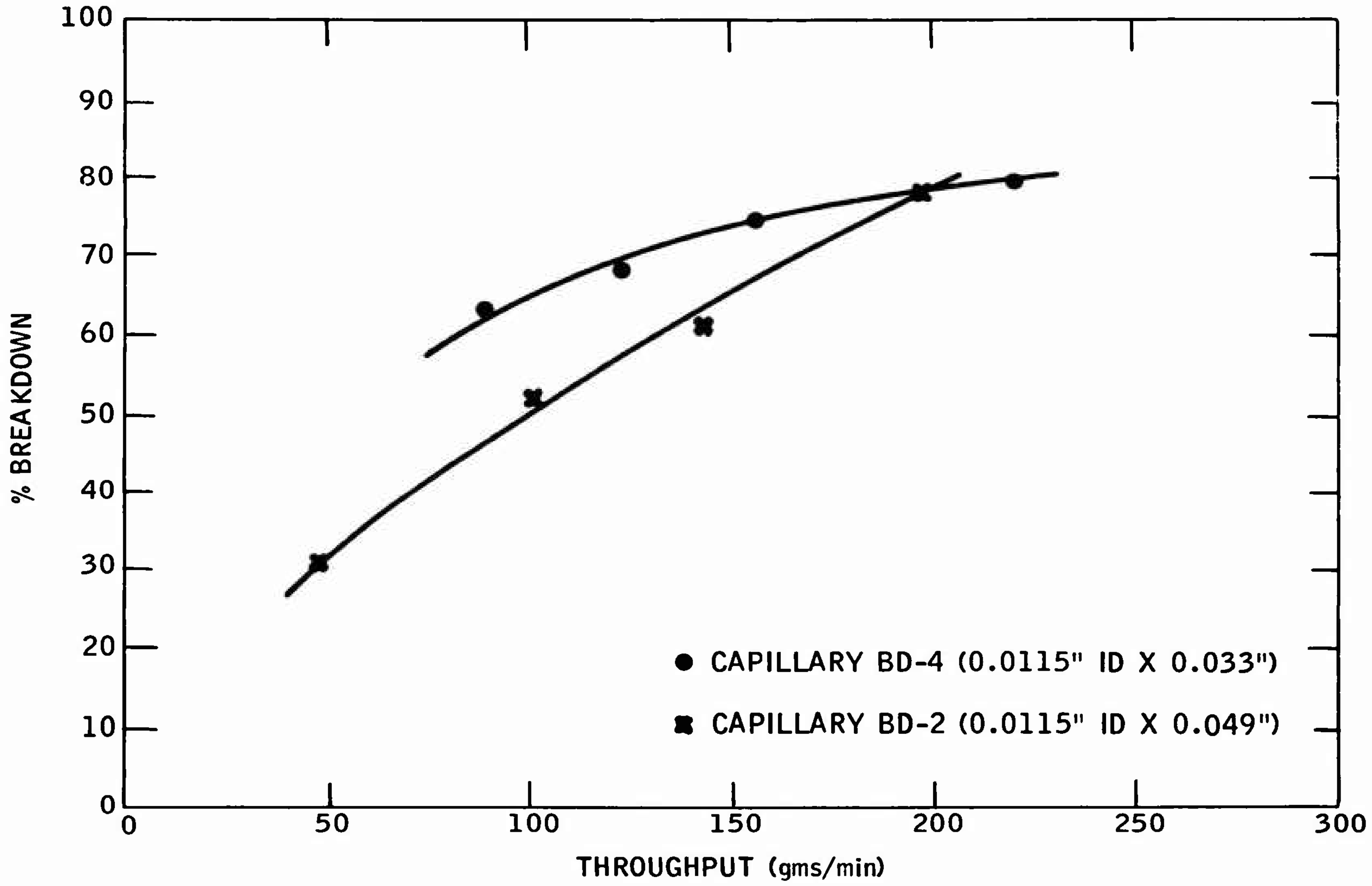


Figure 20. Effect of Capillary Length to Diameter on Breakdown of WSX-7063 Fuel Emulsion.

TABLE 33
THROUGHPUT AND BREAKDOWN DATA ON AGED (30 DAYS)
7165 EMULSIONS ATOMIZED FROM A CAPILLARY*

Fuel	Atomization Pressure (psig)	Throughput (gms/min)	Percent Breakdown
WSX-7165	60	76.0	76.2
	125	118.5	80.6
	200	150.5	82.9
	400	205.8	85.1
7165-A2	60	92.6	63.9
	125	131.8	81.9
	200	164.4	86.9
	400	229.6	94.1

* Capillary Dimensions: 0.01165" ID x 0.033"

TABLE 34
THROUGHPUT AND BREAKDOWN DATA ON AGED (30 DAYS)
7165 EMULSIONS ATOMIZED FROM A CAPILLARY*

Fuel	Atomization Pressure (psig)	Throughput (gms/min)	Percent Breakdown
7165-A3	100	98.6	65.9
	200	139.2	81.3
	300	167.2	86.2
	400	193.4	93.8
7165-A1	100	89.2	49.4
	200	118.0	74.4
	300	169.2	78.4
	400	195.2	82.8

* Capillary Dimensions: 0.0115" ID x 0.049"

TABLE 35
DROPLET SIZE DISTRIBUTION DATA ON ATOMIZED FUELS FROM A CAPILLARY*

	Frequency (percent)							
Droplet Size	15µ	30µ	45µ	60µ	75µ	90µ	105µ	120µ
JP-4	6.4	59.9	25.6	4.8	1.5	1.5	0.5	0.5
WSX-7165 (Fresh)	20.9	26.1	14.1	12.0	8.2	3.3	4.6	4.1
WSX-7165 (Aged 30 Days)	6.7	59.2	24.8	5.5	1.7	1.3	-	0.4
WSX-7063 (Fresh)	20.0	27.2	22.9	10.4	6.0	2.9	2.7	2.4
7165-A2	36.9	22.4	15.0	4.5	2.5	1.0	0.5	1.5
7165-A3	50.1	21.2	13.9	5.8	2.6	1.5	1.9	1.2
7165-A1	8.0	64.6	20.6	4.9	1.4	0.2	0.4	-

*Capillary Dimensions: 0.0115" ID x 0.033".
Atomization pressure used was 125 psig.

TABLE 36
DROPLET SIZE DISTRIBUTION DATA ON ATOMIZED FUELS FROM A CAPILLARY*

	Frequency (percent)							
Droplet Size	15μ	30μ	45μ	60μ	75μ	90μ	105μ	120μ
JP-4	16.7	33.4	27.0	16.1	5.3	0.6	0.3	-
WSX-7165	4.7	43.3	30.2	9.3	4.2	2.8	3.3	1.9
WSX-7063	49.4	18.5	23.4	5.7	1.5	0.4	0.4	0.4
7165-A2	54.6	17.8	14.9	7.9	3.7	0.4	-	-
7165-A1 (Fresh)	54.4	18.8	15.6	5.3	3.4	1.3	0.6	0.3
7165-A1 (Aged 30 Days)	52.2	19.9	15.6	8.5	2.9	0.7	0.4	-
7165-A3 (Fresh)	50.4	22.6	21.2	3.3	1.4	0.5	-	0.5
7165-A3 (Aged 30 Days)	43.8	24.6	16.9	8.8	3.1	1.1	0.6	-

* Capillary Dimensions: 0.0115" ID x 0.049".

Atomization pressure used was 125 psig.

In order to get a color photograph of the jet, it was necessary to use front illumination of the jet rather than back illumination, as was used to obtain the black and white photographs. The dye levels were varied over a wide range to increase their intensity. Despite this, however, it was still not possible to isolate the "free" JP-4 in the atomized jet of broken emulsion.

Effect of Emulsion Aging

The effect of emulsion aging was investigated by storing samples of the emulsions in the laboratory at room temperature and evaluating the emulsion breakdown and degree of atomization. The data obtained from these studies are summarized in Tables 33 through 36. Figures 21 and 22, which present data for emulsions 7165-A3 and WSX-7165, are typical plots of the data obtained for all the emulsions. These show that aging these emulsions for 30 days had no significant effect on their breakdown characteristics in a capillary. It can thus be concluded that these emulsions are stable in storage for 30 days. Further, freshly prepared emulsions and emulsions aged for 30 days should exhibit combustion behavior in the engine in an equivalent manner at high atomization pressures (>125 psig).

The degree of atomization was also investigated for freshly prepared fuel emulsions, for aged (30 days) emulsions, and for JP-4. In this study, all the fuels were atomized at 125 psig and viewed at a distance of 3 inches from the nozzle. Figures 23 and 24 show the sequential breakup of JP-4 and 7165 fuel emulsion, respectively. At an atomization pressure of 125 psig, the sprays for JP-4 and emulsion 7165 appear to be identical. Further, Figures 22 and 23 show that more complete breakup is achieved as one moves away from the capillary.

The droplet size distribution for JP-4 and WSX-7165 fuel emulsion atomized at 125 psig is shown in Figure 22. The droplet size distribution of the atomized sprays was essentially identical for the emulsions and JP-4. Once again, one would expect that at atomization pressures greater than 125 psig for a nozzle having the dimensions of the capillary, the combustion performance of these emulsions should be comparable to that of JP-4.

Figures 26 and 27 show the particle size distribution data plotted for freshly prepared emulsions and emulsions allowed to age for 30 days. The particle size distributions,for the atomized emulsions, whether aged or not, are about the same. Therefore, aging does not appear to have any significant effect on the atomization behavior of these fuel emulsions.

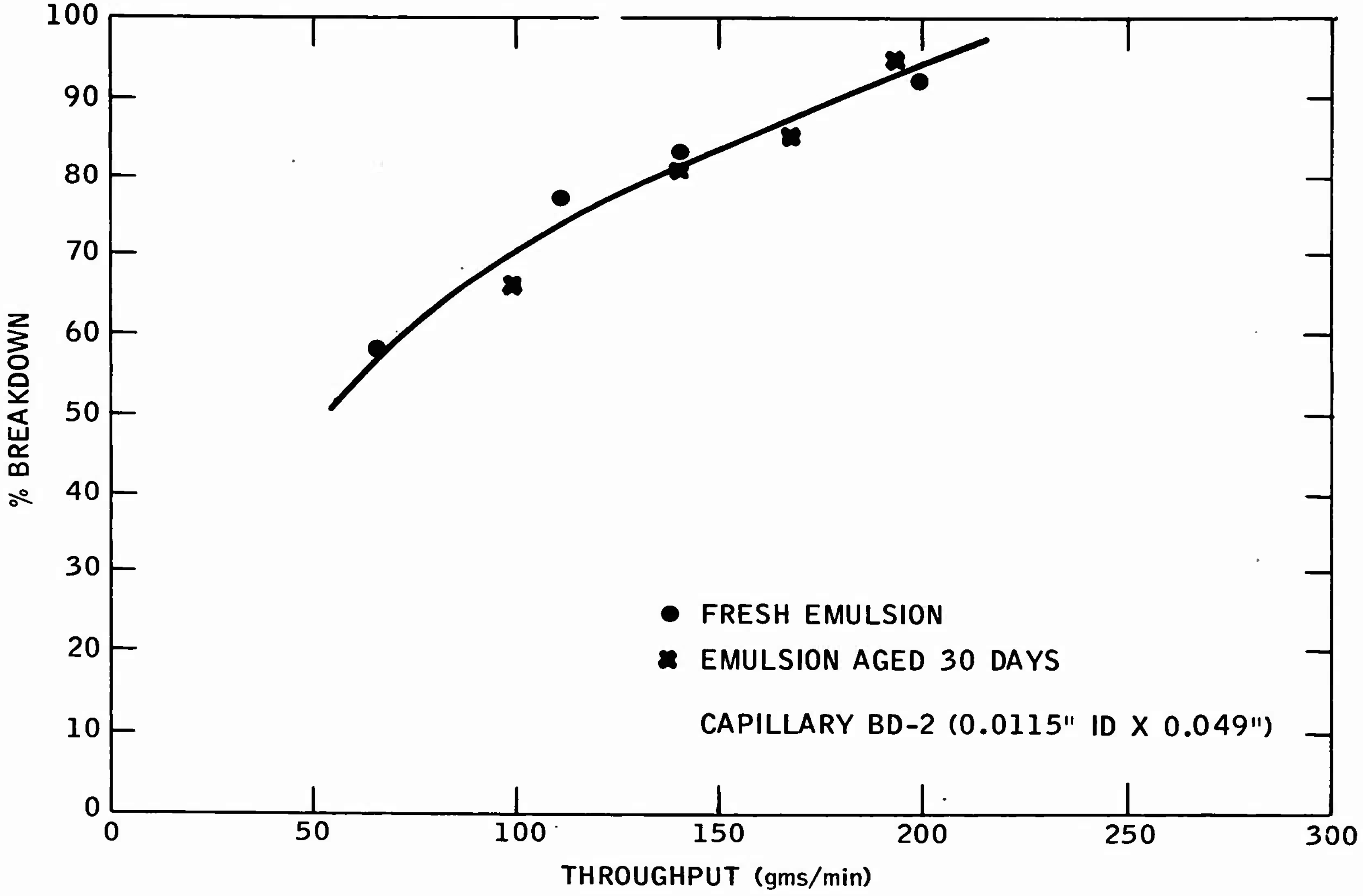


Figure 21. Effect of Aging (30 Days) on the Breakdown Characteristics of Emulsion 7165-A3 in a Capillary.

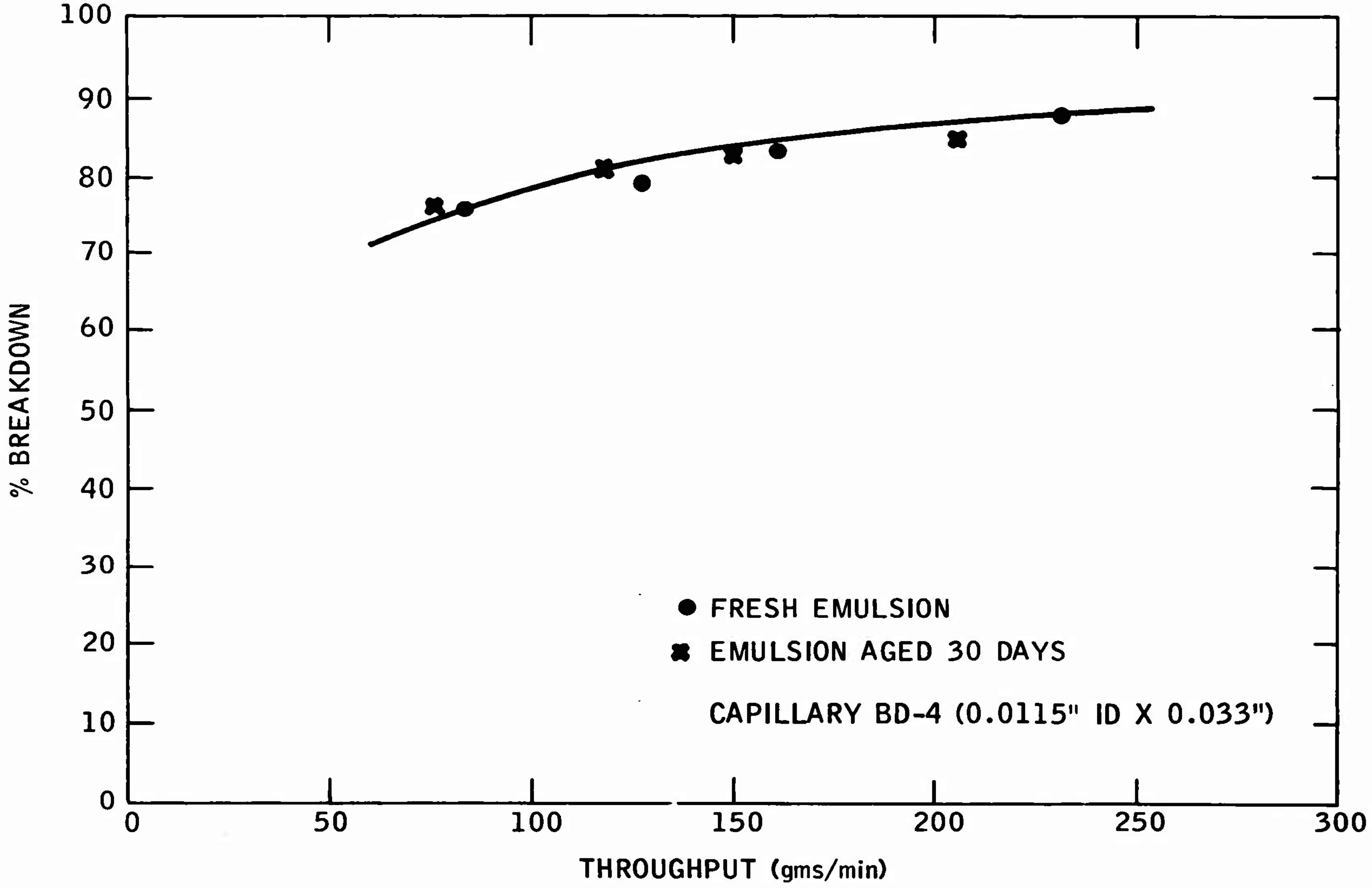
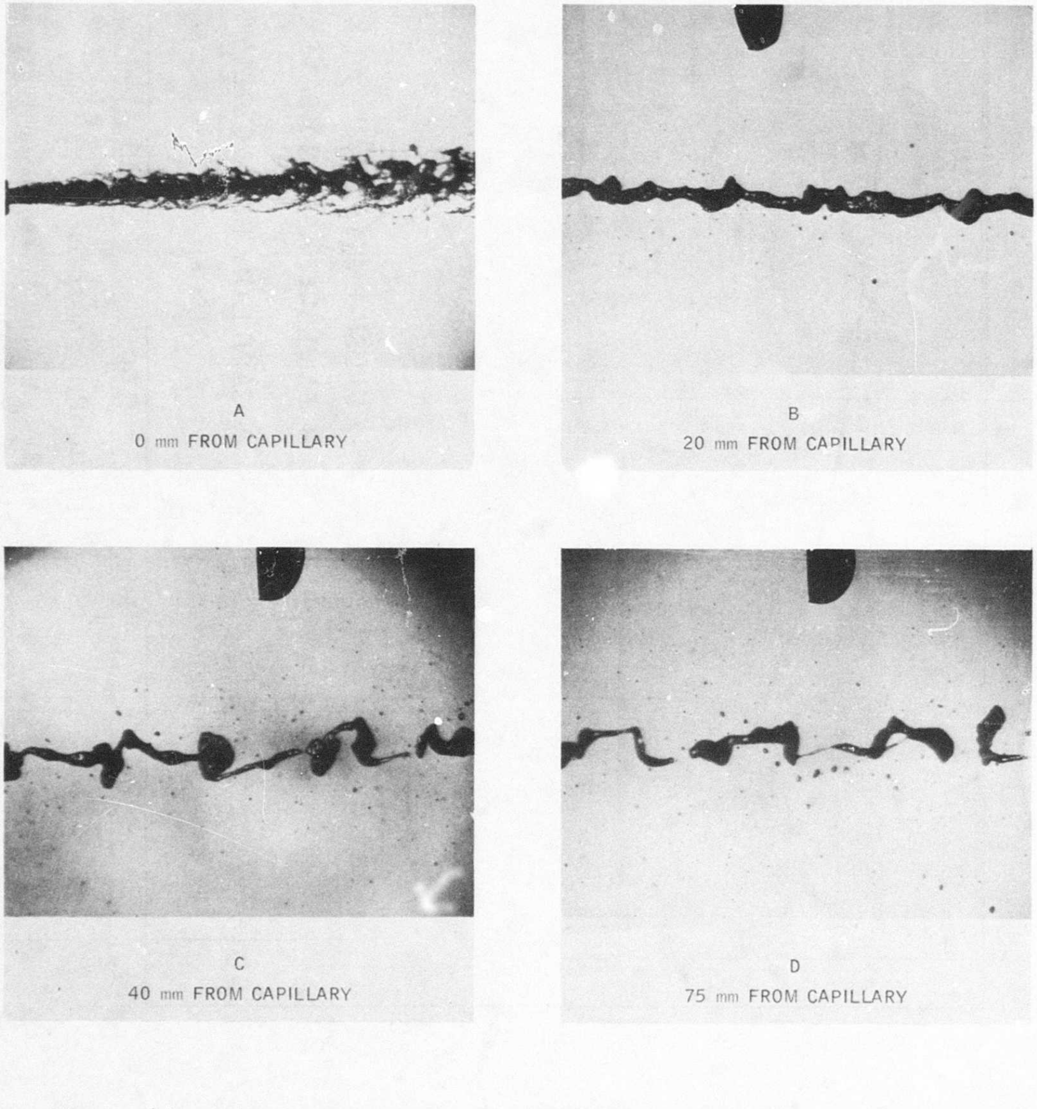


Figure 22. Effect of Aging (30 Days) on the Breakdown Characteristics of Emulsion WSX-7165 in a Capillary.



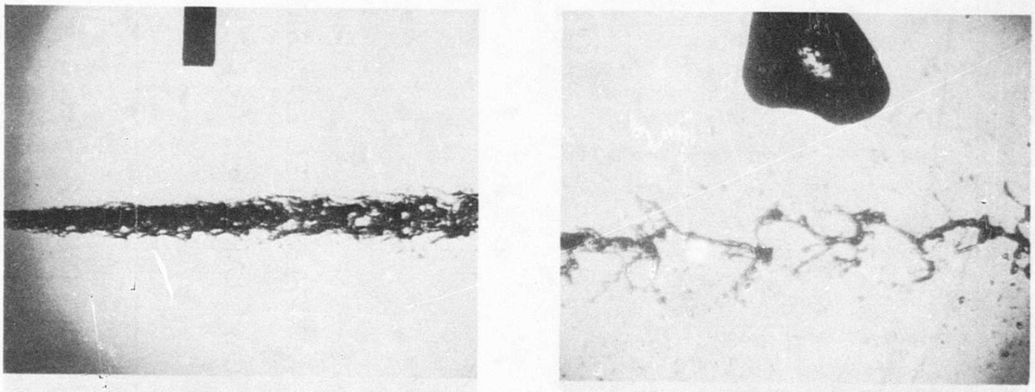
A
0 mm FROM CAPILLARY

B
20 mm FROM CAPILLARY

C
40 mm FROM CAPILLARY

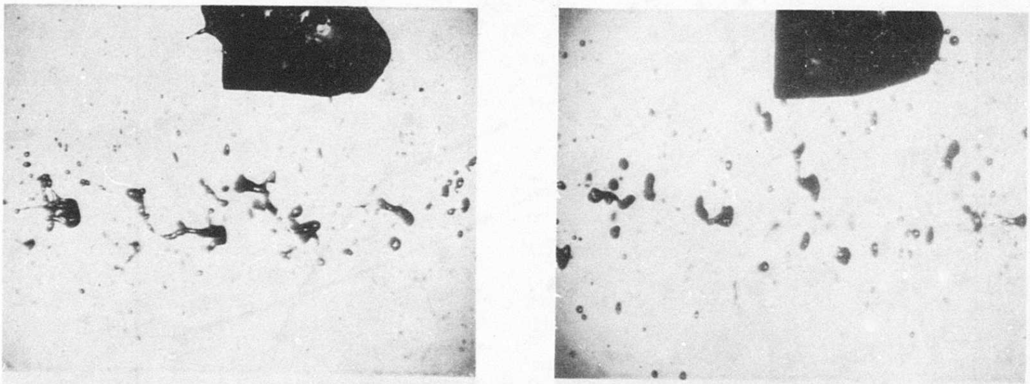
D
75 mm FROM CAPILLARY

Figure 23. Sequential Breakdown of JP-4 Atomized From a Capillary (All Photographs are 11X Magnification).



A
0 mm FROM CAPILLARY

B
20 mm FROM CAPILLARY



C
40 mm FROM CAPILLARY

D
75 mm FROM CAPILLARY

Figure 24. Sequential Breakdown of 7165 Emulsion Atomized From a Capillary (All Photographs are 11X Magnification).

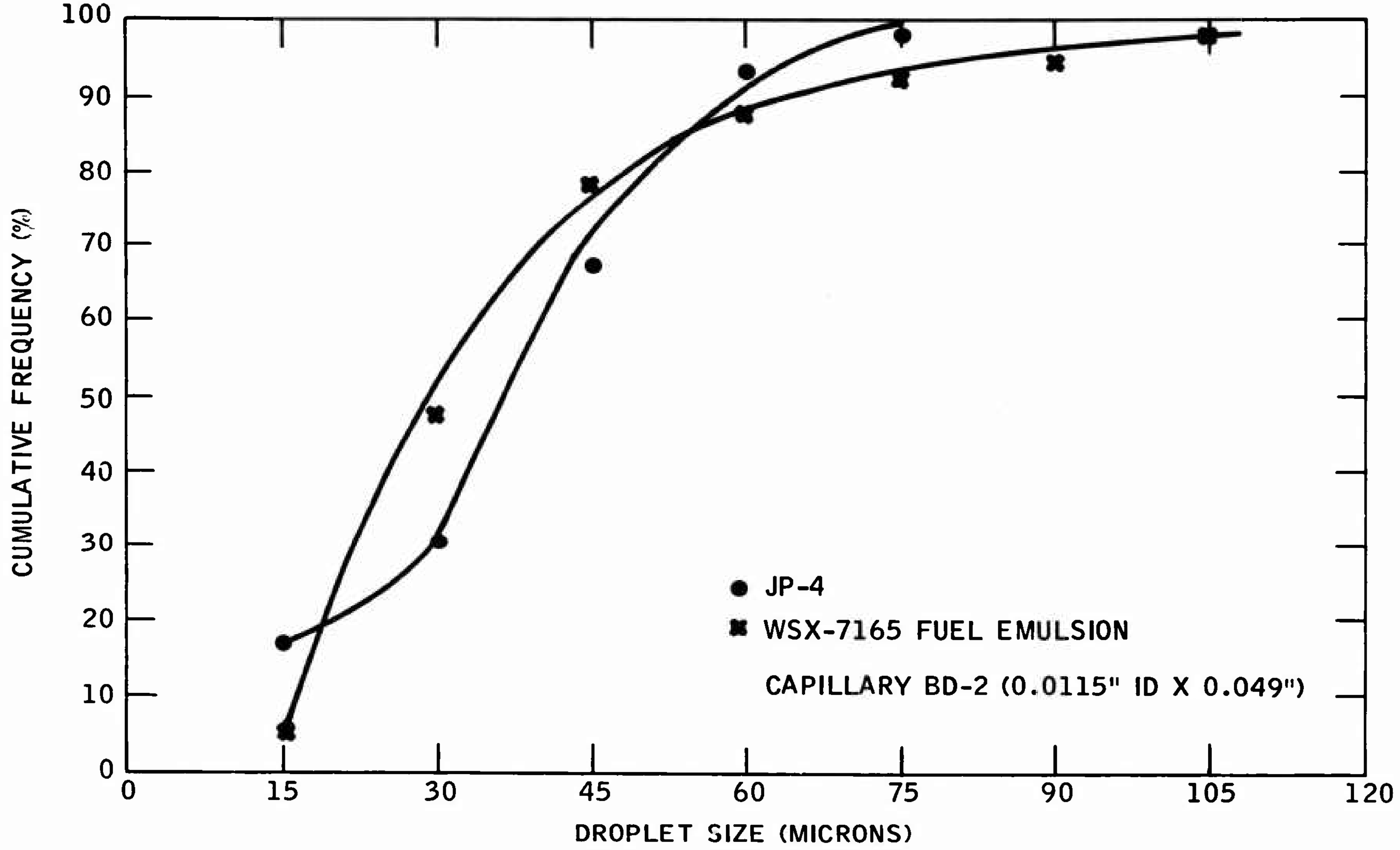


Figure 25. Droplet Size Distribution of WSX-7165 Fuel Emulsion and JP-4 Atomized From a Capillary.

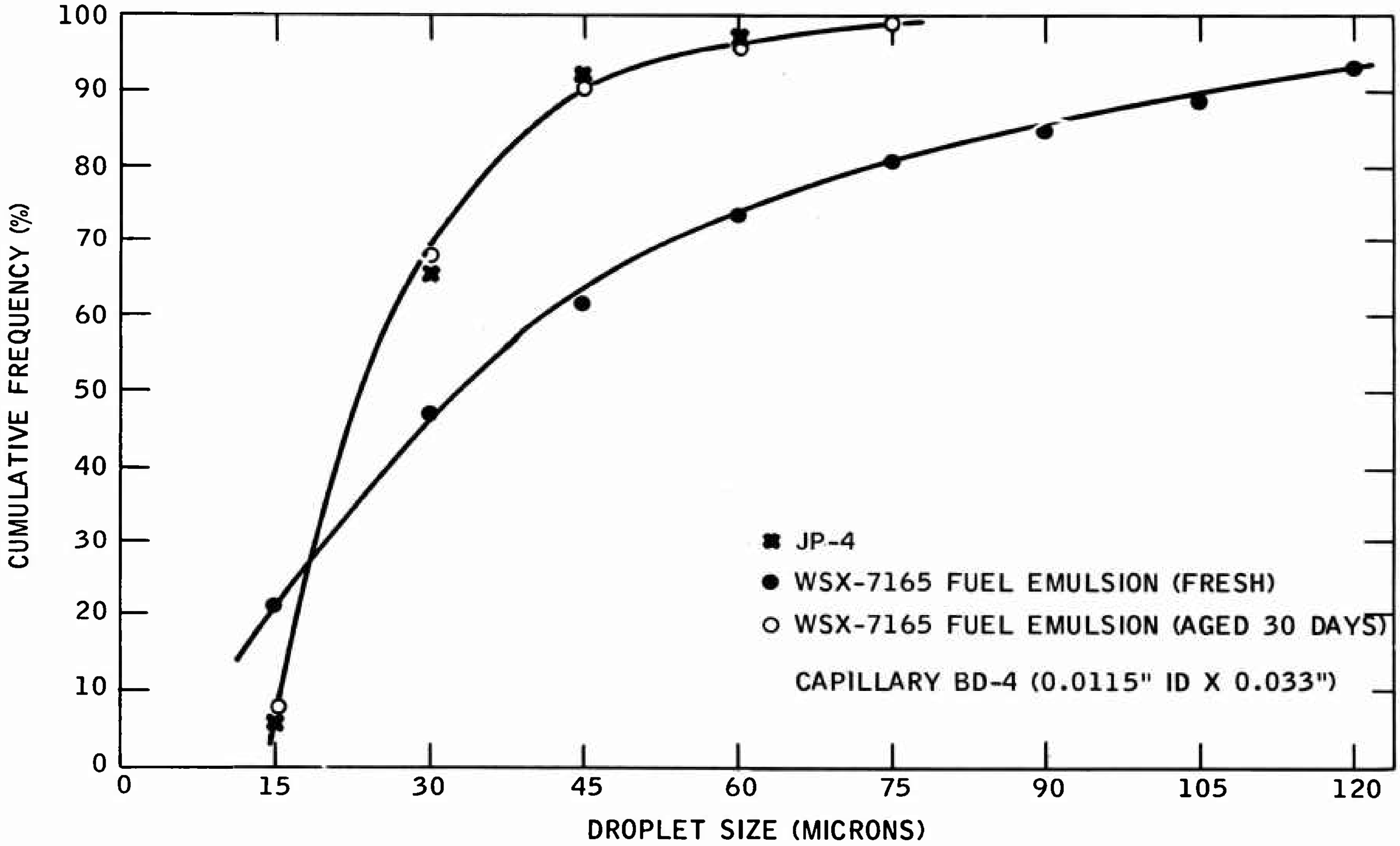


Figure 26. Droplet Size Distribution of WSX-7165 Fuel Emulsion Atomized From a Capillary.

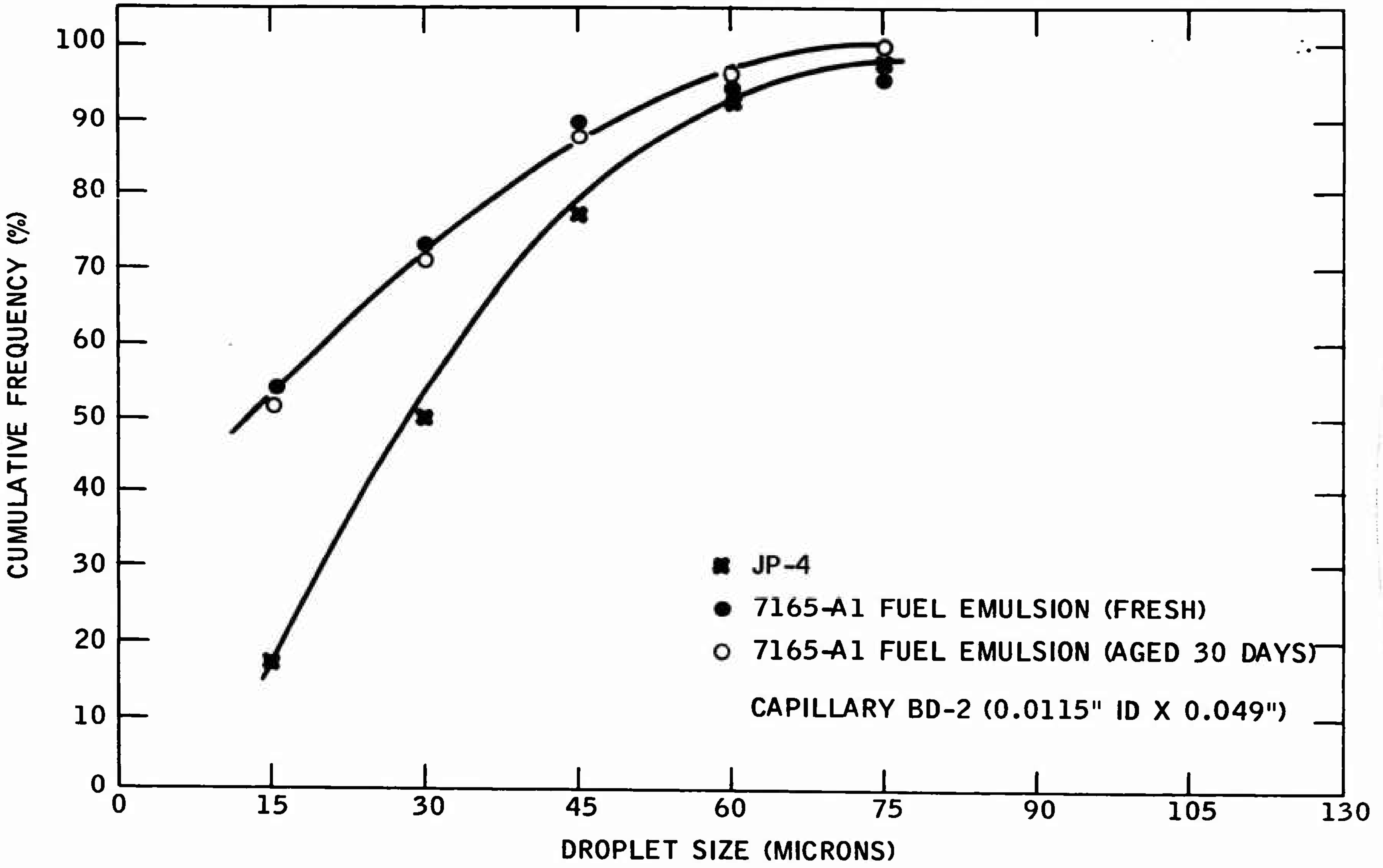


Figure 27. Effect of Emulsion Aging (30 Days) on Droplet Size Distribution of 7165-Al Fuel Emulsion Atomized From A Capillary.

CONCLUSIONS

The flow behavior of the emulsions investigated in this program is identical to that of JP-4 at atomization pressures ranging from 60 to 400 psig. Throughput (M) versus pressure (P) studies show that the emulsions follow a $P \sim M^2$ relationship that is the same as that for JP-4.

Our studies have shown that at high throughputs, the emulsion breakdown is unaffected by changing the capillary length-to-diameter ratio. However, at low throughputs, less emulsion breakdown occurs because the shear stresses within the capillary are in the range which induces emulsification. These facts indicate that emulsion breakdown occurs at the entrance to the capillary and no further breakdown occurs either within or at the exit of the capillary. It was not possible to obtain color photographs which isolated the "free" JP-4 from that of the emulsion to confirm where emulsion breakdown occurs on being atomized from a capillary.

At high atomization pressures (>125 psig), the degree of atomization for the emulsions was comparable to that of JP-4. However, at low atomization pressures (<-60 psig), the emulsions were broken down to about 50% and gave coarser sprays than did JP-4. On this basis, further work is recommended to study the atomization behavior of emulsions at low atomization pressures, as combustion problems can be anticipated under such conditions.

As was found in the combustion phase of this program, emulsifier level is the dominant parameter which determines extent of emulsion breakdown. The presence of corrosion inhibitor has a significant effect on emulsion breakdown characteristics, particularly on the behavior of emulsions at low atomization pressures.

Aging the emulsions for 30 days had no significant effect on the breakdown characteristics of the emulsions studied in capillaries.

VI. CHARACTERIZATION OF OPTIMIZED 7165 FUEL EMULSIONS

INTRODUCTION

To develop the safest possible fuel emulsion, we must consider the properties which make it safe:

- Yield stress
- High mechanical stability (resistant to breakdown by high impact forces)
- High thermal stability (resistant to breakdown when ignited)
- Reduced burning rate, evaporation rate, and flame propagation rate
- Tendency to adhere to the tank (high adhesiveness)

The safest possible fuel emulsion must possess a high yield stress. The exact level required for maximum safety has yet to be determined. Such an emulsion must also be exceedingly stable both thermally and mechanically. Mechanical stability is required to resist breakdown in a crash situation; the impact force that the emulsion is to withstand also needs to be defined. High thermal stability is required for the following reasons: (1) if the emulsion is ignited, to prevent breakdown to form hazardous liquid fuel, and (2) to reduce static evaporation rate and dynamic evaporation, e.g., when the emulsion is sheared as in a crash. Both of these will reduce the flame propagation rate.

The higher the adhesiveness of the emulsion to the tank, the more difficult it will be to expel the fuel from a ruptured tank in a crash.

Since our strategy was to optimize WSX-7165 to produce the safest possible fuel emulsion, we evaluated WSX-7165 in terms of the properties outlined above for a safe emulsion. WSX-7165 can be characterized as having a high yield stress (equilibrium yield stress of 1500 dynes/cm^2) and good thermal stability. Therefore, in our optimization studies, we set out to maintain these good properties along with the following:

- High yield stress (>1400 dynes/cm^2 after 30 days at room temperature)
- Small change in yield stress at 140°F
- Little or no emulsion breakdown as the emulsion burns
- Significantly reduced evaporation of emulsion even after 8 hours at 140°F

WSX-7165 can also be characterized as having only fair mechanical stability, as evidenced by its tendency to break down to varying extents in the following tests:

- Vibration
- Pumping
  - Gear Pumps
  - Centrifugal Pumps

Thus, the program resolved itself into maintaining the good thermal stability (high and low temperature) of WSX-7165 and improving its mechanical stability.

EMULSION PROCESS

All the optimized 7165 formulations were prepared via Process II (Table 1). The corrosion inhibitors in every case were charged to the continuous phase along with the emulsifier ENJ-5728. To evaluate the optimized 7165 fuel emulsions, the emulsions were all prepared in 2500-gram batches in the Hobart mixer. No difficulty was encountered in the laboratory scale-up of the optimized emulsions.

RESULTS AND DISCUSSIONS

Composition of Optimized Formulations

Using the strategy outlined above, five optimized 7165 fuel emulsions were formulated and characterized; three of these were completely characterized in accordance with the contractual requirements. The compositions of these formulations are shown in Table 37.

All of the optimized formulations contain water to enhance the overall stability of these emulsions and a corrosion inhibitor to inhibit their corrosiveness toward mild steel. Both the water and the corrosion inhibitor effectively enhance the mechanical stability of these emulsions. In addition, the optimized emulsions all contain urea and a high ratio of emulsifier Atlas IL-851 to emulsifier ENJ-5728 to give them a high equilibrium yield stress at room temperature and at 140°F.

TABLE 37

COMPOSITIONS OF OPTIMIZED 7165 FUEL EMULSIONS

	Weight Percent				
	7165-1	7165-2	7165-3	7165-4	7165-5
JP-4	97.0	97.0	97.0	97.0	97.0
ENJ-5728	0.15	0.20	0.15	0.20	0.13
Atlas IL-851	0.70	0.70	0.70	0.50	0.32
Urea	0.41	0.40	0.40	0.22	0.22
Formamide	1.64	1.60	1.60	1.98	1.80
N,N'-disalicylidine 1,2-propanediamine	0.10	-	-	-	-
Hydrazine Salt of B-DDSA	-	-	0.15	0.10	0.10
TAMA	-	0.08	-	-	-
B-DDSA	-	0.02	-	-	-
H_2O (by wt. emulsion)	0.50	0.50	0.50	0.50	0.40

Characterization Tests

All of the optimized 7165 fuel formulations were characterized from the standpoint of stability as measured in the screening tests listed on page 2.

The test methods used in this program are described in the appendix of this report. The three optimized emulsion formulations selected for complete characterization were 7165-1, 7165-3, and 7165-4. The other two formulations were not completely characterized; emulsion 7165-2 did not have acceptable corrosion properties toward mild steel and 7165-5 had an equilibrium yield stress which was only about 1000 dynes/cm^2 and was quite similar to 7165-4 composition-wise.

The tests performed on 7165-1, -3, and -4 also included those shown in Table 38. The typical properties of the optimized 7165 emulsions are shown in Tables 39 and 40.

Characterization Test Results

The optimized 7165 fuel formulations contain from 0.50% to 0.90% emulsifiers as compared to 1.0% for WSX-7165 fuel emulsion. The equilibrium yield stress of 7165-1 and 7165-3 is comparable to that of WSX-7165 at all the temperatures investigated. These formulations all contain about the same total emulsifier level. The most significant difference between 7165-4 and 5 and the other formulations is in yield stress. This difference in equilibrium yield stress is due to the difference in emulsifier level between 7165-4 (0.70%), 7165-4 (0.50%), and the other emulsion formulations (≈1%).

Emulsion Stability

The stability of the optimized 7165 emulsions under various conditions is comparable to that of WSX-7165. This is evidenced by stability to vibration, freeze-thaw (-65°F to 140°F), centrifugation, and storage at room temperature in excess of 90 days (Tables 39 and 40).

The conductivity of all the optimized 7165 emulsions is much greater than that of WSX-7165 containing 0.50% water. This suggests that the optimized 7165 emulsions have smaller emulsion droplets which are not as closely packed as the droplets in the WSX-7165 emulsion; that is, the degree of dispersion in the optimized 7165 formulations is greater than that in the WSX-7165 emulsion. Because of this, the continuous phase in the optimized 7165 emulsions is much more free to move about and is, therefore, more conductive. This also means that there is less internal strain from packing in the optimized emulsions.

Emulsion Compatibility

The compatibility of the optimized formulations with respect to elastomers, single metals, and metal couples was investigated at room temperature and 140°F. The results are summarized in Tables 39 to 42. The optimized formulations are, in general, compatible with all the metals and elastomers found to be compatible with WSX-7165. In addition, formulations 7165-1, -3, and -4 are compatible with mild steel at room temperature and 140°F. Formulations 7165-1 and -3 show only a very slight tendency to attack mild steel at 140°F after 1 week.

The compatibility of the emulsion formulations with the following metal couples was also investigated:

- Aluminum - AISI 1010 Steel
- Copper - AISI 1010 Steel
- Aluminum - Copper
- Bronze - Copper
- Aluminum - 316 Stainless
- Aluminum - Bronze
- Copper - 316 Stainless

TABLE 38
CHARACTERIZATION TESTS PERFORMED ON MOST PROMISING EMULSION FORMULATIONS

- Corrosion - Single Metals and Metal Couples
- Vapor Loss at 77°F and 140°F
- Yield Stress vs. Age (90 days)
- Yield Stress at 0°F and 77°F After Aging 7 Days at Room Temperature
- Pumping Tests on Freshly Prepared and Aged (30 Days) Emulsions
  - Centrifugal Pump
  - Gear Pump
- Conductivity and Centrifugation (500 g RCF) After Aging 30 Days
- Conductivity vs. Temperature (-65°F, 0°F, 77°F, and 140°F)
- Heat Transfer Measurements
- Microbial Resistance
- Pressure Drop in Different Pipes
  - Metal (Stainless)
  - Polytetrafluoroethylene
- Stability With Respect to Filtration (40-Micron Filter) vs. Flow Rate
- Effect of Coupling Agents (De-icer, Corrosion, Inhibitor, etc.)

TABLE 39
SOME TYPICAL PROPERTIES OF OPTIMIZED 7165 FUEL EMULSIONS

	Emulsion Formula (Weight Percent)			
Properties	7165	7165-1	7165-3	7165-4
Yield Stress (dynes/cm^2)				
● Initial	2700	3200	3800	2800
● 1 Wk. at R.T.	1500	1920	1850	1525
● 1 Wk. at 140°F	1450	1630	1650	960
● 1 Wk. at -65°F	1900	2100	3100	2300
● 30 Days at R.T.	1450	1875	1725	1125
● 90 Days at R.T.	1725	1450	1850	1000
Stability (wt.% separation)				
● 8 Hrs. Vibration	0.0	0.0	0.0	0.0
● 30 Days at R.T.	0.0	0.0	0.0	0.0
● 90 Days at R.T.	0.0	0.0	0.0	0.0
● Freeze-Thaw*	Stable	Stable	Stable	Stable
● 8 Hrs. Centrifugation (500g RCF)				
- Fresh Sample	0.0	0.0	0.0	0.0
- After Aging 30 Days	0.0	0.0	0.0	0.0
Corrosion-Wt. Loss (mg/in.^{2})				
● 30 Days at R.T. (Steel)	-	0.0	0.8	0.0
● 1 Wk. at 140°F				
- Steel (AISI/1010)	11.1	1.6	2.1	0.0
- Bronze	5.2	10.6	9.1	5.6
- Aluminum	0.2	0.0	0.0	0.0
- 316 Stainless	0.1	0.0	0.0	0.0
- Copper	5.0	13.0	11.3	7.1
● 1 Wk. at R.T.				
- Steel (AISI/1010)	-	0.0	0.2	0.0
- Bronze	-	3.3	3.0	2.3
- Copper	-	4.5	4.2	3.6
Conductivity (microamps)				
● Initial	110	195	450	295
● 1 Wk. at R.T.	220	650	750	750
● 1 Wk. at 140°F	1200	2750	4050	2650
● 1 Wk. at -65°F	135	450	450	325
● 30 Days at R.T.	550	850	1150	1050
● 90 Days at R.T.	-	950	1425	1250

* Six Freeze-Thaw Cycles - 6 Hrs. at 140°F, and 16 Hrs. at -65°F

TABLE 39 (CONTINUED)

Properties	Emulsion Formula (Weight Percent) 7165	7165-1	7165-3	7165-4	7165-5
Four-Ball Wear (mm)*	0.750	0.633	0.533	0.550	0.575
Swelling of Elastomers (% increase)					
Neoprene	37.0	45.5	49.0	38.0	-
Buna N (MS-902)	18.5	16.0	41.6	34.5	-
Buna N (MS-29513)	42.0	45.0	67.0	58.5	-
Silicone	85.0	90.5	81.0	85.7	-
Viton	3.4	4.1	6.2	5.2	-
Resistance To Organisms					
Aerobacter aerogenes at 86°F	30 Days	30 Days	30 Days	30 Days	-
Pseudomonas Aeruginosa at 86°F	30 Days	30 Days	30 Days	30 Days	-
Cladosporium Resinae at 77°F	30 Days	30 Days	30 Days	30 Days	-

* The JP-4 used in the emulsions had a four-ball wear of 0.766 mm; the JP-4 used for the 7165 had a value of 0.450 mm.

TABLE 40
SOME TYPICAL PROPERTIES OF OPTIMIZED 7165 FUEL EMULSIONS

Properties	Emulsion Formula (Weight Percent)	
	7165-2	7165-5
Yield Stress (dynes/cm^2)		
● Initial	3120	3120
● 1 Wk. at R.T.	1725	1300
● 1 Wk. at 140°F	1200	800
● 1 Wk. at -65°F	2050	1605
● 30 Days at R.T.	1605	980
● 90 Days at R.T.	1500	950
Stability (wt.% separation)		
● 8 Hrs. Vibration	0.0	0.0
● 30 Days at R.T.	0.0	0.0
● 90 Days at R.T.	0.0	0.0
● Freeze-Thaw*	Stable	Stable
● 8 Hrs. Centrifugation (500g RCF)		
- Fresh Sample	0.0	0.0
- After Aging 30 Days	0.0	0.0
Corrosion-Wt. Loss (mg/in.^{2})		
● 30 Days at R.T. (Steel)	≈ 2.5	0.0
● 1 Wk. at 140°F		
- Steel (AISI/1010)	5.8	0.0
- Bronze	9.4	4.7
- Aluminum	0.0	0.0
- 316 Stainless	0.0	0.0
- Copper	23.2	11.0
● 1 Wk. at R.T.		
- Steel (AISI/1010)	1.5	0.0
- Bronze	3.1	2.7
- Copper	8.2	4.5
Conductivity (microamps)		
● Initial	205	305
● 1 Wk. at R.T.	450	1050
● 1 Wk. at 140°F	3350	3850
● 1 Wk. at -65°F	205	550
● 30 Days at R.T.	650	1450
● 90 Days at R.T.	1250	1550

* Six Freeze-Thaw Cycles - 6 Hrs. at 140°F and 16 Hrs. at -65°F

The results of these compatibility studies are summarized in Tables 41 and 42 for emulsions 7165-1, 7165-3, and 7165-4. It appears that for the metal couples involving copper and steel, the corrosiveness of the emulsions toward the steel is accentuated. In the case of the metal couple involving copper and bronze, the corrosiveness of the emulsions toward both the bronze and the copper is accentuated. Coupling the other metals does not appear to affect the corrosiveness of the emulsions toward the metals of the five other metal couples involving aluminum-steel, aluminum-copper, aluminum-stainless, aluminum-bronze, and copper-stainless.

The optimized 7165 fuel emulsions are, for the most part, compatible with the same elastomers as is WSX-7165. It does appear, however, that some of the optimized emulsions tend to show higher swelling levels with neoprene (7165-1 and -3) and Buna N (7165-3 and -4) than does 7165 emulsion. The optimized 7165 fuel emulsions are also resistant to bacterial attack as is WSX-7165.

Pumping and Filtration Studies

The results of the pumping and filtration studies are summarized in Tables 43 and 44. The data show that the optimized 7165 formulations are stable with respect to pumping with either a centrifugal pump or a gear pump. The pumping tests also show that the optimized 7165 formulations are more stable mechanically than the WSX-7165 emulsion. Greater evidence of this is obtained when the emulsions are allowed to age for 30 days and are then pumped using a centrifugal pump and a gear pump. There is no emulsion breakdown for the optimized 7165 emulsions by either of these pumps. However, aged WSX-7165 gave 5% breakdown when pumped with the gear pump and about 11% breakdown when pumped with the centrifugal pump. These results are summarized in Table 43.

The optimized 7165 emulsions are more stable mechanically than the WSX-7165 because of the presence of the ionic corrosive inhibitor in these formulations. The inhibitor is concentrated in the interfacial film, where it behaves as an emulsifier. The presence of the ionic material in the interfacial film increases the strength of the emulsifier film, decreases droplet size, and increases surface coverage of the JP-4 droplets. The increased interfacial film strength (smaller droplet) thus accounts for the increased mechanical stability of the emulsions. The smaller droplets also account for much of the higher conductivity of the optimized 7165 emulsions relative to the WSX-7165 emulsion (Tables 39 and 40). The smaller droplets can pack much more efficiently than the larger droplets; therefore, there is greater freedom of the continuous phase, which is manifested in terms of greater emulsion conductivity.

The effect of pipe composition on the pressure drop required to pump the optimized 7165 emulsions is shown in Table 44.

TABLE 41
COMPATIBILITY OF OPTIMIZED 7165 EMULSIONS WITH METAL COUPLES AT ROOM TEMPERATURE (77°F)*

	Weight Loss (mg/in.^{2})		
Metals	7165-1	7165-3	7165-4
Singles			
Aluminum	0.07	0.30	0.6
1010 Steel	0.0	0.20	0.0
Copper (Cu)	4.5	4.2	3.6
Bronze (Br)	3.3	3.0	2.4
Al-1010 Steel Couple			
Aluminum	+0.20	+0.35	+0.37
1010 Steel	+0.16	+0.30	+0.23
Cu-1010 Steel Couple			
Copper	2.1	2.1	1.6
1010 Steel	+0.25	+0.30	+0.30
Al-Cu Couple			
Aluminum	+0.40	+0.45	+0.53
Copper	2.0	2.0	1.6
Br-Cu Couple			
Bronze	1.9	1.8	1.6
Copper	1.9	2.0	1.7

* 1 week

TABLE 42
COMPATIBILITY OF OPTIMIZED 7165 EMULSIONS WITH METAL COUPLES AT 140°F*

Metals	Weight Loss (mg/in.^{2})		
	7165-1	7165-3	7165-4
Singles			
Aluminum (Al)	0.0	0.0	0.0
1010 Steel	1.6	2.1	0.0
Copper (Cu)	13.0	11.3	7.1
Bronze (Br)	10.6	9.1	5.6
316 Stainless	0.0	0.0	0.0
Al-1010 Steel Couple			
Aluminum	0.9	0.47	0.0
1010 Steel	1.6	2.9	1.5
Cu-1010 Steel Couple			
Copper	8.4	9.0	13.3
1010 Steel	6.1	2.0	3.7
Al-Cu Couple			
Aluminum	1.7	0.07	0.07
Copper	12.0	12.9	18.6
Br-Cu Couple			
Bronze	16.7	17.8	17.2
Copper	17.0	15.6	14.1
Al-Stainless Couple			
Aluminum	0.0	0.0	0.0
Stainless	0.0	0.0	+0.2
Al-Bronze Couple			
Aluminum	0.0	0.0	0.0
Bronze	3.5	4.2	3.9
Cu-Stainless Couple			
Copper	10.5	10.8	11.1
Stainless	+0.1	0.0	0.0

* 1 week

TABLE 43
EFFECT OF AGING OPTIMIZED 7165 EMULSIONS ON STABILITY TO PUMPING WITH CENTRIFUGAL AND GEAR PUMPS

	Emulsion Formula			
	7165	7165-1	7165-3	7165-4
Gear Pump Test @ 0.17 gpm				
Fresh Emulsion				
● Yield Stress Before Pumping (dynes/cm^2)	2700	1920	3250	1875
● Yield Stress After Pumping	3250	2300	3500	2175
● Emulsion Condition	No Breakdown	No Breakdown	No Breakdown	No Breakdown
Emulsion Aged 30 Days				
● Yield Stress Before Pumping (dynes/cm^2)	1450	1605	1725	1390
● Yield Stress After Pumping	2185	1750	2300	1815
● Emulsion Condition	1.3% Breakdown	No Breakdown	No Breakdown	No Breakdown
Centrifugal Pump Test @ 1.4 gpm				
Fresh Emulsion				
● Emulsion Condition	5.0% Breakdown	No Breakdown	No Breakdown	No Breakdown
Emulsion Aged 30 Days				
● Emulsion Condition	11-20% Breakdown	No Breakdown	No Breakdown	No Breakdown

TABLE 44
EFFECT OF PIPE COMPOSITION ON PRESSURE DROP REQUIRED TO PUMP OPTIMIZED 7165 EMULSIONS*

Pipe Composition	Pressure Drop (psig) 7165	7165-1	7165-3	7165-4
Stainless	90	20	11	14
Teflon	4	2.8	6.5	3
Polyethylene	3	2.5	3.0	2

* Flow rate = 0.102 cc/sec.
Tube dimensions - 48" length; 1/8" inner diameter
Pump used - SOD viscometer rig (ASTM D 1092) equipped with indicated pipes in place of capillaries.

First, the data in Table 44 show that the optimized 7165 emulsions are much easier to pump through stainless steel pipe than is the WSX-7165 emulsion. Secondly, pumping any of the emulsions through pipes made of low-energy surfaces such as polyethylene or Teflon requires a much lower pressure drop than pumping the emulsions through comparably sized high-energy surface pipes such as stainless. The first effect is due to the fact that the optimized 7165 emulsions contain the ionic corrosion inhibitors which are adsorbed onto the high-energy surface, the stainless, and thereby form a lower energy surface. The emulsion does not significantly wet the lower energy surface, and the result is mainly plug flow. Therefore, for the optimized 7165 emulsions, the pressure drop in pumping these through metal pipes is lower than that for WSX-7165, which adheres to the pipe wall.

Lower pressure drops are required to pump all the emulsions through pipes made of low surface energy materials because none of the emulsions wet the walls of these pipes. Therefore, one gets plug flow where the plug is lubricated by a thin film of the continuous phase.

The data in Table 45 show that the optimized 7165 formulations are stable enough to be filtered through a 40-micron filter having a filter area of 0.10 in.^{2} at rates up to at least 496 gms/min. Up to this filtration rate, no emulsion breakdown was observed with the optimized 7165-1, -3, and -4 fuel emulsions. Filtration data on WSX-7165 under similar conditions show that gross emulsion breakdown occurred at the higher flow rates (496 gm/min) through the 40-micron screen. These filtration data thus further confirm the enhanced mechanical stability of the optimized 7165 emulsions relative to WSX-7165.

Effect of Temperature on Emulsion Yield Stress and Conductivity

The effect of temperature on the yield stress and conductivity of the optimized 7165 formulations relative to WSX-7165 is shown in Table 46. In general, all of the emulsions show only slight increases in yield stress from 77°F down to -65°F. The conductivity of these emulsions changed with respect to temperatures in the expected manner, i.e., increased with increasing temperature, and decreased with decreasing temperature.

Effect of Coupling Agents

The effect of the following coupling agents on the optimized 7165 emulsions was investigated:

- Santolene C
- Jet fuel de-icer
- Butyl alcohol

None of these materials had any beneficial effect on the emulsion properties which could not be achieved by the use of corrosion inhibitors. Because of this, the materials listed above were not incorporated in the optimized emulsion formulations.

Heat Transfer Measurements

In an effort to compare the relative heat transfer properties of the optimized 7165 emulsions to those of JP-4, heat transfer measurements were attempted by using the preheater section of a CFR Fuel Coker. The experimental setup used to make the heat transfer measurements is illustrated in Figure 28. The system consists of the preheater section, thermocouples to measure the inlet temperature and the outlet temperature, a variable-speed gear pump, and a reservoir for holding the fuel.

The preheater section consists of two aluminum tubes (3/8 inch and 9/16 inch in diameter) mounted concentrically between inlet and outlet end bodies. A cartridge-type heating element is mounted inside the inner tube and is used to heat the fuel as it passes between the two concentric tubes. A variac was used to control the output of the cartridge heater, which was about 12 inches long.

In the setup shown in Figure 28, the outer tube was not insulated and no provisions were made to measure the surface temperature of the heated inner tube. Because of this, we cannot discuss the heat transfer of the emulsion relative to that of JP-4 in any quantitative sense. Therefore, everything said about heat transfer based on our experiments will be highly qualitative.

TABLE 45
EFFECT OF PUMPING OPTIMIZED 7165 EMULSIONS THROUGH 40-MICRON FILTER AT DIFFERENT FLOW RATES*

	Emulsion Formula**			
	7165	7165-1	7165-3	7165-4
Initial Yield Stress (dynes/cm^2)	1450	1675	1750	1390
Yield Stress (dynes/cm^2) After Pumping @ Rate of:				
138 gm/min	3120	2300	2300	1400
282 gm/min	2185	2300	2500	1300
496 gm/min	1900	2500	2850	2175
Emulsion Condition After Pumping @ Rate of:				
138 gm/min	<1% Breakdown	No Breakdown	No Breakdown	No Breakdown
282 gm/min	11.5% Breakdown	No Breakdown	No Breakdown	No Breakdown
496 gm/min	15.0% Breakdown	No Breakdown	No Breakdown	No Breakdown
Pressure Drop (psig) at Pumping Rate of				
282 gm/min	12.0	3.0	8.0	4.0

* Filter area was 0.10 in^2.

** All emulsions had aged about 30 days.

TABLE 46
EFFECT OF TEMPERATURE ON YIELD STRESS AND CONDUCTIVITY OF OPTIMIZED 7165 FUEL EMULSIONS

	Emulsion Formula			
	7165	7165-1	7165-3	7165-4
*Conductivity (microamps) Measured at:				
● -65°F	15	25	45	35
● 0°F	-	65	145	255
● 77°F	135	255	750	325
● 140°F	1200	4250	4750	4750
*Yield Stress (dynes/cm^2) Measured at:				
● -65°F	3150	3700	3475	3400
● 0°F	-	3125	3120	2800
● 77°F	1925	2950	2700	2300
● 140°F	1325	1145	1250	640
Initial Yield Stress (dynes/cm^2)	1925	3200	3250	2800

* All measurements from R.T. to -65°F were after emulsion aged 7 days at -65°F; data at 140°F on emulsions aged for 7 days.

The heat transfer coefficient h (in $BTU/hr/ft^2/^oF$) is given by the following expression (Reference 8):

$$h = \frac{Q}{A(LMTD)} \qquad (1)$$

where:

Q = heat transferred to the fluid

A = area of heater surface

$LMTD$ = log mean temperature difference between heater and fuel

$$Q = m\ Cp\ (t_{fo}-t_{fi}) \qquad (2)$$

where:

m = mass flow rate

Cp = specific heat of fuel

t_{fo}, t_{fi} = inlet and outlet temperature of fuel, respectively

The above equations have been presented to show what is involved in the heat transfer process. Since the temperature of the heated surface was not measured, the value of LMTD in equation 2 cannot be evaluated from our experiment.

For the purpose of this discussion, the specific heat of the fuel emulsion and JP-4 can be assumed to be about the same, since the fuel emulsion is 97% by weight of JP-4.

The emulsion and JP-4 were cold-flow tested in the unit (Figure 28) to establish the pump setting required for comparable flow rates. These data are shown in Figure 29. For any given pump setting, the flow rate for the JP-4 is about 20% higher than that for the emulsion.

In the experimental setup shown in Figure 28, since the outer tube is not insulated, heat is effectively being transferred at two surfaces: from the heater to the fluid and from the fluid to the air via the outer tube. Therefore, the temperature of the fluid as it exits from the preheater tube will depend on which rate is faster: that from the heater to the fluid or that involving the transfer of heat from the fluid to the air. Using the approximate wattage input to the heater in the experiments, and using equation (2), it was possible to calculate the amount of heat loss via the outer tube to the air. Our crude calculations show that

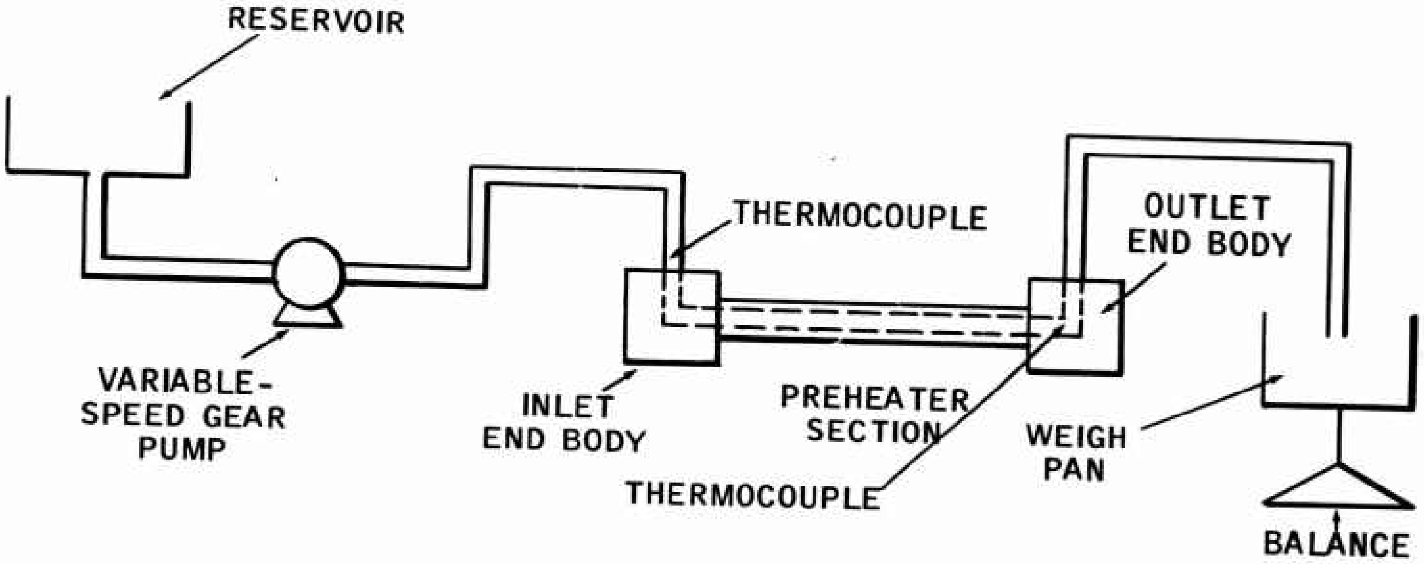


Figure 28. Experimental Setup Used for Heat Transfer Measurements.

the heat loss to the air via the outer tube is about one-half the heat input by the heater. This further indicates the difficulty in attempting to extract any firm conclusions from the experimental data shown in Table 47.

Qualitatively, therefore, if the heat transfer via the outer tube is as great as the calculations indicate, it can be assumed that for the same heat input, the relative temperature change of the fluids passing through the preheater section (Figure 28) could be a qualitative measure of the relative heat transfer properties of the fluids. Thus, the fluid showing the greater temperature change for a given heat input would be expected to have the poorer heat transfer properties.

Table 47 summarizes the data obtained for JP-4 and the 7165 emulsion at two different heat inputs (Variac settings) and at four different flow rates. The temperature change is slightly greater for the emulsion in every case. At first glance, the differences observed could very well be explained by the differences in flow rates. However, when one plots the temperature vs. flow rate for the emulsion and JP-4 as shown in Figure 30, it is obvious that at any given flow rate the temperature change for the emulsion is consistently higher than that for the JP-4. Even though neither the data nor the experimental procedure will allow us to say quantitatively that the fuel emulsion is a poorer heat transfer fluid, it does appear that this might be the case.

When the heat transfer properties were investigated at lower heat inputs (Variac setting 40), only at low flow rates (40 gm/min) are differences in the temperature change for the JP-4 and the emulsion great enough to suggest that the emulsions have poorer heat transfer properties. At higher flow rates, there is a crossover in the heat transfer properties. This, in itself, could indicate poorer heat transfer properties for the emulsion relative to JP-4. That is, at the lower heater input, less heat is being transferred from the heater to the emulsion than is the case for that of JP-4. Because of this, at low heater input and high mass flow rates, the emulsion is cooler when it exits from the preheater.

The above discussion indicates the need for quantitative heat transfer studies on fuel emulsions. To obtain meaningful heat transfer data on the emulsions relative to JP-4, more sophisticated experimental techniques will be required. Until these experiments are carried out, one can only assume that the heat transfer properties of fuel emulsions are somewhat poorer than those of JP-4.

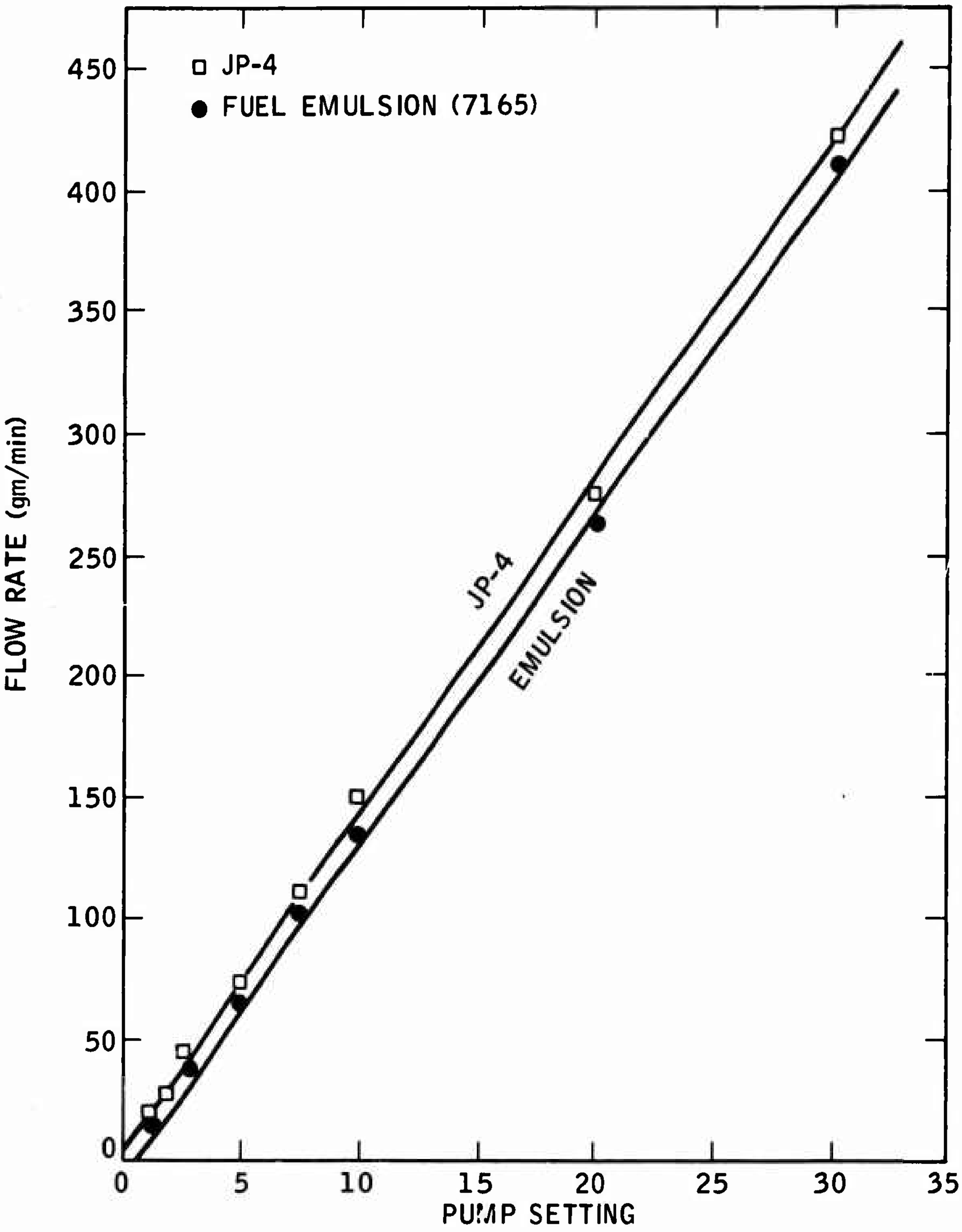


Figure 29. Heat Transfer Measurements--Cold Flow Test of JP-4 and 7165 Emulsion.

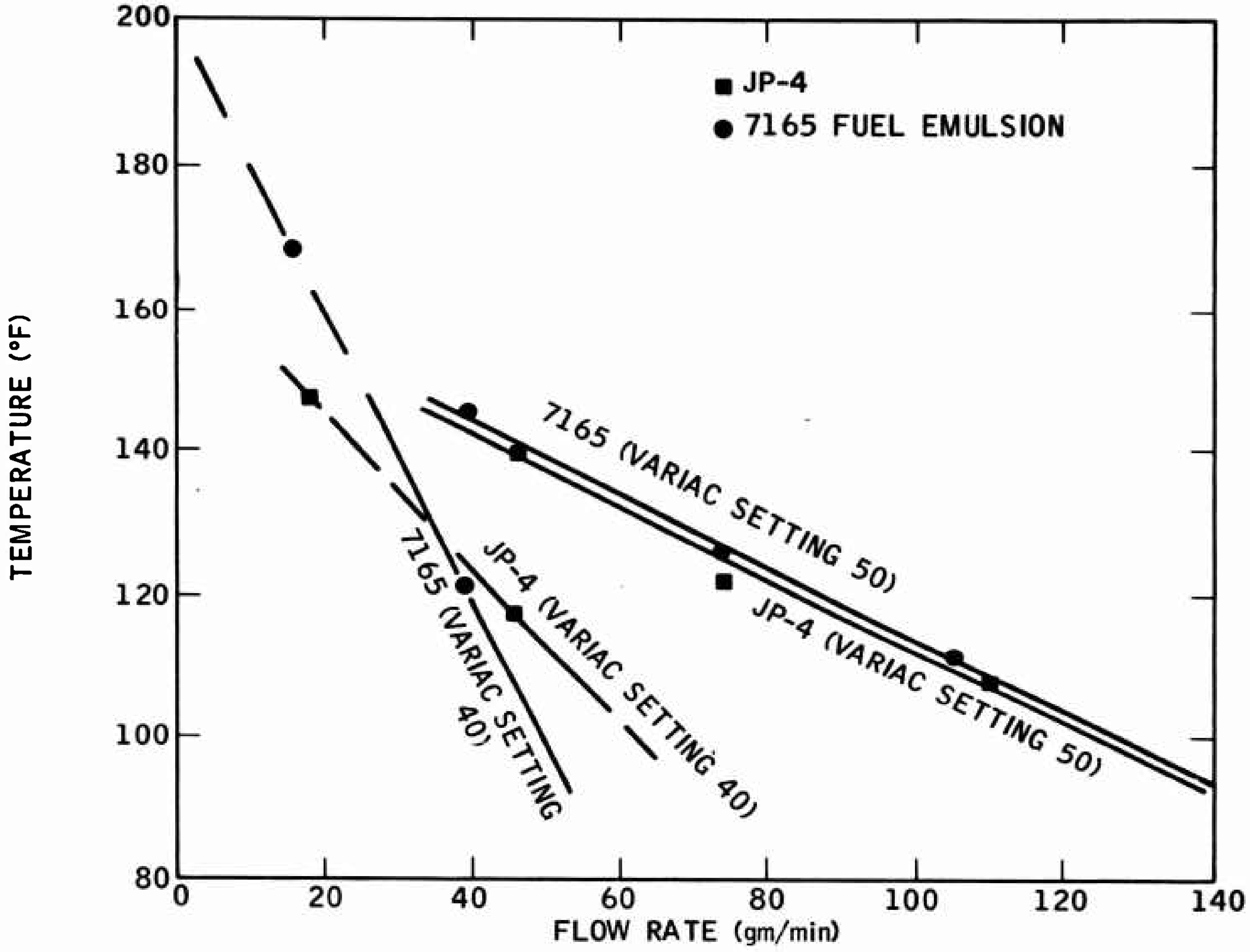


Figure 30. Effect of Flow Rate on Heat Transfer of JP-4 and Emulsified JP-4 (7165).

TABLE 47

HEAT TRANSFER CHARACTERISTICS OF 7165 EMULSION RELATIVE TO JP-4

Fluid	Flow Rate (gm/min)	Variac Setting	Inlet Temp (°F)	Outlet Temp (°F)	ΔT (outlet-inlet)
JP-4	18.3	40	76	147	71
7165 Emulsion	15.0	40	76	170	94
JP-4	44.0	40	76	118	42
7165 Emulsion	39.3	40	76	120	44
JP-4	45.7	50	76	140	64
7165 Emulsion	39.3	50	76	144.5	68.5
JP-4	74.0	50	76	122	46
7165 Emulsion	73.0	50	76	127	51
JP-4	110	50	76	108	32
7165 Emulsion	105	50	76	112	36

Evaporation Loss

Evaporation loss data for the five optimized formulations are shown in Figures 31, 32 and 33. All of the emulsions showed the same extent of evaporation at room temperature, including WSX-7165. At 140°F, emulsions 7165-1 and 7165-4 showed evaporation losses comparable to WSX-7165. Emulsion 7165-5, which has only 0.5% emulsifier, had an evaporation loss at 140°F (Figure 32), which is significantly greater than that of WSX-7165. This effect is attributable to the difference in emulsifier levels for these emulsions and indicates the significantly greater thermal stability for those emulsions containing the higher emulsifier levels.

The most interesting effect was observed with emulsion 7165-2, which had a significantly lower evaporation loss relative to WSX-7165 at 140°F. This can be attributed only to the corrosion inhibitor (TAMA-B-DDSA). For some reason, the interfacial film probably remains quite strong relative to that of WSX-7165 even when the temperature is raised. In any event, this indicates again what strong effects small concentrations of emulsifying agents or corrosion inhibitors have on the properties of fuel emulsions.

Emulsion Lubricity

The lubricity as indicated by four-ball wear results was measured for all five of the optimized 7165 emulsions. The four-ball data are summarized in Table 39. The lubricity is taken as being inversely related to the four-ball wear; i.e., the higher the four-ball wear, the lower the lubricity. The lubricity of the optimized formulations is at least as good as, if not better than, that for WSX-7165 fuel emulsion. The presence of the corrosion inhibitor appears to increase emulsion lubricity. This effect is due to the inhibitor's being adsorbed onto the metal surface and thereby reducing lubricity in the same way as the pressure drop required to pump the emulsions through metal pipes.

Because fuel lubricity is such an important property of the fuel, and our data indicate that this property might be different for the fuel emulsion and JP-4, more work is needed to study the emulsion parameters which affect this important property. Studies carried out on JP-4 have indicated the strong effect of water and trace quantities of various additives on the lubricity of jet fuel (Reference 1). In these studies, water was found to have a very detrimental effect on the lubricity of jet fuel. Because all of the fuel emulsions being evaluated contain water, it is imperative to study the effect of water and other materials, e.g., emulsifiers, corrosion inhibitors, and continuous phase, on the lubricity of fuel emulsions.

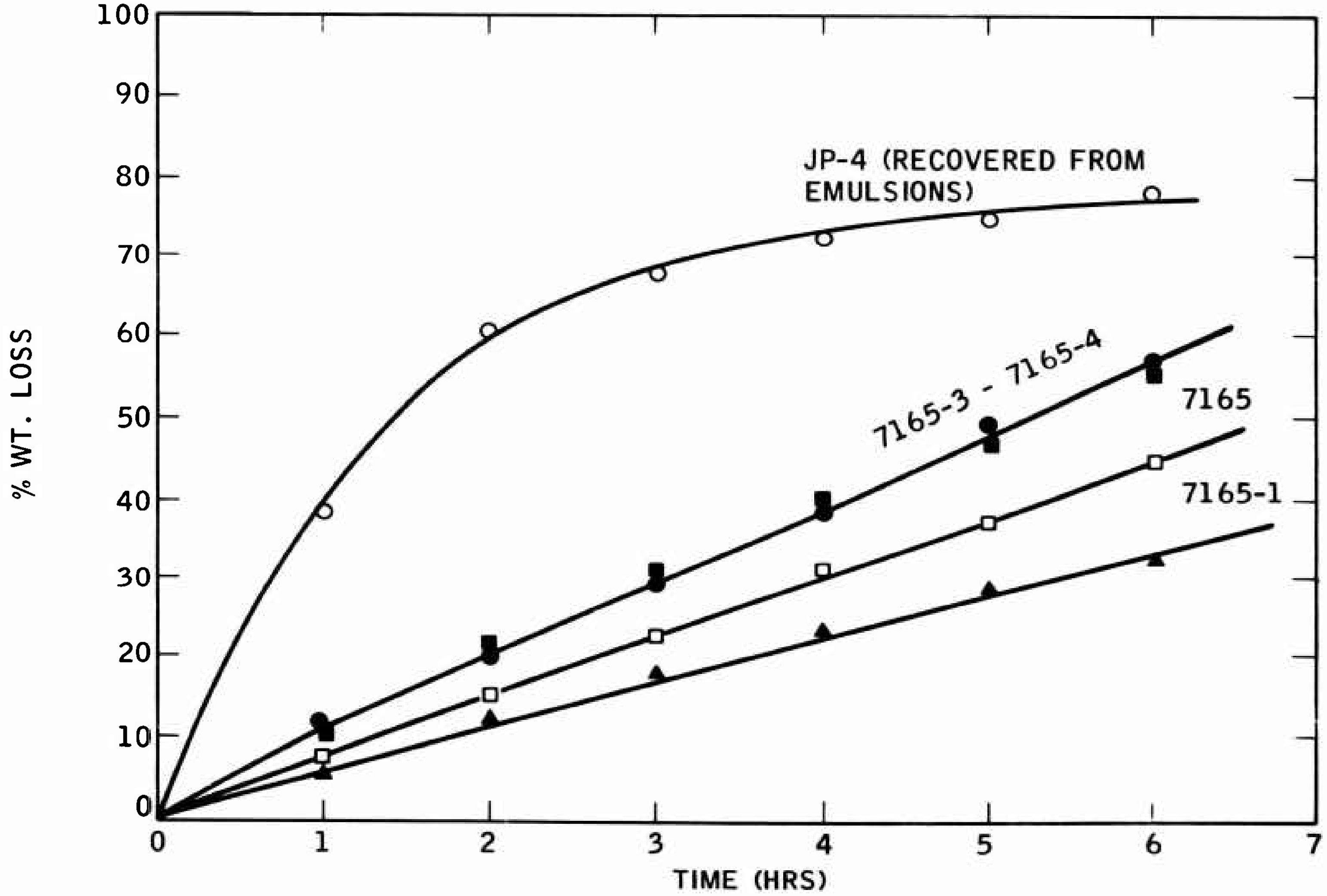


Figure 31. Evaporation Loss at 140°F for Optimized 7165 Fuel Emulsions.

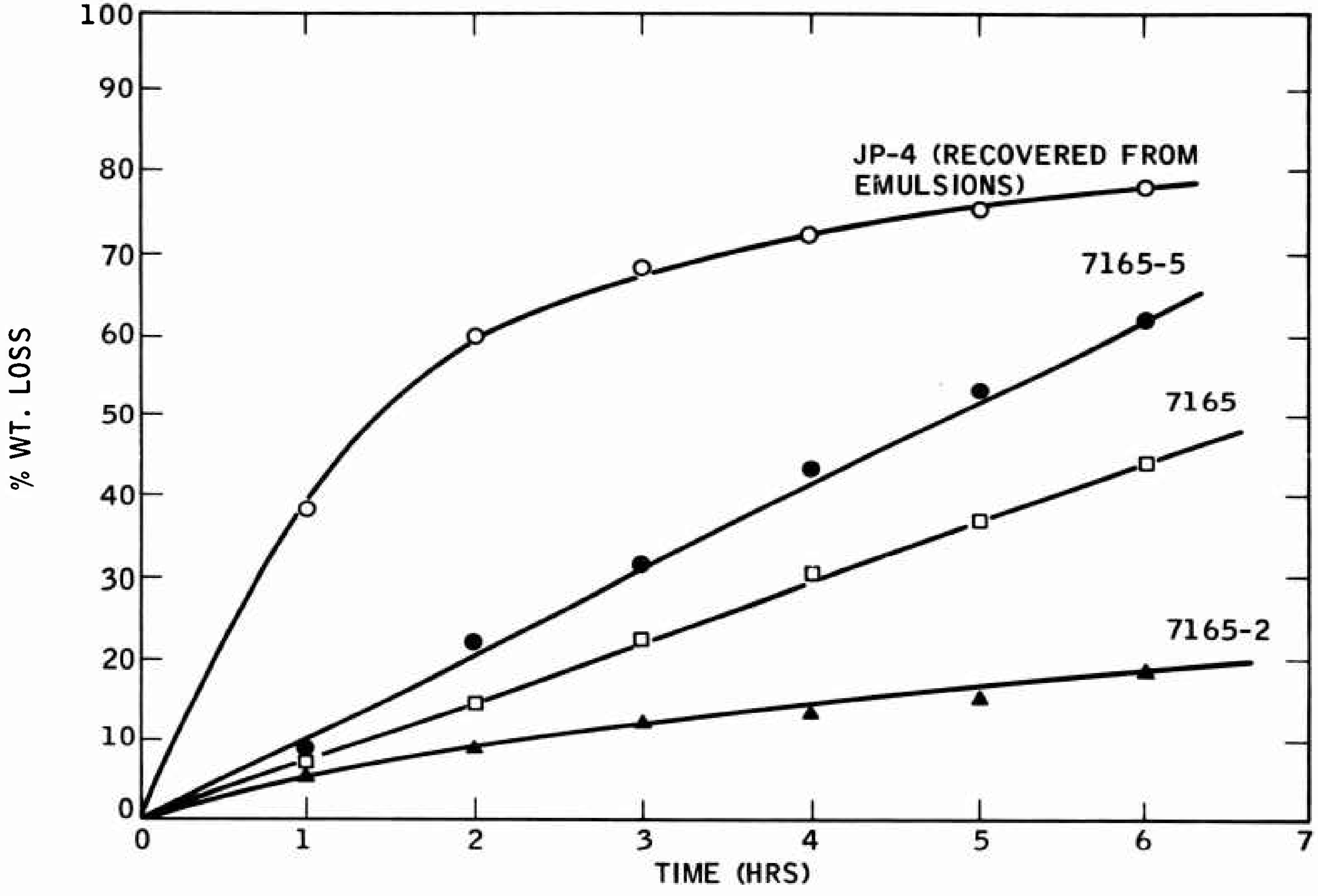


Figure 32. Evaporation Loss at 140°F for Optimized 7165 Fuel Emulsions.

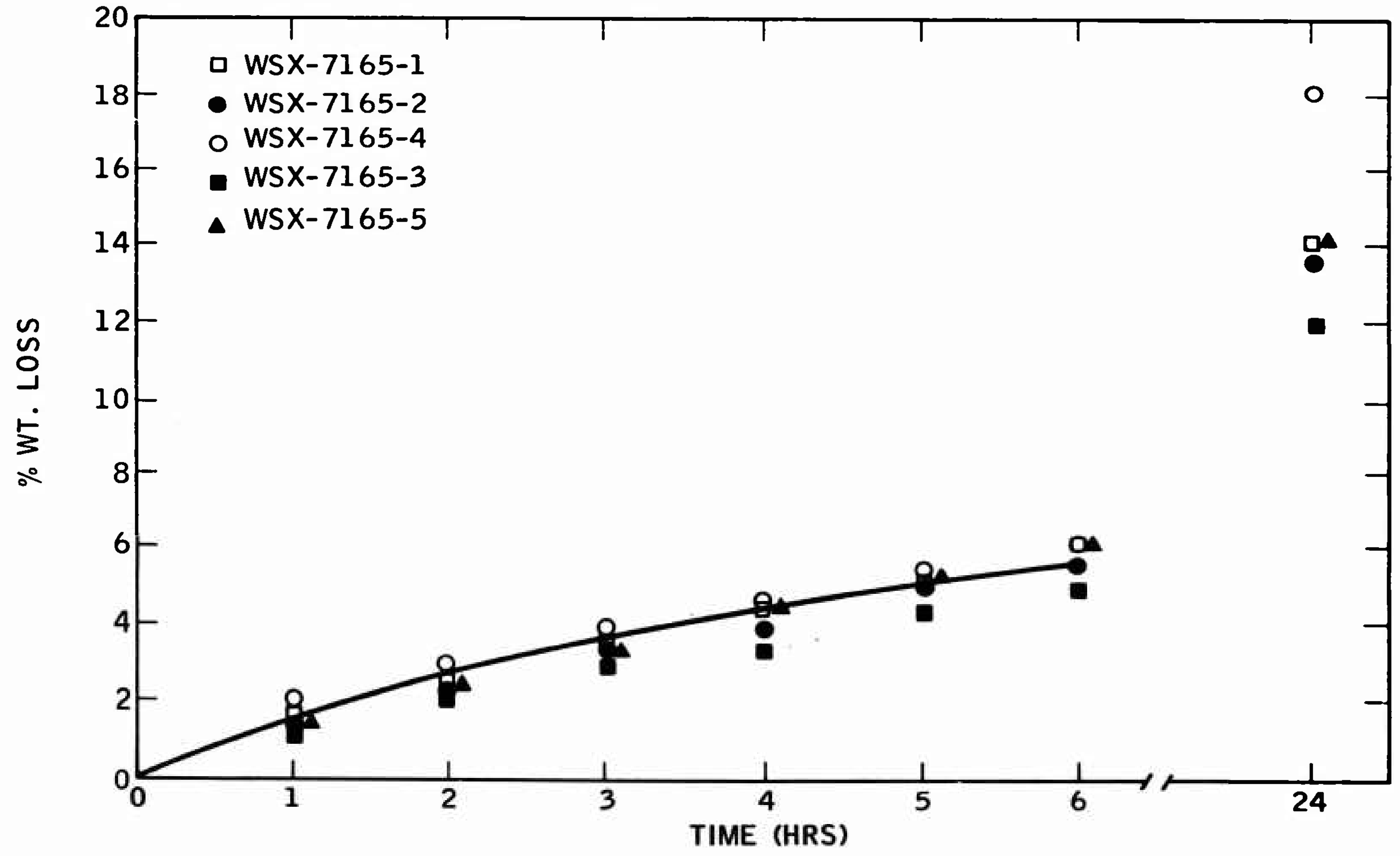


Figure 33. Evaporation Loss at Room Temperature (77°F) for Optimized 7165 Emulsions.

CONCLUSIONS

Five optimized 7165 emulsions have been formulated and characterized. All of these emulsions are more stable to mechanical forces and less corrosive toward mild steel than is WSX-7165. For the four emulsion formulations containing from 0.7% to 1.0% emulsifiers, the optimized formulations have thermal and storage stabilities comparable to WSX-7165.

The heat transfer properties of the emulsions appear to be somewhat poorer than those of JP-4 under the crude experimental conditions investigated.

The optimized emulsions are, in general, compatible with the same elastomers and metals as WSX-7165. As noted above, the optimized formulations are considerably more compatible with mild steel than is WSX-7165.

Pumping studies show that the optimized 7165 emulsions can be pumped with either a centrifugal pump (1700 RPM helicopter boost pump) or a gear pump without breakdown even after the emulsions have aged for 30 days. The emulsions also can be filtered using a 40-micron filter without breakdown.

It has been shown that significantly lower pressure drops are required to pump all the emulsions through Teflon or polyethylene pipes (low-energy surfaces). However, the optimized 7165 fuel emulsions require significantly lower pressure drops than WSX-7165 to pump through pipes of stainless steel.

The lubricity of the optimized 7165 emulsions appears to be better than that for WSX-7165. The data indicate that this is due to the corrosion inhibitor that the optimized formulations contain. However, because of the effect of water and other polar constituents even at trace levels on the lubricity of jet fuel, more work is needed to assess the effect of these materials on the lubricity of fuel emulsions.

VII. CONCLUSIONS

Based on the results obtained in this program, the following conclusions can be made:

1. Several optimized 7165 fuel emulsions have been formulated and characterized which are more stable to mechanical forces than is WSX-7165. They represent improvements over WSX-7165 in that they are compatible with mild steel and stable to pumping with either centrifugal or gear pumps.

2. The addition of corrosion inhibitors and small quantities of water improve the overall stability of 7165 type emulsions, the greatest effect being on their low-temperature stability and their stability to mechanical forces, e.g., to vibrational forces and pumping.

3. Stable formulations of 7165 can be made which contain as little as 0.5% emulsifier provided the emulsions contain at least 0.5% water. Such emulsions, however, have an equilibrium yield stress less than 1000 dynes/cm^2 and would, therefore, not be suitable safety fuel candidates.

4. Emulsion conductivity is a good measure of degree of dispersion for 7165-type fuel emulsions. This appears to be related to emulsion stability, e.g., stability at low temperatures and stability to mechanical forces.

5. Emulsifier concentration is the dominant factor which determines the breakdown characteristics of the fuel emulsion.

6. Emulsions having a yield stress <1500 dynes/cm^2 exhibit combustion properties comparable to those of JP-4.

7. The use of an air-assist nozzle significantly improves the combustion efficiency of high yield stress emulsions (>1500 dynes/cm^2).

8. The fuel emulsion is broken as it enters the nozzle, and no further breakup occurs after the emulsion has left the nozzle.

9. At high atomization pressures (>125 psig), in the capillary rheometer, the fuel emulsions are atomized to about the same degree as JP-4. At low atomization pressures, however, fuel emulsions are poorly atomized relative to JP-4.

VIII. RECOMMENDATIONS

The following recommendations are made as a result of this program:

1. Because emulsion 7165-1 has improved mechanical stability and corrosion properties relative to WSX-7165, it is recommended that emulsion 7165-1 be used for immediate future evaluations until further data indicate otherwise. This particular formulation is further recommended because its formulation represents the least departure from formulation WSX-7165.

2. It is recommended that emulsion 7165-4 be considered as a backup emulsion to emulsion 7165-1 because of its good corrosion properties and because it contains less emulsifiers. The latter should be quite advantageous from the combustion standpoint.

3. Because the effect of yield stress on emulsion safety has not been established, it is recommended that two of the emulsions (yield stresses 1500 dynes/cm^2 and 5000 dynes/cm^2) be evaluated in crash tests.

4. Because emulsion conductivity appears to be a good parameter to relate to emulsion quality, it is recommended that further work be carried out to quantify the relationship between emulsion conductivity and emulsion quality.

5. Because emulsion properties, e.g., lubricity, conductivity, and cleanliness, must be measured quickly and accurately, it is recommended that work be carried out to develop tests to measure these key properties.

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APPENDIX

EXPERIMENTAL TEST PROCEDURES

1. Yield Stress - Emulsion yield stress was determined using modified ASTM Method D-217. The yield stress via this method simply equals the cone assembly weight over the wetted cone area.

2. 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 small glass jar using metal tongs. The metal was completely immersed in the emulsion,and the jar was capped and stored at 140°F for 1 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 steel wool, washed with alcohol to remove products of corrosion, and then weighed. The data were presented as weight loss per square inch.

3. 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 140°F for 1 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 percentage of weight increase.

4. Four-Ball Wear - The lubricity as measured by the four-ball wear test was determined by ASTM test D2266. The test conditions were 7.5 Kg, 130°F, and 1800 RPM for 1 hour.

5. Evaporation Loss - To measure evaporation loss, 100 grams of the emulsion was added to a petri dish that was 5 inches in diameter and 2-1/2 inches deep. The emulsion was spread out smoothly to cover the bottom of the dish. The dish was then stored either in the oven (forced air) at 140°F or at room temperature. The weight loss of the sample was followed as a function of time. The results were reported as percentage weight loss.

6. Current Flow - Current flow was measured 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 in the emulsion to a depth of 6 inches.

7. Vibration Stability - Vibration stability 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 yield stress of the emulsion was measured before and after the test. If any emulsion breakdown occurred, the percentage of breakdown was determined and reported.

8. Pumping Tests - In these tests, a Zenith gear pump connected to a variable speed gear was used to determine the effect of pumping on emulsion breakdown.

To determine the effect of pumping the emulsions with a centrifugal pump, a 7100-rpm helicopter boost pump was used. Both tests were once-through operations, and the emulsions were collected and the percentage of breakdown, if any, was determined.

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13. ABSTRACT

This report summarizes the work aimed at the optimization of two nonaqueous fuel emulsions, WSX-7165 and WSX-7063, to improve their quality for possible use in gas turbine engines. Several optimized fuel emulsions that meet the initial established contractual requirements were formulated and characterized. These fuel emulsions are stable under a variety of conditions, ranging from -65°F up to at least 140°F. The emulsions are compatible, in general, with the same elastomers and metals of construction as the WSX-7165 fuel emulsion. In addition, the optimized emulsions are also compatible with mild steel. The combustion and rheological behavior of the optimized emulsion formulations was also investigated. At high atomization pressures, the combustion efficiency of the emulsions approaches that of JP-4, provided the emulsion yield stress is less than 1500 dynes/cm^2. It was also found that the presence of corrosion inhibitors has a profound effect on the combustion behavior of these emulsions.

It is concluded on the basis of this program that burning of the safest possible fuel emulsions directly in turbine engines will require certain fuel system modifications. The hardware changes envisaged will have to involve systems which will aid the breakdown of the emulsion in or prior to the nozzle. This will be required for improved performance at the low atomization pressures involved during engine idling.

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Air-Assist Atomization						