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A STUDY OF THE EFFECTS OF  
DETERGENTS ON TYPICAL BILGE WATERS  
AND CORRELATION OF OIL PARTICLE SIZES

U.S.C.G. REPORT CG-D-177-75 - A STUDY OF THE EFFECTS OF DETERGENTS ON TYPICAL BILGE WATERS AND CORRELATION OF OIL PARTICLE SIZES



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*W. L. King*

W. L. KING  
Captain, U. S. Coast Guard  
Chief, Environmental and  
Transportation Technology Division  
Office of Research and Development  
U. S. Coast Guard Headquarters  
Washington, D.C. 20590

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16. Abstract Oil removal systems for treating bilge water are drastically affected by the condition, composition, and character of the incoming bilge water-oil mixture. The presence of various detergents and cleansers causes emulsification of hydrocarbon products already present. The extent of emulsification caused by synthetic detergents on eight oils was studied at a fixed agitation rate and intensity as a function of detergent type (cationic, anionic, or non-ionic) and concentration as well as temperature, pH and salinity of the continuous (external) phase (distilled water). Laboratory test emulsions were generated using ultrasonic agitation, coupled with high speed non-aerating dispersion to simulate the type of emulsions produced by action of a centrifugal pump. A HIAC Particle Counter was used to determine the amount of oil emulsified. The conclusions indicated that: (1) Detergents with cationic-active ingredients would promote a higher degree of emulsification than those with non-ionic or anionic type surfactants. (2) The amount of oil emulsified under fixed agitation rate and intensity and fixed oil concentration does not increase proportionally with increasing detergent concentrations. (3) The concentration of emulsified oil tends to approach a nearly constant value with increasing detergent concentration. (4) At low concentrations of detergent, 100 ppm, the effect of some detergents seems to be one of de-emulsification. An appendix is included in this report covering a correlation of particle size data generated by a number of investigators.			
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### LIST OF ABBREVIATIONS

CMC	-Critical Micelle Concentration
$\bar{d}_v$	-Volumetric mean diameter
D.O.C.	-Dispersed oil concentration
$\mu$	-microns
mg/l	-milligrams per liter
NDO	-Navy Distillate Oil
NSFO	-Navy Special Fuel Oil
O/W	-Oil in water emulsion
ppm	-parts per million
PSD	-Particle size distribution
Syndets	-Synthetic detergents
TOM	-Trace Oil Monitor

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## 1.0 INTRODUCTION

### 1.1 Statement of Problem

A concerted effort is currently being expended by various government agencies and laboratories to develop efficient oil removal systems for treating discharged bilgewaters. The oil-removing efficiency of any oil-water separator is grossly affected by the condition of the incoming bilge-water-oil mixture. Under most circumstances the oil in the bilge usually has sufficient residence time to naturally separate from the water (ship in port) or else is only loosely emulsified (ship at sea) thereby presenting little difficulty in removal from the bilge water during or prior to discharge.

However, all bilges are usually collection points for other various and sundry liquids which find their way into the bilge spaces. Of great interest would be any rinse or wash waters generated during clean-up operations and it is likely that various detergents and cleaners would be used to "cut" grease and oily matter from machinery, decks, bulkheads, etc. and this highly emulsified liquid would find its way into the bilge spaces. These detergents and cleaners would then react with or emulsify to some extent any of the hydrocarbon products already present, especially when this mixture has to be pumped. These more stable detergent-oil-water emulsions would then have an adverse effect on the efficiency of the bilgewater oil removal system and/or would increase the maintenance schedule of the system. For example, it has been shown that some coalescing filter cartridge type separators are disarmed by detergent<sup>1</sup>. That is, upon exposure to detergents, the filter fibers lose their ability to coalesce oil. The exact phenomenon is not known but it is suspected that the surfactants change the oleophilic (oil-loving) characteristics of the fiber surface to a more oleophobic (oil-hating) condition.

Therefore, since elimination of the use of detergents and cleaning compounds on board ship is not practical, it would be desirable to specify those formulations having minimum effect on separators and monitoring equipment. For that reason, this study focused on pure synthetic detergents and high-molecular weight polymers, as well as several commercial formulations of interest.

### 1.2 Purpose of Study

This study had a four-fold purpose. First, this study was conducted to measure the effect which a group of selected detergents and cleansers have on various oils under controlled conditions by making particle size distribution and population measurements. These data then allowed calculation of oil volume emulsified (dispersed) as a function of detergent type and concentration.

Second, a study was also made into the effects of various high molecular polymers, used to reduce fluid friction in pipes, on oil particle size distribution.

Third, the scope of this program included testing the effects of detergents on the performance of the breadboard oil-in-water monitor, being developed at General Electric under contract DOT-CG-32370-A.

Fourth, during the proposed program, a study of selected existing data on oil particle size distribution and analysis was conducted. In order to better correlate these data, it was proposed to convert the data to some common base. It would then be possible to more directly compare the results of these previous investigations. In this way a more complete understanding of small oil particle generation and behavior under various conditions of agitation rate and intensity would be possible and would be of great value to later investigations. Applicable data from the first phase of this study was also included in this correlation.

### 1.3 Intended Applications

The test results were expected to show which detergent-cleanser formulations could be predicted to produce highly stable emulsions in bilge-waters. From this data, it was hoped that it would be possible to specify those formulations which would have minimal effect on bilgewater separator performance. Finally, the data might make it possible to specify new "tailored" formulations which would have minimal effect on bilgewater separator systems.

## 2.0 TECHNICAL DISSERTATION

Detergents and cleansers can be chemically classified as to their mode of allowing oily matter to be rinsed or washed from various surfaces and suitably dispersed by or into water. The term water herein is meant to include fresh, salt and brackish-type waters. The term detergent, by definition, formerly meant a substance or mixture which has a cleansing action due to a combination of properties including lowering of surface tension, wetting action, emulsifying and dispersing action and foam formation. Ordinary soap is the best known example. However, the word detergent is now coming to mean the synthetic variety, in distinction to "soap" which is derived from natural fats and oils. Synthetic detergents, according to reference 2, are materials which have a cleansing action like soap but are derived directly from substances other than the natural fats and oils. Synthetic detergents are surface-active agents which have structurally unsymmetrical molecules containing both hydrophobic groups and hydrophilic hydrocarbon chains.

There are three main types of detergents:

- (1) Anionic detergents form negatively charged ions containing the oil-soluble portion of the molecule, the ionizable group is the hydrophilic portion. Soap is an example of this class and the synthetic members of this class are sodium salts of organic sulfonates or sulfates.
- (2) Cationic detergents or invert soaps, ionize so that the oil-soluble portion is positively charged and the principle examples are

quaternary ammonium halides. Outstanding germicidal activity overshadows the detergent applications of this type which accounts for only about 10% of the total synthetic detergent production in the United States.

(3) Nonionic detergents do not ionize but acquire hydrophilic character from a oxygenated sidechain usually poly-oxyethylene. The oil-soluble part of the molecule may come from fatty acids, alcohols, amides or amines. By suitable choice of the starting materials and regulations of the length of the polyoxyethylene chain, the wetting, foaming or detergent properties of the nonionic may be greatly varied. Furthermore, they can be used in combination with either anionic or cationic detergents.

In commercial formulations the variations depend on the intended application. This is evidenced by the wide variety of products one finds on the shelves of any supermarket or automotive supply store. Regardless, all detergents are made of some variation of the three basic types of detergents, i.e., anionic, cationic, nonionic species; however, they also include perfumes, optical brighteners, soil-suspending agents, moisturizers, etc. A typical heavy-duty detergent might consist of 20% organic surfactant, 45% phosphate detergent builder, 25% sodium sulfate, silicate, other organic builders and 10% of the miscellaneous matter mentioned above. The purpose of this study has been to examine more closely the behavior of each specific detergent class using three of each type. As will be pointed out later, the study utilized a select number of oil types which might be found in a typical bilge and two crude oil types which might be found in a cargo tank during tank cleaning operations. A complete description of the test matrix will be presented later.

## 2.1 Basic Emulsion Theory

"An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another liquid in the form of droplets, whose diameters, in general, exceed  $0.1\mu$ . Such systems possess a minimal stability, which may be accentuated by such additives as surface-active agents, finely-divided solids, etc." (p.2 reference 3)

Also (from pp. 2-3, reference 3), in discussing emulsions, it is necessary to distinguish clearly each of the two liquid phases present. The phase which is present in the form of droplets is called the disperse or internal phase; the phase in which these droplets are suspended is called the continuous or external phase.

When two immiscible liquids are in contact with each other, the free energy between them at the lowest possible level is when one (oil) is simply a layer on the other (water) in some containing vessel (bilge). This free energy is a function of the surface or interfacial tension of each liquid against the other, usually expressed in dynes/cm. If the one liquid (oil) becomes a disperse phase in the other (water) continuous phase or vice versa, the interfacial free energy increases with the increase in area of contact between the two phases. The smaller the droplets in the disperse phase

(increase in area) the greater the free energy present. Since such systems tend toward a minimum free energy, processes which lower interfacial area and free energy, such as flocculation and coalescence, will tend to occur.

Flocculation and coalescence are the result of instability, however, emulsion stability improves with the presence of additives; surface-active agents (such as synthetic detergents), finely divided solids, etc. as stated previously. In certain cases, an additive in either phase may affect the stability by changing the interfacial tension.

Another phenomenon which can be measured and which indicates the stability of an emulsion is that property known as the Zeta Potential. The Zeta Potential is the electrical potential at the plane of shear between the mono-layer of charged particles adsorbed on the droplet (the Nernst layer), and the bulk of continuous phase. If the oil droplets, in the case of interest, become charged, by adsorption of surfactant ions for example, the droplets will repel each other whenever they tend to collide (like charges repel) and flocculation/coalescence will not readily take place. When the Zeta Potential (ZP) is above -40 millivolts, the emulsion (suspension) is expected to show good stability and emulsions with ZP of -80 to -125 millivolts would show maximum stability.<sup>4</sup>

## 2.2 Surface Activity

The effect of surface active materials on interfacial tension and/or zeta potential within an emulsion system is quite striking (a surface-active agent is defined as any substance which shows a marked tendency to adsorb at a surface or interface). Experiments have shown that surface-active agents such as 0.001 Molar ( $\sim$ 300 ppm) sodium oleate, can reduce interfacial tension by a factor of 4,000, or from a stability standpoint, the surfactant would produce a more stable emulsion.

Bulk properties (those of the emulsion as a whole) of solutions of surface active compounds are also quite unusual with increasing surfactant concentration. Conductivity values show a deviation towards increased conductivity, while colligative or osmotic properties decrease. One postulation which explains why these phenomena occur and which relates surface to bulk properties is the micelle theory, advanced in 1925 by J. W. McBain. (p. 36-37 reference 3)

As background for the micelle theory, it was recognized that surface active molecules are characterized by the presence of a polar group (which has high affinity for other polar groups and molecules, including water) and a non-polar group which has a low affinity for water. In an aqueous solution of a surfactant, minimum contact between the non-polar groups of the surfactant molecules and water molecules is accomplished by a clustering of surfactant molecules so that the non-polar groups are in contact with each other, yet are surrounded and hidden by the polar (hydrophilic) groups of the surfactant molecules.

### 2.3 Properties of Oil/Water Mixtures Containing Surfactants

Simply stated, the existence of micelles would account for the behavior of surfactant solutions mentioned. That is, the reduction of the total number of particles (ions or undissociated molecules) by micelle formation would account for non-ideal behavior with respect to colligative and similar properties. Furthermore, micelles would be more electrically conductive than in the unassociated form.

Aqueous solutions of surfactants also generally exhibit a marked change in their physical properties over a rather narrow surfactant concentration range. This rapid change is thought to be due to micelle formation; the surfactant concentration at which micelle concentration suddenly becomes appreciable is referred to as critical micelle concentration (CMC). At concentrations greater than CMC, surface tension of the solution does not decrease further with an increase of surfactant concentration. Foaming and detergency often are at a maximum at the CMC, although ability of surfactant solutions to "solubilize" water-insoluble materials (oils) starts at CMC and increases with concentration of micelles. That is, as long as sufficient surfactant is present to completely cover each oil droplet generated, the oil will be "solubilized" or emulsified. Below CMC, the oil droplets will tend to flocculate and coalesce because of incomplete coverage of surfactant on each oil droplet.

The value of CMC of ionic surfactants is also affected by the presence of salts or polar compounds, structure of surfactants, and temperature. Salts lower the CMC value with the amount of depression governed by the concentration of ions in the water of opposite charge to that of the surface-active molecules. This has been explained earlier as due to the micelle substantial surface charge density compared with single ions in solution. Repulsion between ions and micelles of the same charge produce a greater separation than between ions of the same charge. Ions of opposite charge to micelles are more strongly attracted.

When oil/water mixtures containing surfactants are mixed or agitated by some means the micelles which form have the non-polar portion attached to the oil droplets and the polar end faces out in an oil/water emulsion, and the opposite if a water/oil emulsion forms. At certain oil/water ratios, it would also be possible to obtain both types of emulsions, both of which could be extremely stable. In bilge applications, it has been shown that at oil concentrations approaching 1% and above it is highly likely that the water/oil emulsion (or reverse emulsion) will begin forming. This is usually the cream inversion one sees at the interface between separated oil and the water.

### 2.4 Emulsion Behavior

It has been recognized for a long time that most good emulsifying agents were surface active materials, or materials which have a marked tendency to adsorb at the oil/water interface. Hence, the surfactant will affect the

interfacial tension. The significance of this, in emulsion formation/stability can be shown in the following example (See p. 96. Reference 3). If ten cubic cm of olive oil is dispersed into droplets of 0.1 $\mu$  radius, the total interfacial area created is 300 sq. meters. The interfacial tension of this oil against water at 20°C is 22.9 dynes/cm. The work required to do this would be 1.64 gram - calories. The work necessary to emulsify 100 pounds (45,400 gms) of olive oil would be 8.09 Kilogram - calories (Kg-cal.); this represents a substantial amount of potential energy stored in the system and hence a considerable degree of thermodynamic instability, as described in Section 2.1, Basic Emulsion Theory.

If the same amount of olive oil was emulsified in a 2% soap solution, the work required (or the interfacial energy) would be only 0.75 Kg-cal, as the soap would reduce interfacial tension to as low as 2 dynes/cm. Although this lowering of surface tension is significant, it is not the only factor in explaining stabilizing effects of emulsifying agents since other non-surface active materials (gums, fine solids) are also effective stabilizers.<sup>1</sup>

The depression of interfacial tension implies that the emulsifier is concentrated at the interface, forming an interfacial film which has a stabilizing influence. In the presence of emulsifiers (compared with the simple oil/water emulsion), collisions between dispersed droplets will result in flocculation/coalescence less frequently, due to the protective interfacial film covering the many droplets. The same protection can be provided by gums which would form a mineral coat on the surface. Of course, combinations of any of the above phenomena would also contribute to the stability of an oil/water emulsion and all are likely to occur in a ship's bilge.

Regardless, dispersed liquid droplets will eventually tend to coalesce since the interfacial energy must be dissipated. One way to decrease this energy is to reduce the interfacial area and this is accomplished by flocculation and coalescence. The interfacial energy is at a minimum when dispersed droplets have finally coalesced into one large liquid mass. Hence, given sufficient time varying from seconds to years, an emulsion will eventually revert to two continuous phases separated by a single interface.

This occurs due to three inter-related forms of instability: sedimentation, flocculation and coalescence. Since the dispersed oil droplets are usually of lower density than the continuous phase, they will tend to accumulate at the top of the emulsion. Rise rate depends upon density difference between the two phases, particle size, and viscosity of the continuous phase (Stoke's Law). Rise velocities, given by Stoke's Law are frequently quite low and essentially negligible for most oil drops smaller than ten microns.

Flocculation is agglomeration of dispersed droplets into a loose cluster, in which particles retain individual character. Forces responsible for this process are London-vander Walls attractive forces. Effective particle size is increased when flocculation occurs, hence increasing oil droplet rise rate.

<sup>1</sup> Emulsions: Theory & Practice, page 96

Flocculation probably occurs even in emulsions stabilized by emulsifying agents especially if the interfacial film on the droplets is incomplete. Dispersed droplets may meet at the points which are not covered with adsorbed emulsifier, flocculate and rise out of the bulk solution. By definition, an emulsion is not considered "broken" unless coalescence follows flocculation since flocculated particles are easily redispersed by mild agitation. Coalescence is generally the slow step in the process of emulsion breaking, thus the rate of coalescence determines emulsion stability.

It is generally recognized that the interfacial film of an adsorbed emulsifier on dispersed droplets is the barrier which prevents coalescence. If displacement of an adsorbed emulsifier layer at the interface occurs, or droplets have incomplete monolayer coverage, coalescence may proceed. Unlike flocculation, coalescence is irreversible. So the stability of an oil/water emulsion is dependent on many factors and depends on complex interactions even under ideal laboratory conditions. The complexity increases by orders of magnitude when one considers the complexity of waste water produced in a ship's bilge.

The foregoing is a rather simplified discussion of the complexity of small oil particle behavior in water where other additional substances present in minute amounts can grossly affect the behavior of the oil particles. Many volumes have been written on the subject of emulsions and a great deal of energy (dollars) has been and will always be expended to produce stable emulsions (figuratively and literally). This study has been more concerned with gross overall effects of detergents on the amount of dispersed or emulsified oil generated under controlled conditions. The emulsion stability is of interest for the short time span of minutes not months or years as is the concern in the commercial aspects of emulsion technology. This technology area is extremely complex and an understanding of some of the theories behind emulsion behavior was felt to be in order.

### 3.0 EXPERIMENTAL PROCEDURE

#### 3.1 Emulsion Preparation and Stability Discussion

Emulsion study and experimentation does not lend itself to simple procedure. Preparation of emulsions where all of the oil is completely dispersed into some finite particle size range is a monumental task in itself. Even as the oil passes into the agitation zone of a centrifugal pump, the emulsion formed immediately upon the exit of the zone is undergoing coalescence because of the high collision rate and energy of the system. Going back one step, the amount of oil which is emulsified at the impeller blades is a function of the oil break-up rate versus the re-coalescing rate. Because of the very short residence time in the agitation zone, it is not surprising that only small amounts of the oil become emulsified (dispersed). Previous investigators have found that a simple centrifugal pump, usually thought to produce a high degree of emulsification, actually emulsifies only about 5% of the input oil concentration.

When an emulsion or more correctly, dispersed mixture, is allowed to settle after agitation, the mixture will not be completely stable. Droplets larger than 15-25 microns, obeying Stoke's Law, will rise, and these plus other smaller droplets will be colliding or flocculating and coalescing to varying degrees, depending on existing physical and chemical conditions. This partly describes the so-called "instability" of the mixture. Finally, after some time, minutes to hours or even days, a more stable condition exists. At some point in time the experimenter must make his measurements in order to attempt to relate his finding to some earlier time or time zero.

In this study it was felt that a settling time of two minutes after agitation was terminated would be a suitable point in time to take a representative sample of the mixture for measurement. In a practical sense, this two minute interval is about the residence time in an oil/water separator downstream of the pump (agitation source). Since the analytical process also required some time span, the data reported was actually obtained three minutes later or at T+5 minutes.

Because of the instabilities of oil/water emulsions, a series of measurements were also made over 2-3 minute intervals up to T+45 minutes to determine whether the representative sample itself was undergoing any significant changes during the analysis in the instrument. The results of these longer count time measurements will be discussed later.

#### 3.2 Selection of Detergent Candidates

Since one of the main points of interest in this study involved basic detergent ingredients, a number of pure surfactant compounds were obtained from chemical manufacturers. Those companies which supplied chemicals for this study are listed in Table 3.1. From a total of fifty-two detergents submitted, twelve were selected for testing: three of cationic type, three of anionic type, three non-ionic type, and three commercial types. These three classifications of syndets, plus three commercial products were included in order to evaluate detergent effect as a function

TABLE 3.1

CHEMICAL MANUFACTURERS

SUPPLYING DETERGENTS

COMPANY

E. I. Dupont deNemours and Co.  
Crompton and Knowles Corporation  
Rohm and Haas Company  
American Cyanamid Company  
Wyandotte Chemical Corporation  
Atlas Chemical Industries  
Shell Chemical Company  
Monsanto  
Retzloff Chemical Company  
Witco Chemical Company  
Jefferson Chemical Company  
Lever Brothers

of chemical nature. The three representative compounds selected in each classification, however, were different formulations (Table 3.2) in an attempt to investigate as many surfactants as possible. Three high-molecular weight polymers were included as a special case for study. A mixture of surfactants was also to be formulated and evaluated, but additional study of a few of the selected surfactants was deemed more necessary especially in observing their effect at higher concentrations.

### 3.3 Basic Technique Description and Test Parameters

Particle count and size measurements were made on all the test emulsions to evaluate the effect of synthetic detergents on oily water mixtures, with respect to the amount of dispersed oil in the presence of detergent, and stability of the oil-water-detergent emulsion. From this data, the particle size distribution and volume of oil dispersed within a given size range was obtained. By comparison of data obtained for baseline dispersions of test oils in distilled water containing no detergent with that of mixtures of oil, water, and detergent, the detergent effect on oil emulsification could be determined.

To more completely establish the effects of syndets on oil-water emulsions, several different water conditions were also investigated. For this part of the study, emulsions were also generated in salt water (50% salinity), in slightly acidic (pH 6) and slightly alkaline (pH 8) conditions, and at a high temperature (120° F), ambient (73° F) and cold temperatures (40° F).

In studying these oil-water-detergent mixtures, as they would apply to bilge water, the oil type was also taken into account. Since bilges are a collection point for various oils and wash waters, eight separate oil types were included for testing.

### 3.4 Preliminary Test Parameter Investigation

The original test matrix proposed each oil type input concentration of 5000 parts per million (ppm) to be agitated with each detergent in concentrations of 0, 50, 250, and 1000 ppm; and concentrations of 10, 50, and 250 ppm high molecular weight polymers with three selected oils. The mixtures were to be generated using a high speed non-aerating dispersator, and particle size distribution (as population) obtained by recording particle count taken with a HIAC particle counter, every minute after a two minute settling period for five minutes, then a last reading at ten minutes after the settling period, see Table 3.3.

Perhaps the most difficult, and also the most crucial procedure was the preparation of laboratory emulsions which were of reproducible size distribution and Concentration. The proper agitation and dispersion was one which approximated that produced by a centrifugal pump, since the purpose of this work was to study oily water emulsions similar to those of bilge water subjected to centrifugal pump agitation. Previous investigators have shown that only about 5% of an input oil concentration of 1% is emulsified into droplets of diameters less than ten microns on one pass through an Ingersoll-Rand centrifugal pump operating at 60 psi and 50 gpm. <sup>5</sup>

5 Foster-Miller "Laboratory Evaluation of the Emulsifying Characteristics of Pumps" Contract DOT-CG-24287-A

TABLE 3.2

DESCRIPTION OF SELECTED DETERGENTS USED IN THIS STUDY

	<u>TRADE NAME</u>	<u>CHEMICAL FORMULATION</u>
<u>ANIONIC</u>	Klearfac AB-270	Mono substituted ortho-phosphate ester
	Alkanol 189-S	Sodium alkyl sulfonate
	Aerosol OT-75	Dioctyl ester of sodium sulfo succinic acid
<u>CATIONIC</u>	Product BCO	C-type cetyl betaine
	Aerosol C-61	Ethanolated alkyl guanidine amine complex
	Retarder LAN	Quaternary ammonium compound
<u>NON-IONIC</u>	Intravon SO	Mixture of surfactants especially effective for removal of oil and grease
	Triton X-100	Octyl phenoxy polyethoxy ethanol
	Span 80	Sorbitan mono-oleate
<u>HIGH M.W.</u>	Pluradot HA510	Polyoxyalkylene glycols
	Pluronic L 101	Condensate of ethylene oxide with hydrophobic bases formed by condensing propylene oxide with propylene glycol
	Merpol SH	Higher fatty alcohol - SH ethylene oxide condensate
<u>COMMERCIAL</u>	Concentrated All	
	Rirso	
	Zif	

TABLE 3.3

PRELIMINARY STUDY OF DISPERSION METHODS

A: 5000 ppm Marine Diesel Kraft Model S-30 Dispersator at 3000 RPM  
For 2 Minutes; Particle Counts/ml After 2 Minutes Settling Time

	<u>2-5 <math>\mu</math></u>	<u>5-10 <math>\mu</math></u>	<u>10-20 <math>\mu</math></u>	<u>20-40 <math>\mu</math></u>	<u>40-60 <math>\mu</math></u>
1 min after	118	16	3	0	0
2 min after	153	15	5	0	0
3 " "	196	20	4	0	0
4 " "	193	24	2	0	0
5 " "	208	21	2	0	0
10 " "	214	17	4	0	0

B: 5000 ppm Marine Diesel Kraft Model S-25 Dispersator at 1000 RPM  
For 2 Minutes; Particle Counts/ml After 2 Minutes Settling Time

	<u>2-5 <math>\mu</math></u>	<u>5-10 <math>\mu</math></u>	<u>10-20 <math>\mu</math></u>	<u>20-40 <math>\mu</math></u>	<u>40-60 <math>\mu</math></u>
1 min	216	17	6	0	0
2 "	315	17	3	0	0
3 "	366	22	4	1	0
4 "	375	32	7	1	0
5 "	335	22	4	0	0
10 "	419	32	5	0	0

TABLE 3.3 (cont'd.)

C: 5000 ppm Marine Diesel S-25 Stirrer at 6000 RPM For 1 Minute  
2 Minute Settling Time

Particle Counts/Ml

	<u>2-5 <math>\mu</math></u>	<u>5-10 <math>\mu</math></u>	<u>10-20 <math>\mu</math></u>	<u>20-40 <math>\mu</math></u>	<u>40-60 <math>\mu</math></u>
1 min	1797	1840	982	748	1284
2 "	3029	3138	2705	2396	4566
3 "	2799	2997	2811	2601	5079
4 "	2813	3089	2746	2540	5174
5 "	2885	3024	2763	2541	5070
10 "	2944	3098	2838	2694	4694

D: 5000 ppm Marine Diesel S-25 Stirrer at 4500 RPM for 10 Minutes  
2 Minute Settling Time

Particle Counts/Ml

	<u>2-5 <math>\mu</math></u>	<u>5-10 <math>\mu</math></u>	<u>10-20 <math>\mu</math></u>	<u>20-40 <math>\mu</math></u>	<u>40-60 <math>\mu</math></u>
1 min	3819	3300	2596	2012	3074
2 min	3796	3323	2551	1962	3091
3 min	3917	3317	2507	2066	3072

Since any oil/water dispersion is a dynamic, ever-changing system, a series of tests were conducted where particle counts were monitored every minute up to five minutes then periodically up to forty five minutes after final mixing. This was done to determine if significant changes in particle size distribution had occurred. A number of test emulsions were counted in this manner and the data at and beyond five minutes after mixing showed minor ( $\leq 5\%$ ) deviations, well within the instrumental and experimental error.

### 3.5 Final Experimental Procedure

Based on the data, observations and background of more than 70 separate preliminary emulsification experiments, the mixing technique and sequence of operations involved in making the particle count and size distribution were finalized and fixed for all subsequent test sample procedures. This sequence, as well as the laboratory equipment used, is listed below with a brief discussion of the HIAC Particle Counter:

The following equipment was used in this study:

- a) HIAC Particle Counter, Model SSTA, Model D2-60 Cell
- b) Kraft Non-Aerating Dispersator, Model S-25
- c) Sonagen Ultrasonic Bath
- d) HIAC Bottle Sampler, Model AB-110
- e) Glass Syringe, 30 cc
- f) Hi-Purity Nitrogen Gas Cylinder and Regulator
- g) Brooks Sho-rate Flow-meter
- h) Pyrex Glassware
- i) Graylab Labtimer
- j) Bausch & Lomb Dynazoom Dynoptic Microscope and Camera
- k) Coulter Counter, Model TA

#### 3.5.1 Description of HIAC Particle Counter

The HIAC Particle Counter utilizes an optical method to count and size particles. Sample fluid flows through a small rectangular fluid passage and past a window which is a tiny glass fiber with a square cross-section. The fluid passage is exactly the same width as the window so that all particles are observed. Particles passing by the window are counted one by one as long as the specified particle concentration limits are not exceeded. Light from a tungsten lamp is formed by the window to a parallel beam of exact size and directed onto a photodetector. Each particle as it passes the window reduces the light reaching the detector, in proportion to the size of the particle. It is only necessary for the particles to have a different index of refraction from that of the fluid. This causes a specific reduction in base voltage of the photodetector, proportional to the particle size. Five counting channels, with preset variable thresholds tally particles by size.

As with most analytical instrumentation, operational problems in measuring and counting oil droplets with the HIAC Particle Counter do exist. First, for proper particle counting, the window in the sensor must be clean. Oil, detergents, and oil-water-detergent mixtures caused some clouding of the window, and since the window is inaccessible, cleaning had to be carried

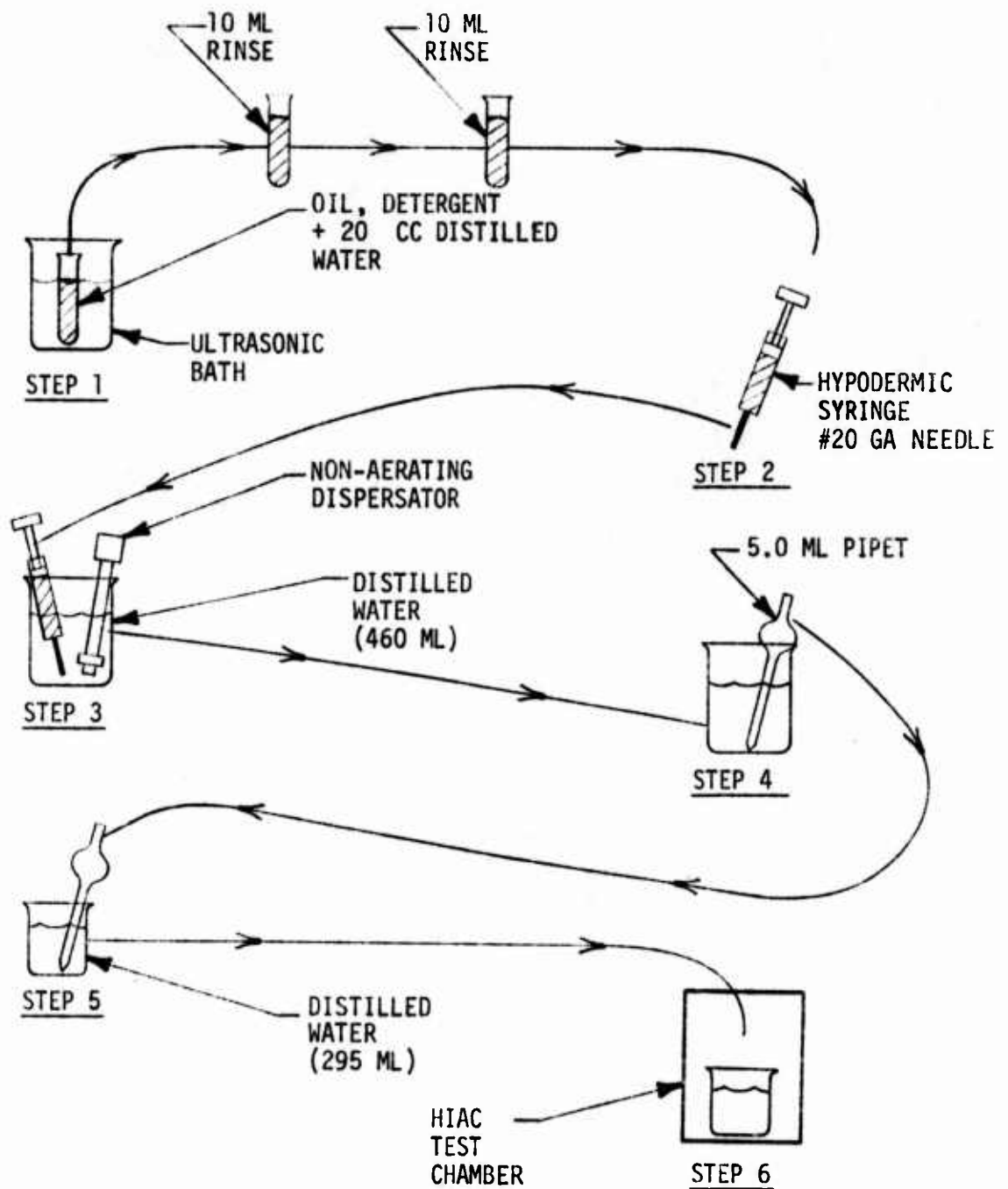
out by passing solvents and distilled water through the sample line. This flushing technique usually worked well except with Navy Special Fuel oil which posed more of a cleaning problem.

Second, and more important, any dispersion is a dynamic system with processes such as flocculation/coalescence and re-dispersion constantly occurring. These processes were likely to be occurring to some unknown extent in the sample container and in the line which led from the sample container to the sensor. The number of particles between two and four microns often increased noticeably up to five minutes after mixing, probably due to flocculation and coalescence of droplets smaller than two microns which are not detected by this system. Microscopic examination of emulsion samples did show presence of oil droplets smaller than 2 microns. Also, flocculation of oil droplets, may be detected as one larger oil droplet diameter if the flocculated oil passes the sensor intact. Such occurrences do not necessarily invalidate the experimental data, as one objective was to determine emulsion stability or instability, as evidenced by the amount of flocculation and coalescence taking place in the oil/water mixture.

### 3.5.2 Sample Manipulation Technique

The preparation of each dispersion test was carried out in the following manner. The technique is shown schematically in Figure 3.1.

- a) Pipet test oil (0.25 ml - 500 ppm) into clean 20 x 145 mm Pyrex Test Tube
- b) Add detergents (0, 25, 50, 100 ppm) by micropipet or Hamilton microliter syringe.
- c) Add 20.0 ml distilled water by pipet. Immerse test tube in ultrasonic bath.
- d) Immediate ultrasonic agitation (60 m amp plate current) for 45 seconds.
- e) Place S-25 non-aerating stirrer in 460-ml volume distilled water, operating at 2000 RPM.
- f) Emulsion from step (d) poured into the hypodermic syringe (plunger removed), test tube rinsed with 2 10-ml portions distilled water and added to the syringe.
- g) The syringe contents were immediately injected into the 460-ml volume of water. Injection was directed at intake side of dispersator over 15 seconds with stirring action continued for 25 seconds total elapsed time.
- h) The dispersator was removed. The beaker containing the emulsion was then allowed to settle quietly for 2 minutes.
- i) A 5.0 ml aliquot for analysis in HIAC particle counter was withdrawn by pipet from within 10 mm of the bottom and diluted 1:60 in distilled water. The oil accumulated on the surface was prevented from entering the pipet by gently forcing air through the pipet as it was being inserted. The diluted sample was then placed in the counting sample chamber.
- j) Sample flow of 10 cc/min in the HIAC assembly was accomplished using pressurized gas (Figure 3.2); the channels on the HIAC Particle Counter were calibrated to count particles in the following ranges:

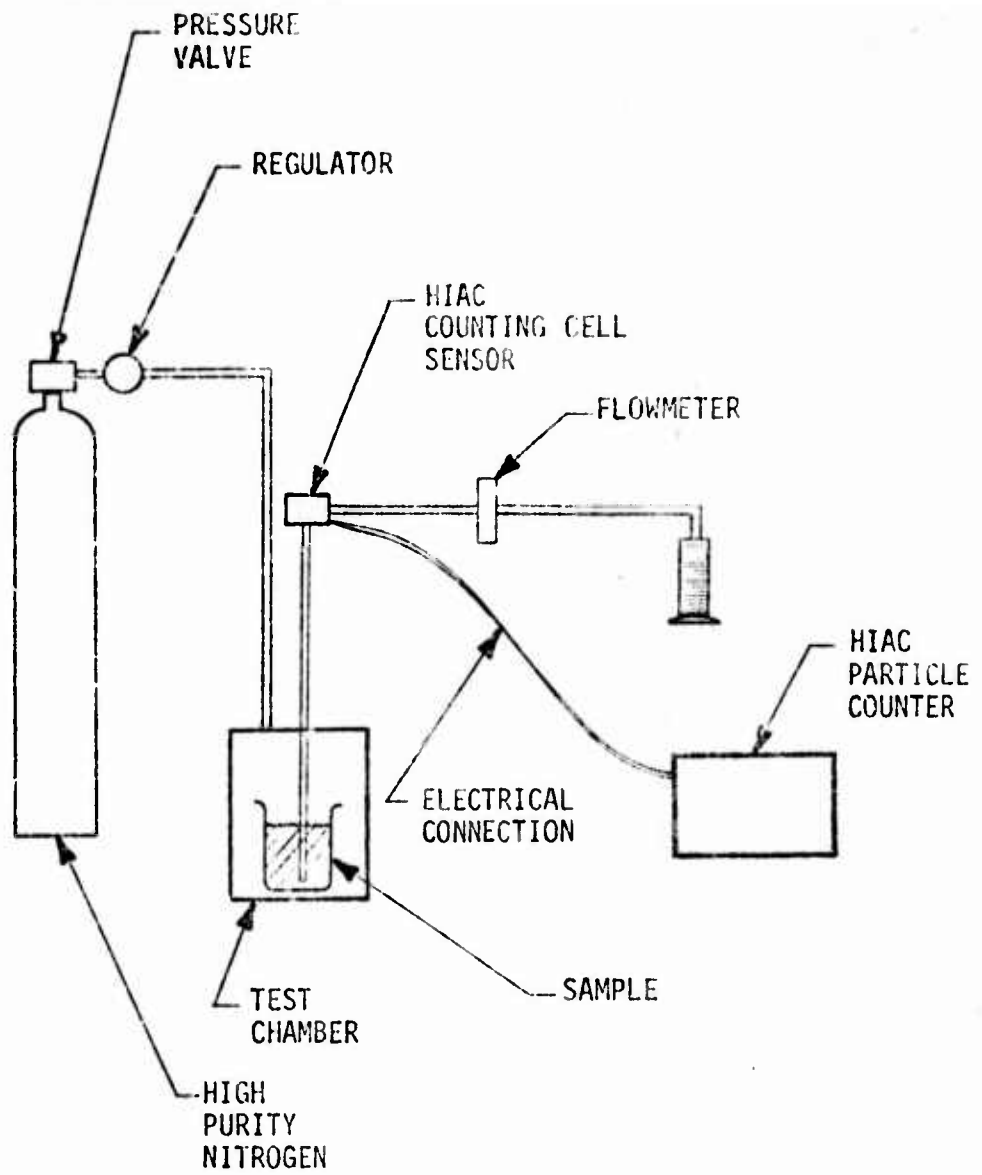


LABORATORY  
EMULSIFICATION PROCEDURE

USED IN EVALUATING EFFECT OF DETERGENTS.

Note: See photographs in Raw Data Appendix.

Figure 3.1



EXPERIMENTAL TEST SETUP FOR MEASURING  
PARTICLE SIZE DISTRIBUTION

FIGURE 3.2

Note: See photographs in Raw Data Appendix.

Channel 1	2-4u
Channel 2	4-7u
Channel 3	7-10u
Channel 4	10-15u
Channel 5	15-60u

- k) Three particle counts over 0.5 min. were taken starting at 3 min after mixing, then one 0.5 min count at 5 min, 7 min, and 10 min after mixing. Background counts of distilled water were recorded prior to each run, which were used as a check on the cleanliness of the HIAC cell and system, and were also subtracted from the total count.

### 3.6 Final Test Matrix

Due to the instrumental limitations of the HIAC Particle Counter, the efficiency of the emulsification process, and the objectives of this study, the proposed test matrix was revised to its final form, Table 3.4. Oil input concentration was set at 500 ppm, with detergent concentration similarly decreased to 100, 50, 25 and 0 ppm. The concentration of high molecular weight polymers was set at 125, 25 and 5, and 0 ppm, for three selected oils. Emulsions of oil-water-detergent were prepared using the method outlined in section 3.5.2 and particle counts obtained. This data was compared with the particle counts obtained for the simple oil-water mixtures in order to evaluate the effect of detergent on the dispersed oil concentration and stability of the emulsion.

The effect of the condition of the water (salinity, pH or temperature) on emulsion stability was also included in the scope of the study as can be seen from the Final Test Matrix, Table 3.4.

The pH, (6-8) salinity (25, 50, 100%) and temperature (40°, 120° F) of the water were the three conditions of interest, and were to be varied with selected oils.

Tests with the Trace Oil Monitor, a device prototype designed by GE for detecting 1-100 ppm oil in water, were also included in the test matrix.

### 3.7 Additional Experimental Effort

In order to obtain a more complete and thorough picture of the emulsifying effect of synthetic detergents on oily water mixtures, some additional experimental work was carried out. The areas of investigation are mentioned below and the results will be discussed in greater detail in Section 4.0 and 5.0.

TABLE 3.4 FINAL TEST MATRIX

		A B C D E F G H (OIL CODE LETTERS)											
DET. CONC. PPM		TEST CODE NO.	KUMAIT CRUDE	2190-TEP	MARINE DIESEL	NAVY DISTILLATE (NDO)	NAVY SPECIAL FUEL OIL (NSFO)	LUBRICATING OIL 9250	HYDRAULIC OIL	SO. LOUISIANA CRUDE			
<b>ANIONIC</b>			PSD	PSD	PSD	PSD	PSD	PSD	PSD	PSD			
Klearfac AB-270	100	1	↓	↓	↓	↓	↓	↓	↓	↓	TOM		S
	50	2	↓	↓	↓	↓	↓	↓	↓	↓		pH	T
	25	3	↓	↓	↓	↓	↓	↓	↓	↓			
Alkanol 189-S	100	4	↓	↓	↓	↓	↓	↓	↓	↓	pH		S
	50	5	↓	↓	↓	↓	↓	↓	↓	↓		T	TOM
	25	6	↓	↓	↓	↓	↓	↓	↓	↓			
Aerosol OT-75	100	7	↓	↓	↓	↓	↓	↓	↓	↓	T		
	50	8	↓	↓	↓	↓	↓	↓	↓	↓		TOM	
	25	9	↓	↓	↓	↓	↓	↓	↓	↓			pH
<b>CATIONIC</b>			PSD	PSD	PSD	PSD	PSD	PSD	PSD	PSD			
Product BCO	100	10	↓	↓	↓	↓	↓	↓	↓	↓	TOM		S
	50	11	↓	↓	↓	↓	↓	↓	↓	↓		pH	T
	25	12	↓	↓	↓	↓	↓	↓	↓	↓			
Aerosol C-61	100	13	↓	↓	↓	↓	↓	↓	↓	↓	pH		S
	50	14	↓	↓	↓	↓	↓	↓	↓	↓		T	TOM
	25	15	↓	↓	↓	↓	↓	↓	↓	↓			
Retarder LAN	100	16	↓	↓	↓	↓	↓	↓	↓	↓	T		
	50	17	↓	↓	↓	↓	↓	↓	↓	↓		TOM	
	25	18	↓	↓	↓	↓	↓	↓	↓	↓	S		pH
<b>NON-IONIC</b>													
Intravon SO	100	19	↓	↓	↓	↓	↓	↓	↓	↓	TOM		S
	50	20	↓	↓	↓	↓	↓	↓	↓	↓		pH	T
	25	21	↓	↓	↓	↓	↓	↓	↓	↓			
Span 80	100	22	↓	↓	↓	↓	↓	↓	↓	↓	pH		S
	50	23	↓	↓	↓	↓	↓	↓	↓	↓		T	TOM
	25	24	↓	↓	↓	↓	↓	↓	↓	↓			
Triton X-100	100	25	↓	↓	↓	↓	↓	↓	↓	↓	T		
	50	26	↓	↓	↓	↓	↓	↓	↓	↓		TOM	
	25	27	↓	↓	↓	↓	↓	↓	↓	↓	S		pH

LEGEND: PSD - Particle Size Distribution  
 TOM - Trace Oil Monitor  
 S - Salinity 100, 50, 25, 0%  
 T - Temperature 120°F, 73°F, 40°F  
 PH - 6 or 8

TABLE 3.4 FINAL TEST MATRIX (CONTINUED)

		DETERGENT CODE NO.		A	B	C	D	E	F	G	H	OIL CODE
		PPM		KUMAIT CRUDE	2190-TEP	MARINE DIESEL	NAVY DISTILLATE (NDO)	NAVY SPECIAL FUEL OIL (NSFO)	LUBRICATING OIL 9250	HYDRAULIC OIL	SO. LOUISIANA CRUDE	
<b>COMMERCIAL</b>												
All	100	28	PSD	PSD	PSD	PSD	PSD	PSD	PSD	PSD	PSD	
	50	29	↓	↓	↓	↓	↓	↓	↓	↓	↓	
	25	30	↓	↓	↓	↓	↓	↓	↓	↓	↓	
Rinso	100	31	↓	↓	↓	↓	↓	↓	↓	↓	↓	
	50	32	↓	↓	↓	↓	↓	↓	↓	↓	↓	
	25	33	↓	↓	↓	↓	↓	↓	↓	↓	↓	
Zif	100	34	↓	↓	↓	↓	↓	↓	↓	↓	↓	
	50	35	↓	↓	↓	↓	↓	↓	↓	↓	↓	
	25	36	↓	↓	↓	↓	↓	↓	↓	↓	↓	
<b>HIGH MOLECULAR WEIGHT POLYMERS</b>												
Merpol SH	125	37			PSD							TOM
	25	38			↓							
	5	39										
Pluronic L-101	125	40	PSD									TOM
	25	41	↓									
	5	42	↓									
Pluradot HAS10	250	43							PSD			TOM
	125	44							↓			
	25	45							↓			
	5	46							↓			

### 3.7.1 Effect of High Detergent Concentration on Emulsification

Since relatively minimal effect on PSD of these test oils in water was noted with detergent concentrations 1/5, 1/10, 1/20 of the oil concentration, emulsions with detergent and oil in 1:1, 2:1, 10:1 ratios were generated, and PSD obtained. A sample of each anionic, cationic, non-ionic detergent type was tested with marine diesel and 2190-TEP. These data are presented in the next Section 4.0.

### 3.7.2 HIAC Counter vs. Coulter Counter Study

As a check on the HIAC Particle Counter, particle size distributions, based on percent by volume, were obtained for the emulsions listed below using a Coulter Counter. In this instrument, particles are sized by passing the emulsion through a narrow orifice, which has a conductivity electrode on either side. The conductivity of the oil particles, suspended in an electrolyte, is much lower than that of the continuous phase. As each particle passes through the aperture and displaces its own volume of electrolyte, the resistance (the reciprocal of the conductance) in the path changes; the magnitude of this change is directly proportional to the volumetric size of the particle. Samples diluted in isotonic water to a 0.5 concentration index see note.

All initial oil concentrations 500 ppm.

NOTE: Concentration index is a part of the Coulter Counter, the reading indicates when an adequate amount of the test emulsion has been added to insure reliable data, yet not exceed coincidence limits.

2190 - TEP/50 ppm Klearfac AB-270  
Hydraulic Oil/25 ppm Klearfac AB-270  
South Louisiana Crude Oil/50 ppm Aerosol C-61  
South Louisiana Crude Oil/100 ppm Span 80  
Navy Special Fuel Oil/100 ppm Aerosol OT-75  
Lubricating Oil 9250/100 ppm Aerosol OT-75  
Lubricating Oil 9250/50 ppm Klearfac AB-270  
Kuwait Crude Oil/50 ppm Alkanol 189-S

The particle size distributions for these emulsions appear in the Raw Data Appendix.

Since the Coulter Counter sizes and counts particles by volume, the particle size distributions of oil and detergent mixtures show maximums in the large particle size range (over fifteen microns) because these particles make such a large contribution to the total volume.

In order to compare the particle size data obtained for oil/water and detergent emulsions with these two instruments, several test emulsions were generated and particle counts recorded using both instruments. In Figure 3.3 the data obtained with the Coulter Counter showed maximum particle density (based on volume) in the fifty-sixty micron size range. The comparison of population-based data, from the HIAC Particle Counter with Coulter Counter volume-based data is presented in Figure 3.4.

**COULTER COUNTER Model T & TA**      **PARTICLE SIZE ANALYSIS**

OPERATION: \_\_\_\_\_

OPERATOR: \_\_\_\_\_

EQUIPMENT: \_\_\_\_\_

SAMPLE: \_\_\_\_\_

DISPERSED: \_\_\_\_\_

ELECTROLYTE: \_\_\_\_\_

Time 40.8 sec  
for 25K

500 ppm Kuwait Crude  
50 ppm Alkano1 189-S  
45 Sec U. Sonic

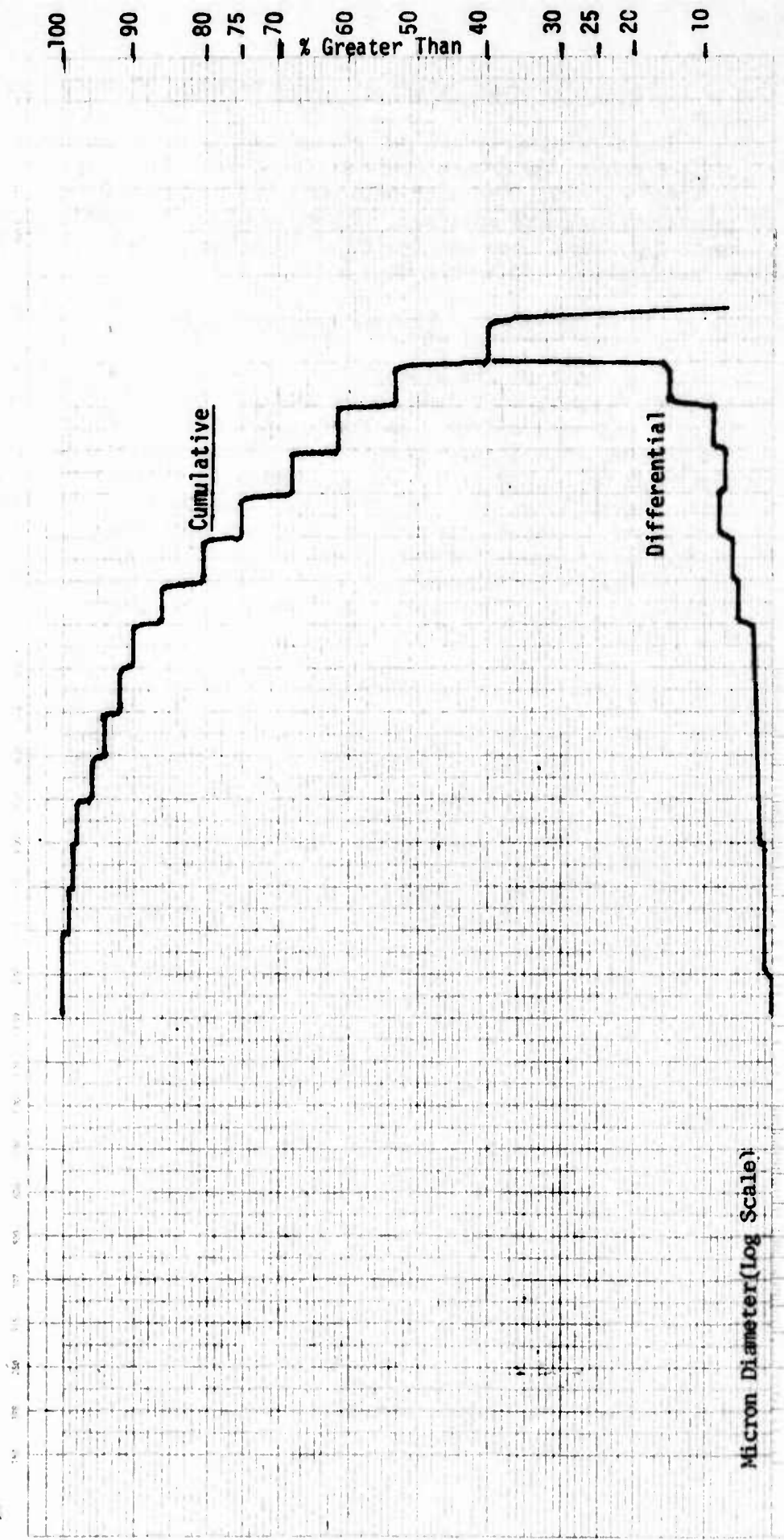


FIGURE 3.3 - Coulter Counter Particle Size Analysis



As would be expected, the population-based data showed the highest percentages of particles in the smallest size range. Without calculations to convert population count to volume, or vice-versa, the two forms of data can not be directly compared.

The sample handling for these two instruments differ which also introduces a factor which could affect the measurement. For Coulter Counting, the oil/water emulsion had to be diluted in background electrolyte, an isotonic solution containing ten parts per thousand salinity. The effect of these additional ions, in large excess compared to amount of emulsified oil droplets and in the presence of cationic and anionic detergents, is unknown and quite complex. If the interfacial layer present on the oil droplets is discharged or the surface film rendered more soluble in either the oil or water (a change in droplet surface tension), then one would expect that the oil emulsion stability during analysis would be affected. If this is true, then questions arise concerning the validity of any oil/water emulsion data taken by a Coulter Counter. This possibility should be examined more closely since many investigators have used and continue to use the Coulter Counter to measure oil particle size distribution.

The above phenomenon is not as pronounced using the HIAC Counter since the diluting medium is distilled water. There may be a simple dilution or solution of oil droplet surface films but the end result would not be expected to have as drastic an effect as ionized water would have. Additional study in this area of instrumental particle counting and sizing of oil in water is indicated.

### 3.7.3 Agent-in-Oil Versus Agent-in-Water Study

An alternate order of mixing test emulsions was investigated during this program. The method which had been used for generating all test emulsions discussed previously was the agent-in-oil method, in which an emulsifying agent is dissolved in the oil phase with water added to the mixture, followed by agitation. In the preparation of oil-in-water emulsions the finest particle-size is ordinarily obtained by first forming, and then inverting, a water-in-oil emulsion. Thus, the emulsifier was dissolved in the oil and the aqueous phase was then added to the oil phase, followed by ultra sonic agitation to form a water-in-oil emulsion. Upon dispersion of this w/o emulsion into additional water an oil-in-water emulsion formed.

The method examined in this case was the agent-in-water technique, which involves dissolving the emulsifier in water, and injecting the test oil while subjecting the mixture to ultrasonic agitation. The agent-in-water procedure is considered to make oil-in-water emulsions more directly. The amounts of emulsified oil resulting from this mixing method are found in Table 4.17. Comparison of the agent-in-water with agent-in-oil mixing methods for the two test oils showed similar volumes of dispersed oil present in droplets smaller than ten microns. In the cases of 100 and 500 ppm Alkanol 189-S with Marine Diesel, the agent-in-water method produced emulsions with higher concentrations of emulsified oil than the agent-in-oil method. Since the volume of oil present in droplets smaller

than ten microns stayed essentially the same for both mixing methods, the additional dispersed oil was present as larger droplets (10 to 35 $\mu$ ) which accounts for the higher concentration of emulsified oil with the agent-in-water method. This observation seemed to imply that the agent-in-water method generated less stable emulsions than the agent-in-oil method, as more oil was present in the larger particle sizes.

With lower detergent concentrations (less than or equal to 100 ppm), emulsions of Marine Diesel and Alkanol 189-S (anionic type) generated by both methods had essentially the same concentrations of dispersed oil (<35  $\mu$ ). However, the emulsion generated using the agent-in-water technique had a larger fraction of the total dispersed oil present in the smaller size ranges (< 10  $\mu$ ). This size distribution difference indicated that agent-in-water produced a more stable emulsion, with less oil being removed from the mixture by flocculation or coalescence.

## 4.0 EXPERIMENTAL RESULTS

### 4.1 PRESENTATION OF DATA

The basic experimental data was obtained from the HIAC Particle Counter display and manually recorded as particle counts in five size ranges for five milliliters of test sample. Counts were accumulated over a 0.5 min interval at a ten milliliter/minute sample flow in the sensing cell. These numbers included background counts in the dispersing medium and diluting medium (distilled water usually) which was subtracted from the total count giving oil particle counts for five milliliters of mixture, diluted 1:60 from the original test sample. A representative sequence of typical counts is shown below:

Oil Type: Navy Special Fuel Oil at 500 ppm  
Detergent Type: Span 80, Conc. 25 ppm

Channels	1	2	3	4	5
	(2-4 $\mu$ )	(4-7 $\mu$ )	(7-10 $\mu$ )	(10-15 $\mu$ )	(15-60 $\mu$ )
Sample Background	318	28	1	1	0
Total time after final mixing (min.)					
3-3.5	3177	500	67	40	0
3.5-4.0	3700	619	82	48	0
4.0-4.5	3943	631	84	35	0
4.5-5.0	4008	704	81	53	0
7.0-7.5	4016	756	99	55	0
10.0-10.5	3971	684	79	62	0

As can be seen, the first three counts from 3 to 4.5 minutes showed the count rate approaching a nearly constant level. The later counts were approximately equal, within instrument efficiency and counting accuracy. Therefore, the count at 5.0-5.5 minutes after mixing was taken as the equilibrium point and was used to determine the amount of finely dispersed oil in the test emulsion and in determining the particle size distribution.

There are a number of methods for presenting and reducing the above basic data. See Appendix 1 for a discussion of methods used by various investigators. The simplest form would involve plotting particle counts in each size range as a percentage of the total count versus particle diameter. This is known as the particle size distribution curve.

A more sophisticated format would involve plotting the cumulative percent of total count greater than each size (or less than) as a log function versus the size as a normal function on log-probability graph paper. The advantages of this technique are that the curve is a straight line and standard deviation, mean diameter, direct conversions to cumulative volume percent may be more directly obtained.

The real purpose of this experimental effort was to determine the amount (volume or mass) of finely dispersed oil generated in each test as a function of the various parameters and additives under study. Since dispersed oil concentration in each case provided this measure of any emulsifying effects which had occurred, a format of data presentation and reduction which indicated this function was deemed most appropriate. To obtain this information, the total volume of dispersed oil and the cumulative volume percent for each size range was calculated from the particle counts obtained (less background) using a desk-side computer and program.

To calculate the volume of dispersed oil from particle counts, it was first necessary to determine the average diameter of particles counted in each channel. Since calculations of volume were to be made and volume is a function of the diameter to the 3rd power, the arithmetic mean diameter for each size range could not be used. Instead, a volumetric mean diameter was calculated for each size range. Since volume =  $\pi d^3/6$ , the mean volume is equal to  $\pi \bar{d}^3/6$  where  $\bar{d}$  is the "mean volumetric diameter". The total volume represented by counts in each channel was found by integration from the lower limit of each size range,  $d_1$ , to the upper limit  $d_2$  of each counting channel. Thus:

$$V = \sum n_i V_i$$

$$\bar{V} = \frac{\pi \bar{d}^3}{6}$$

$$\bar{V} = \frac{1}{d_2 - d_1} \int_{d_1}^{d_2} \frac{n \pi d^3}{6} d(d) = \frac{\pi \bar{d}^3}{6}$$

where n = number of counts.

Also, due to the nature of the instrument, Channel 5 counted all particles between fifteen and sixty microns. However, the two minute settling period eliminated oil droplets larger than thirty five microns from the sample (Stoke's Law). For this reason, computations of volumetric mean diameter used 35  $\mu$  as the upper limit for the last size range. These volumetric mean diameters were:

	<u>Setting</u>	<u><math>\bar{d}_v</math></u>
Channel 1	2-4 $\mu$	3.1
Channel 2	4-7 $\mu$	5.6
Channel 3	7-10 $\mu$	8.6
Channel 4	10-15 $\mu$	12.6
Channel 5	15-60 $\mu$	26.6

This "volumetric mean diameter" was subsequently used to calculate the volume of oil represented by particle counts in each size ranges. The total volume (in ppm) of emulsified oil, and the cumulative percent of this volume in each size range appeared on the computer printout. Included in the computations were corrections for dilution, flow rate and time of counting in order to

obtain particle counts per milliliter.

The particle size distributions for eight test oils in water, as cumulative volume percent, are shown in Table 4.1. These concentrations of emulsified oil with no detergent present were used as baselines for evaluating the emulsifying activity of syndets. The cumulative particle size distributions of the oil-water mixtures are also presented in non-cumulative form (viz., volume-fraction of emulsified oil present in each size range) in Table 4.2.

All raw data, as particle counts at 5 minutes after mixing for test emulsions of oil, water and detergent can be found in Appendix 2 (see Test Matrix for oil-detergent code). Raw data for all tests with all experimental parameters was treated in the same manner; the calculated volumes of emulsified oil (ppm) with the stated concentrations of the detergent samples are tabulated in Tables 4.3 thru 4.7. Discussion and graphical presentations of these tabulated data follow in Section 5.0.

TABLE 4.1

PARTICLE SIZE DISTRIBUTION OF TEST OILS IN DISTILLED

WATER AS CUMULATIVE VOLUME PERCENT

Oil input concentration - 500 ppm

Data at 5 minutes after mixing

	CUMULATIVE PERCENT OF VOLUME					VOLUME OF DISPERSED OIL, PPM
	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-35 $\mu$ *	
Marine Diesel	9.8	35.6	49.2	67.5	100.0	2.1
Navy Distillate	16.7	49.7	63.7	75.2	100.0	2.3
Kuwait Crude	23.2	63.6	78.7	89.7	100.0	23.3**
So. Louisiana Crude	17.8	42.5	54.7	65.8	100.0	3.0
Navy Special Fuel Oil (NSFO)	11.2	21.4	29.4	42.4	100.0	2.2
Lubricating Oil 9250	7.9	26.5	38.1	58.1	100.0	5.2
2190-TEP	25.6	44.4	47.8	62.2	100.0	1.5
Hydraulic Oil	35.7	69.9	78.7	90.0	100.0	2.3

\* Oil droplets larger than 35 microns in diameter settled out of the mixture in the two minutes prior to sampling

\*\* Refer to Section 5.0

TABLE 4.2

PARTICLE SIZE DISTRIBUTIONS OF TEST OILS IN DISTILLED  
WATER AS VOLUME FRACTION PER INCREMENT

Data at 5 min. after final mixing

INPUT OIL CONC.: 500 PPM	PERCENT OF VOLUME					VOLUME OF DISPERSED OIL, PPM
	2-4u	4-7u	7-10u	10-15u	15-35u	
Marine Diesel	9.8	25.8	13.6	18.3	32.5	2.1
Navy Distillate	16.7	33.0	14.0	11.5	24.8	2.3
Kuwait Crude	23.2	40.4	15.1	11.0	10.3	23.3
So. Louisiana Crude	17.8	24.7	12.2	11.1	34.2	3.0
Navy Special Fuel Oil	11.2	10.2	8.0	13.0	57.6	2.2
Lubricating Oil 9250	7.9	8.6	11.6	20.0	41.9	5.2
2190-TEP	25.6	18.8	3.4	14.4	37.8	1.5
Hydraulic Oil	35.7	34.2	8.8	11.3	10.0	2.3

NOTE: The above data is plotted in Figures 5.1 and 5.2. See section 5 for further discussion.

TABLE 4.3

\*  
DISPERSED OIL CONCENTRATION, PPM  
IN PRESENCE OF NON-IONIC TYPE SURFACTANTS

All oil input concentrations 500 ppm. Data at 5 minutes after final mixing.

<u>DETERGENT CONCENTRATION</u>	100 ppm	50 ppm	25 ppm	0 ppm
<u>TRITON X-100</u>	oil concentration in disperse phase, ppm			
Marine Diesel	35.8	55.1	34.2	2.1
Navy Distillate	34.6	33.7	22.8	2.3
Kuwait Crude	—	14.5	—	23.3
South Louisiana Crude	—	13.1	—	3.0
Navy Special Fuel Oil	—	20.3	—	2.2
Lubricating Oil 9250	3.7	5.1	3.4	5.2
Hydraulic Oil	17.3	19.7	7.9	2.3
<u>SPAN 80</u>				
Navy Distillate	54.2	16.0	48.4	2.3
Kuwait Crude	30.7	12.0	19.6	23.3
South Louisiana Crude	19.6	19.7	22.9	3.0
Lubricating Oil 9250	9.5	5.4	6.8	5.2
2190-TEP	7.6	7.2	5.0	1.5
Hydraulic Oil	15.2	18.5	13.2	2.3
<u>INTRAVON SO</u>				
Marine Diesel	11.1	16.8	8.9	2.1
Navy Distillate	12.9	6.3	19.3	2.3
Kuwait Crude	9.8	4.9	10.9	23.3
Navy Special Fuel Oil	—	4.3	—	2.2
2190-TEP	4.4	1.6	2.6	1.5
Lubricating Oil 9250	4.1	4.5	3.5	5.2
Hydraulic Oil	5.6	9.8	4.2	2.3

\* as droplets 2-35  $\mu$  in diameter (NOTE: see Figures 5.5, 5.6, 5.7, 5.9 & 5.15)

DISPERSED\* OIL CONCENTRATIONSIN PRESENCE OF CATIONIC TYPE SURFACTANTS

Oil input concentrations 500 ppm. Data for 5 minutes after final mixing.

DETERGENT CONCENTRATION	100 ppm	50 ppm	25 ppm	0 ppm
Oil concentration, ppm, in disperse phase				
<u>AEROSOL C-61</u>				
Marine Diesel	—	—	58.6	2.1
Navy Distillate	26.8	—	38.4	2.3
Kuwait Crude	—	—	34.2	23.3
2190-TEP	11.5	11.1	9.2	1.5
Lubricating Oil 9250	—	3.7	—	5.2
<u>RETARDER LAN</u>				
Marine Diesel	—	29.5	—	2.1
Kuwait Crude	—	—	37.4	23.3
South Louisiana Crude	—	21.8	—	3.0
Lubricating Oil 9250	—	2.1	12.1	5.2
2190-TEP	—	—	7.7	1.5
Hydraulic Oil	—	18.4	—	2.3
<u>PRODUCT BCO</u>				
Marine Diesel	44.1	24.7	23.8	2.1
Kuwait Crude	—	—	36.4	23.3
South Louisiana Crude	—	—	31.4	3.0
Lubricating Oil 9250	—	2.4	—	5.2
2190-TEP	3.3	5.4	6.4	1.5
Hydraulic Oil	—	—	21.9	2.3

\* as droplets 2-35  $\mu$  in diameter  
 (Note: see also Figure 5.13)

TABLE 4.5

DISPERSED\* OIL CONCENTRATION IN PRESENCE OF ANIONIC TYPE SURFACTANTS

All oil input concentration 500 ppm. Data at 5 minutes after mixing.

SURFACTANT CONCENTRATION	100 ppm	50 ppm	25 ppm	0 ppm
<u>AEROSOL OT-75</u>				
Marine Diesel	—	—	16.3	2.1
Navy Distillate	—	14.8	—	2.3
Kuwait Crude	27.2	11.6	12.3	23.3
South Louisiana Crude	16.0	—	11.3	3.0
Navy Special Fuel Oil	—	25.9	5.5	2.2
Lubricating Oil 9250	4.8	3.6	1.9	5.2
2190-TEP	3.1	—	2.3	1.5
Hydraulic Oil	6.7	—	—	2.3
<u>KLEARFAC AB-270</u>				
Marine Diesel	—	22.1	10.6	2.1
Navy Distillate	—	—	21.1	2.3
Kuwait Crude	—	—	15.3	23.3
South Louisiana Crude	—	—	32.4	3.0
Navy Special Fuel Oil	—	—	12.4	2.2
Lubricating Oil 9250	—	14.0	3.8	5.2
2190-TEP	4.0	7.2	5.0	1.5
Hydraulic Oil	—	—	14.5	2.3
<u>ALKANOL 189-S</u>				
Marine Diesel	6.0	10.2	11.5	2.1
Navy Distillate	17.9	—	—	2.3
Kuwait Crude	—	36.3	—	23.3
South Louisiana Crude	—	8.3	—	3.0
Navy Special Fuel Oil	5.4	4.4	5.6	2.2
Lubricating Oil 9250	2.2	4.5	6.8	5.2
2190-TEP	0.8	1.4	1.1	1.5
Hydraulic Oil	—	3.1	4.3	2.3

\* as droplets 2-35  $\mu$  in diameter

(NOTE: see Figures 5.3, 5.8)

TABLE 4.6

DISPERSED\* OIL CONCENTRATIONS WITH COMMERCIAL DETERGENTS

(in 2-35 microns diameters)

All oil input concentrations 500 ppm. Data at 5 minutes after mixing.

DETERGENT CONCENTRATION	100 ppm	50 ppm	25 ppm	0 ppm
Oil concentration, ppm in disperse phase				
<u>ALL</u>				
Navy Distillate	10.2	7.1	8.5	2.1
2190-TEP	4.6	2.0	—	1.5
Lubricating Oil 9250	1.2	6.5	2.0	5.2
<u>RINSO</u>				
Marine Diesel	—	—	4.0	2.1
Navy Distillate	—	16.0	16.3	2.3
Navy Special Fuel Oil	8.0	—	6.7	2.2
Lubricating Oil 9250	2.4	2.9	—	5.2
Hydraulic Oil	—	—	7.9	2.3
<u>ZIF</u>				
Navy Distillate	6.4	8.0	—	2.1
Lubricating Oil 9250	—	3.5	—	1.5
Navy Special Fuel Oil	—	0.5	—	2.2

\* as droplets 2-35 $\mu$  in diameter

TABLE 4.7

DISPERSED\* OIL CONCENTRATION, HIGH MOLECULAR WEIGHT POLYMERS

All oil input concentrations 500 ppm. Data at 5 minutes after mixing.

<u>POLYMER CONC.</u>	250 ppm	125 ppm	25 ppm	5 ppm	0 ppm
	Oil concentration, ppm, in disperse phase.				
<u>Pluradot HA-510</u>					
Lubricating Oil 9250	4.4	3.6	1.9	—	5.2
<u>Merpol SH</u>					
2190-TEP	—	7.6	2.6	1.5	1.5
<u>Pluronic L-101</u>					
Kuwait Crude	18.2	14.0	8.4	—	23.3

\* as droplets 2-35  $\mu$  in diameter

Note: (See Figures 5.3 and 5.8)

This following group of tables deals with the first attempt made to more clearly understand what the experimental data might reveal.

The first reduction of the foregoing mass of data of primary interest would be that portion of the dispersed oil which would represent the most stable or hardest-to-separate oil droplets. From Stoke's Law alone, gravity would have very little effect on particles up to about 10 microns in diameter. Therefore it is likely that this segment of an oil/water mixture would not be separated in a gravity - type separator. For this reason, it was felt desirable to calculate the volume represented by this size fraction (2-10 microns) from the foregoing data. Tables 4.8 through 4.12 present these calculations for each of the tests conducted. Additional discussion of this data is presented in Section 5.0

TABLE 4.8.

DISPERSED OIL PRESENT AS DROPLETS SMALLER THAN TEN MICRONS WITH NON-IONIC SURFACTANTS

All input oil concentrate 500 ppm. Data at 5 minutes after mixing.

SURFACTANT CONCENTRATION	D.O.C. > 2 $\mu$ < 10 $\mu$		TOTAL D.O.C. PPM < 35 $\mu$	
	%	PPM		
<u>SPAN 80</u>				
Navy Distillate	100	26.7	14.5	54.2
	50	40.2	6.4	16.0
	25	34.5	16.7	48.4
	0	63.7	1.4	2.3
Kuwait Crude	100	42.4	13.0	30.7
	50	61.1	7.3	12.0
	25	46.4	9.1	19.6
	0	78.7	18.4	23.3
South Louisiana Crude	100	31.3	6.1	19.6
	50	29.1	5.7	19.7
	25	78.6	6.5	22.9
	0	54.7	1.6	3.0
Lubricating Oil 9250	100	51.2	4.9	9.5
	50	44.8	2.4	5.4
	25	49.5	3.4	6.8
	0	38.1	2.0	5.2
2190-TEP	100	51.2	4.9	9.5
	50	44.8	2.4	5.4
	25	49.5	3.4	6.8
	0	38.1	2.0	5.2
<u>TRITON X-100</u>				
Marine Diesel	100	34.5	12.4	35.8
	50	42.9	23.6	55.1
	25	32.2	11.0	34.2
	0	49.2	1.0	2.1
Navy Distillate	100	52.6	18.2	34.6
	50	34.9	11.7	33.7
	25	38.0	8.4	22.0
	0	63.7	1.4	2.3
Lubricating Oil 9250	100	57.4	2.1	3.7
	50	43.7	2.2	5.1
	25	47.6	1.6	3.4
	0	38.1	2.0	5.2

TABLE 4.8 (CONTINUED)

All Oil Input Conc.-  
500 ppm Data At 5  
Min After Mixing

DISPERSED OIL PRESENT  
WITH NON-IONIC SURFACTANTS

	SURFACTANT CONC.	DOC, ( $> 2\mu < 10\mu$ )		TOTAL DOC* PPM $< 35\mu$
		%	PPM	
<u>INTRAVON SO</u>				
Navy Distillate	100	36.7	4.7	12.9
	50	58.2	3.6	6.3
	25	49.3	9.5	19.3
	0	63.7	1.4	2.3
Marine Diesel	100	38.2	4.2	11.1
	50	34.3	5.8	16.8
	25	45.1	4.0	8.9
	0	49.2	1.0	2.1
2190-TEP	100	44.9	2.0	4.4
Lub. Oil 2190-TEP	50	46.2	0.8	1.6
	25	46.8	1.2	2.6
	0	47.8	0.7	1.5
Lubricating Oil 9250	100	45.6	1.8	4.1
Lub. Oil 9250	50	41.2	1.8	4.5
	25	52.1	1.8	3.5
	0	38.1	2.0	5.2
Kuwait Crude	100	68.5	6.7	9.8
	50	53.6	2.6	4.9
	25	54.0	5.8	10.9
	0	78.7	18.4	23.3
Hydraulic Oil	100	61.0	3.4	5.6
	50	44.7	4.4	9.8
	25	56.7	2.4	4.2
	0	78.7	1.8	2.3

\* D.O.C. Dispersed oil concentration between two and thirty-five microns

TABLE 4.9

DISPERSED OIL PRESENT AS DROPLETS SMALLER THAN TEN MICRONS WITH CATIONIC SURFACTANTS

All oil input concentration 500 ppm. Data at 5 minutes after mixing.

	DETERGENT CONCENTRATE	D.O.C. $> 2\mu < 10\mu$		TOTAL D.O.C. PPM $\leq 35\mu$
		%	PPM	
<u>AEROSOL C-61</u>				
Marine Diesel	25	57.6	33.7	58.6
	0	49.2	1.0	2.1
Navy Distillate	100	61.3	16.4	26.8
	25	63.5	21.2	38.4
	0	63.7	1.4	2.3
Kuwait Crude	25	83.9	28.7	34.2
	0	78.7	18.4	23.3
Lubricating Oil 9250	50	71.1	2.6	3.7
	0	38.1	2.0	5.2
2190-TEP	100	61.4	7.0	11.5
	50	51.5	5.7	11.1
	25	74.6	6.7	9.2
	0	47.8	0.7	1.5
<u>RETARDER LAN</u>				
Marine Diesel	50	75.5	22.3	29.5
	0	49.2	1.0	2.1
South Louisiana Crude	50	75.5	16.4	21.8
	0	54.7	1.6	3.0
Lubricating Oil 9250	50	62.5	1.3	2.1
	25	74.2	9.0	12.1
	0	38.1	2.0	5.2
2190-TEP	25	74.2	5.7	7.7
	0	4.0	0.0	1.5
<u>PRODUCT BCO</u>				
Marine Diesel	100	48.2	21.2	44.1
	50	67.4	16.6	24.7
	25	63.3	15.0	23.8
	0	49.2	1.0	2.1
Kuwait Crude	25	59.0	20.5	36.4
	0	78.7	18.3	23.3
South Louisiana Crude	25	58.4	18.3	31.4
	0	54.7	1.6	3.0
Lubricating Oil 9250	50	51.6	1.2	2.4
	0	38.1	1.9	5.2
2190-TEP	100	74.0	2.4	3.3
	50	53.9	2.9	5.4
	0	47.8	0.7	6.5

TABLE 4.10

All Oil Input Conc. 500 PPM Data At 5 minutes After Mixing

DISPERSED OIL PRESENT IN DROPLETS SMALLER THAN TEN MICRONS WITH ANIONIC SURFACTANTS

	DETERGENT CONC.	DOC > 2 $\mu$ < 10 $\mu$ )		TOTAL DOC *
		%	PPM	PPM < 35 $\mu$
<u>KLEARFAC AB-270</u>				
Navy Distillate	25	49.2	10.4	21.1
	0	63.7	1.4	2.3
Marine Diesel	25	51.3	5.4	10.6
	50	33.5	7.4	22.1
	0	49.2	1.0	2.1
Lubricating Oil 9250	50	40.6	5.6	14.0
	25	54.9	2.0	3.8
	0	38.1	2.0	5.2
2190-TEP	100	62.7	2.5	4.0
	50	44.4	3.2	7.2
	25	52.0	2.6	5.0
	0	47.8	0.7	1.5
South Louisiana Crude	25	39.7	12.8	32.4
	0	54.7	1.6	3.0
Kuwait Crude	25	72.1	11.0	15.3
	0	78.7	18.4	23.3
Navy Special Fuel Oil	25	38.7	4.8	12.4
	0	29.4	0.6	2.2
<u>AEROSOL OT-75</u>				
2190-TEP	100	48.5	1.5	3.1
	25	40.9	1.0	2.3
	0	47.8	0.7	1.5
Lubricating Oil 9250	100	64.4	3.1	4.8
	50	62.6	2.2	3.6
	25	51.5	0.9	1.9
	0	38.1	2.0	5.2
Navy Distillate	50	41.6	6.2	14.8
	0	63.7	1.4	2.3
Navy Special Fuel Oil	50	40.1	10.4	25.9
	25	47.3	2.6	5.5
	0	29.4	0.6	2.2
Kuwait Crude	100	46.5	12.6	27.2
	50	77.7	9.0	11.6
	25	43.9	5.4	12.3
	0	78.7	18.4	23.3

\* D.O.C. - Dispersed oil concentration between two and thirty five microns

TABLE 4.10 (CONTINUED)

DISPERSED OIL PRESENT IN DROPLETS SMALLER THAN  
TEN MICRONS WITH ANIONIC SURFACTANTS

ALL OIL INPUT CONCEN. - 500 PPM

D.O.C. - DISPERSED OIL CONCENTRATION

DATA AT 5 MINUTES AFTER FINAL MIXING

	SURFACTANT CONC.	D.O.C. >2 $\mu$ <10 $\mu$		TOTAL D.O.C. PPM <35 $\mu$
		%	PPM	
<u>ALKANOL 189-S</u>				
Lubricating Oil 9250	100	43.2	1.0	2.2
	50	57.4	2.6	4.5
	25	50.5	3.4	6.8
	0	38.1	2.0	5.2
2190-TEP	100	36.1	0.3	0.8
	50	81.4	1.1	1.4
	25	55.2	0.6	1.1
	0	47.8	0.7	1.5
Marine Diesel	100	55.3	3.3	6.0
	50	31.1	3.2	10.2
	25	43.3	5.0	11.5
	0	49.2	1.0	2.1
Navy Distillate	100	41.7	7.5	17.9
	0	63.7	1.4	2.3
Hydraulic Oil	50	38.1	1.0	2.8
	0	78.7	1.8	2.3
Navy Special Fuel Oil	100	50.2	2.7	5.4
	50	42.6	1.9	4.4
	25	30.4	1.7	5.6
	0	29.4	0.6	2.2
South Louisiana Crude	50	39.5	3.4	8.3
	0	54.7	1.6	3.0
Kuwait Crude	50	65.3	23.7	36.3
	0	78.7	18.4	23.2

TABLE 4.11

DISPERSED OIL PRESENT AS DROPLETS SMALLER THAN  
TEN MICRONS WITH COMMERCIAL DETERGENTS

ALL INPUT OIL CONCEN. - 500 ppm

D.O.C. - DISPERSED OIL CONCENTRATION

DATA AT 5 MINUTES AFTER FINAL MIXING

	DET. CONC.	D.O.C. $> 2\mu < 10\mu$		TOTAL D.O.C.
		%	PPM	PPM $< 35\mu$
<u>Rinso:</u>				
Lubricating Oil 9250	100	34.5	0.8	2.4
	50	47.3	1.4	2.9
	0	38.1	2.0	5.2
Hydraulic Oil	100	72.6	6.0	8.2
	50	65.6	3.8	5.8
	25	59.0	4.7	7.9
	0	78.7	1.8	2.3
Navy Distillate	50	35.2	5.6	16.0
	0	63.7	1.4	2.3
Navy Special Fuel Oil	100	49.2	3.8	8.0
	25	60.2	4.0	6.7
	0	29.4	0.6	2.2
<u>All</u>				
Marine Diesel	50	40.5	7.3	17.9
	25	38.7	2.9	7.6
	0	49.2	1.0	2.1
Lubricating Oil 9250	100	57.9	2.6	4.6
	25	23.1	0.3	1.4
	0	38.1	2.0	5.2
Navy Distillate	50	52.7	3.7	7.1
	25	40.5	3.4	8.5
	0	63.7	1.4	2.3
2190-TEP	100	76.6	0.9	1.2
	50	72.1	4.8	6.5
	25	46.4	0.9	2.0
	0	47.8	0.7	1.5

TABLE 4.11  
(CONT.)

ALL INPUT OIL CONCEN. - 500 ppm

D.O.C. - DISPERSED OIL CONCENTRATION

DATA AT 5 MINUTES AFTER FINAL MIXING

	DET. CONC.	D.O.C. > 2u < 10u		TOTAL D.O.C.
		%	PPM	PPM < 35u
<u>Zif</u>				
Lubricating Oil 9250	50	43.4	1.5	3.5
	0	38.1	2.0	5.2
Navy Distillate	100	26.4	1.8	6.9
	50	37.2	3.0	8.0
	0	63.7	1.4	2.3
Navy Special Fuel Oil	50	74.7	0.4	0.5
	0	29.4	2.6	2.2

TABLE 4.12

DISPERSED OIL PRESENT AS DROPLETS SMALLER THAN TEN  
MICRONS WITH HIGH MOLECULAR WEIGHT POLYMERS

ALL OIL INPUT CONC. - 500 PPM

D.O.C.- DISPERSED OIL CONCENTRATION

DATA AT 5 MINUTES AFTER FINAL MIXING

	POLYMER CONC. PPM	D.O.C. > 2 $\mu$ < 10 $\mu$		TOTAL D.O.C. PPM < 35 $\mu$
		%	PPM	
<u>Pluradot HA 510</u>				
Lubricating Oil 9250	250	71.1	3.1	4.4
	125	55.1	2.0	3.6
	25	78.8	1.5	1.9
	0	38.1	2.0	5.2
<u>Merdol SH</u>				
2190-TEP	125	42.8	3.3	7.6
	25	44.8	1.2	2.6
	5	53.3	0.8	1.5
	0	47.8	0.7	1.5
<u>Pluronic L-101</u>				
Kuwait Crude	125	40.9	7.4	18.2
	25	65.3	8.6	14.0
	5	65.6	5.5	8.4
	0	78.7	18.4	23.3

The following group of tables present the data obtained for the tests involving the other parameters called out in the test matrix. Table 4.13 presents the temperature effects study grouped according to oil type. Table 4.14 presents the effects of CH grouped according to oil type. Table 4.15 presents the salinity effects study grouped according to oil type.

TABLE 4.13

EFFECT OF TEMPERATURE ON DISPERSED\* OIL CONCENTRATION

All oil input conc. -500 ppm, data at 5 minutes after final mixing

<u>TEMP.</u>	<u>OIL</u>	<u>DETERGENT</u>	<u>DETERGENT CONC. -PPM</u>	<u>DISPERSED OIL CONC.* -PPM</u>
73°F	Lubricating Oil 9250	Intravon SO	25	3.5
120°F	Lubricating Oil 9250	Intravon SO	25	3.0
73°F	Lubricating Oil 9250	Alkanol 189-S	50	4.5
120°F	Lubricating Oil 9250	Alkanol 189-S	50	1.6
73°F	Lubricating Oil 9250	Aerosol C-61	50	3.7
120°F	Lubricating Oil 9250	Aerosol C-61	50	14.0
120°F	Hydraulic Oil	Aerosol C-61	50	32.4
73°F	Hydraulic Oil	Aerosol OT-75	100	6.7
120°F	Hydraulic Oil	Aerosol OT-75	100	3.2
73°F	Hydraulic Oil	Span 80	50	18.5
120°F	Hydraulic Oil	Span 80	50	13.2
73°F	Hydraulic Oil	Alkanol 189-S	50	3.1
40°F	Hydraulic Oil	Alkanol 189-S	50	6.0
120°F	2190-TEP	Klearfac AB-270	25	11.4
73°F	2190-TEP	Klearfac AB-270	25	5.0
73°F	2190-TEP	Intravon SO	25	2.6
120°F	2190-TEP	Intravon SO	25	2.0
120°F	Navy Distillate	Product BCO	25	12.1
73°F	Navy Distillate	Intravon SO	25	19.3
120°F	Navy Distillate	Intravon SO	25	9.3
73°F	Navy Distillate	Klearfac AB-270	25	21.1
120°F	Navy Distillate	Klearfac AB-270	25	11.4
73°F	South Louis. Crude	Klearfac AB-270	25	32.4
120°F	South Louis. Crude	Klearfac AB-270	25	30.7
40°F	South Louis. Crude	Klearfac AB-270	25	27.8
73°F	Navy Special Fuel Oil	Klearfac AB-270	25	12.4
120°F	Navy Special Fuel Oil	Klearfac AB-270	25	8.6
40°F	Navy Special Fuel Oil	Product BCO	25	1.9
120°F	Marine Diesel	Retarder Lan	100	15.9
120°F	Kuwait Crude	Aerosol C-61	50	48.7
120°F	Kuwait Crude	Span 80	50	36.3

\* as droplets 2-35u in diameter

TABLE 4.14

EFFECT OF pH ON DISPERSED\* OIL CONCENTRATION

All oil input conc. -500 ppm, data at 5 minutes after mixing

<u>pH</u>	<u>OIL</u>	<u>DETERGENT</u>	<u>DET. CONC. PPM</u>	<u>DISPERSED OIL CONC. PPM</u>
6	Kuwait Crude	Span 80	50	32.3
8	Kuwait Crude	Klearfac	50	25.3
6	Kuwait Crude	Klearfac	50	14.2
7	Kuwait Crude	--	-	23.3
7	Marine Diesel	---	-	2.3
7	Marine Diesel	Klearfac	50	22.1
6	Marine Diesel	Klearfac	50	24.6
6	Marine Diesel	Triton	25	24.4
6	Marine Diesel	Intravon 50	100	23.6
7	Marine Diesel	Triton	25	34.2
7	Marine Diesel	Intravon 50	100	11.1
6	Marine Diesel	Span 80	100	81.3
6	Marine Diesel	Product BCO	50	27.2
7	2190-TEP	--	-	1.5
7	2190-TEP	Klearfac AB-270	50	7.2
6	2190-TEP	Klearfac AB-270	50	9.8
7	2190-TEP	Retarder	25	7.7
6	2190-TEP	Retarder	25	5.5
6	2190-TEP	BCO	50	4.0
7	2190-TEP	Alkanol 189-S	100	0.8
8	2190-TEP	Alkanol	100	1.9
8	2190-TEP	Triton	25	6.2
7	2190-TEP	Span 80	50	7.2
6	2190-TEP	Span 80	50	7.7
7	Lubricating Oil 9250	---	-	5.2
7	Lubricating Oil 9250	Intravon	100	4.1
6	Lubricating Oil 9250	Intravon	100	3.4
7	Lubricating Oil 9250	Alkanol	100	2.2
6	Lubricating Oil 9250	Alkanol	100	3.6
7	Lubricating Oil 9250	BCO	50	2.4
6	Lubricating Oil 9250	BCO	50	11.0
7	Lubricating Oil 9250	Klearfac	50	14.0
6	Lubricating Oil 9250	Klearfac	50	6.4
7	Lubricating Oil 9250	Span 80	50	5.4
6	Lubricating Oil 9250	Span 80	50	8.2

NOTE: pH is 7 except where noted

\* as droplets 2-35u in diameter

TABLE 4.14 (CONTINUED)

EFFECT OF pH ON DISPERSED OIL CONCENTRATION

<u>pH</u>	<u>OIL</u>	<u>DETERGENT</u>	<u>DETERGENT CONC. ppm</u>	<u>DISPERSED OIL CONC. ppm</u>
7	Hydraulic Oil		---	2.3
6	Hydraulic Oil	Klearfac	50	11.4
8	Hydraulic Oil	Product BCO	50	11.5
8	Hydraulic Oil	Alkanol	100	9.1
6	Hydraulic Oil	Span 80	50	8.5
7	Hydraulic Oil	Span 80	50	18.5
8	Hydraulic Oil	Span 80	50	19.7
6	Hydraulic Oil	Product BCO	50	6.7
7	Navy Distillate			3.3
6	Navy Distillate	Span 80	50	46.5
7	Navy Distillate	Span 80	50	16.0
8	Navy Distillate	Span 80	50	33.3
6	Navy Distillate	Klearfac	50	29.9
6	Navy Distillate	Retarder	25	20.7
6	Navy Distillate	BCO	50	26.4
7	South Louisiana Crude			3.0
6	South Louisiana Crude	Klearfac AB-270	50	14.9
6	South Louisiana Crude	Product BCO	50	41.1
6	South Louisiana Crude	Span 80	50	68.7

\* as droplets 2-35 $\mu$  in diameter

TABLE 4.15

EFFECT OF SALINITY ON DISPERSED\* OIL CONCENTRATION

All oil input conc. -500 ppm, Data at 5 minutes after final mixing

<u>% SALINITY**</u>	<u>OIL</u>	<u>DETERGENT</u>	<u>DET. CONC.</u>	<u>DISPERSED OIL CONC. PPM</u>
0%	Marine Diesel	Product BCO	100	44.1
50%	Marine Diesel	Product BCO	100	30.5
0%	Marine Diesel	Klearfac	50	22.1
50%	Marine Diesel	Klearfac	100	9.5
0%	Kuwait Crude	Span 80	100	30.7
50%	Kuwait Crude	Span 80	100	14.4
0%	2190-TEP	Product BCO	100	3.3
50%	2190-TEP	Product BCO	100	4.2
50%	Lubricating Oil 9250	Klearfac AB-270	100	7.2
50%	Navy Distillate	Klearfac AB-270	100	37.2
50%	Lubricating Oil 9250	Product BCO	100	8.3
50%	Navy Distillate	Product BCO	100	74.3
50%	Marine Diesel	Span 80	100	75.4

\*\*NOTE: Salinity is represented as % of seawater salinity.

\* as droplets 2-35u in diameter

## 4.2 OTHER EXPERIMENTAL RESULTS

Since the data generated (and reduced) from the randomized test sequence indicated that the critical micelle concentration was not being reached, additional experiments involving higher detergent concentrations were included for study. The results of these high surfactant concentration studies are presented in Table 4.16. The data will be discussed and graphically presented in Section 5.0.

Table 4.17 presents the data generated in a series of test wherein the effects of adding the detergent to water followed by the oil (agent-in-water method) was studied. Data from the previous comparable agent-in-oil method are included to show the change in dispersion observed.

It should also be noted that the test matrix called for a number of tests using the Trace Oil Monitor under development by G.E. be conducted to determine the effects of detergent on the performance of this device. Three separate attempts were made to observe these effects and the instrument test system did not allow any significant or reliable measurements to be made. In each case the detergent used in the test would enhance the formation of emulsion in a continuously increasing amount so rapidly that the meter would promptly be driven off-scale. This was a function of the agitation rate and intensity introduced by the mixing devices in the test system. Modification of the system was not considered to be possible without affecting the parameters required for operating the Trace Oil Monitor. The oil dispersion was so unstable that a measurement could not be reliably made. It should be possible to obtain data on these effects when the current prototype in development is completed.

TABLE 4.16

DISPERSED OIL PRESENT AS DROPLETS SMALLER THAN TEN MICRONS

WITH HIGH SURFACTANT CONCENTRATIONS

ALL OIL INPUT CONC. - 500 ppm

D.O.C. - DISPERSED OIL CONCENTRATION

DATA AT 5 MINUTES AFTER FINAL MIXING

SURFACTANT	SURFACTANT CONC. PPM	OIL TYPE	D.O.C. > 2μ < 10μ		TOTAL D.O.C. PPM < 35μ
			%	PPM	
Alkanol 189-S (anionic)	5000	Marine Diesel	54.6	8.9	16.3
	1000	Marine Diesel	44.2	10.5	23.8
	500	Marine Diesel	43.0	7.7	17.8
	0	Marine Diesel	49.2	1.0	2.1
Intravon SO (non-ionic)	5000	Marine Diesel	29.6	16.0	54.1
	1000	Marine Diesel	31.0	17.0	55.0
	500	Marine Diesel	32.2	12.5	38.7
	0	Marine Diesel	49.2	1.0	2.1
Product BCO (cationic)	5000	Marine Diesel	32.4	17.0	52.5
	1000	Marine Diesel	45.5	14.3	40.4
	500	Marine Diesel	35.9	7.9	22.0
	0	Marine Diesel	49.2	1.0	2.1
Alkanol 189-S (anionic)	5000	2190-TEP	40.4	2.1	5.2
	1000	2190-TEP	42.4	2.2	5.3
	500	2190-TEP	38.0	1.0	2.6
	0	2190-TEP	47.8	0.7	1.5
Intravon SO (non-ionic)	5000	2190-TEP	33.6	5.0	14.9
	1000	2190-TEP	34.1	3.8	11.1
	500	2190-TEP	32.5	2.1	6.6
	0	2190-TEP	47.8	0.7	1.5
Product BCO (cationic)	5000	2190-TEP	45.6	4.4	9.7
	1000	2190-TEP	58.9	1.9	3.3
	500	2190-TEP	58.5	3.3	5.7
	0	2190-TEP	47.8	0.7	1.5

TABLE 4.17

COMPARISON OF DISPERSED OIL CONCENTRATIONS FOR  
AGENT-IN-OIL AND AGENT-IN-WATER MIXING METHODS

All oil input concentrations - 500 ppm  
Data at 5 min. after mixing

<u>ALKANOL 189 - S</u> <u>(Anionic)</u>	<u>SURFACTANT</u> <u>CONC.</u>	<u>TOTAL PPM</u>		<u>D.O.C.* 2u &lt; 10u PPM</u>	
		<u>AGENT IN</u> <u>WATER METH.</u>	<u>35u</u> <u>AGENT IN OIL</u> <u>METHOD</u>	<u>AGENT IN</u> <u>OIL METH.</u>	<u>AGENT IN</u> <u>WATER METHOD</u>
Marine Diesel	5000	40.9	16.3	8.9	9.2
	1000	37.2	23.8	10.5	13.1
	500	27.3	17.8	7.7	12.4
	100	15.8	6.0	3.3	11.3
	50	13.7	10.2	3.2	5.7
	25	19.3	11.5	5.0	16.4
	0	2.1	2.1	1.0	1.0
2190 TEP	5000	7.5	5.2	2.1	3.7
	1000	2.6	5.3	2.2	1.0
	500	4.6	2.6	1.0	2.2
	100	2.4	0.8	0.3	1.2
	0	1.5	1.5	0.7	0.7

\*D.O.C. - Dispersed Oil Concentration

## 5.0 Results and Discussion

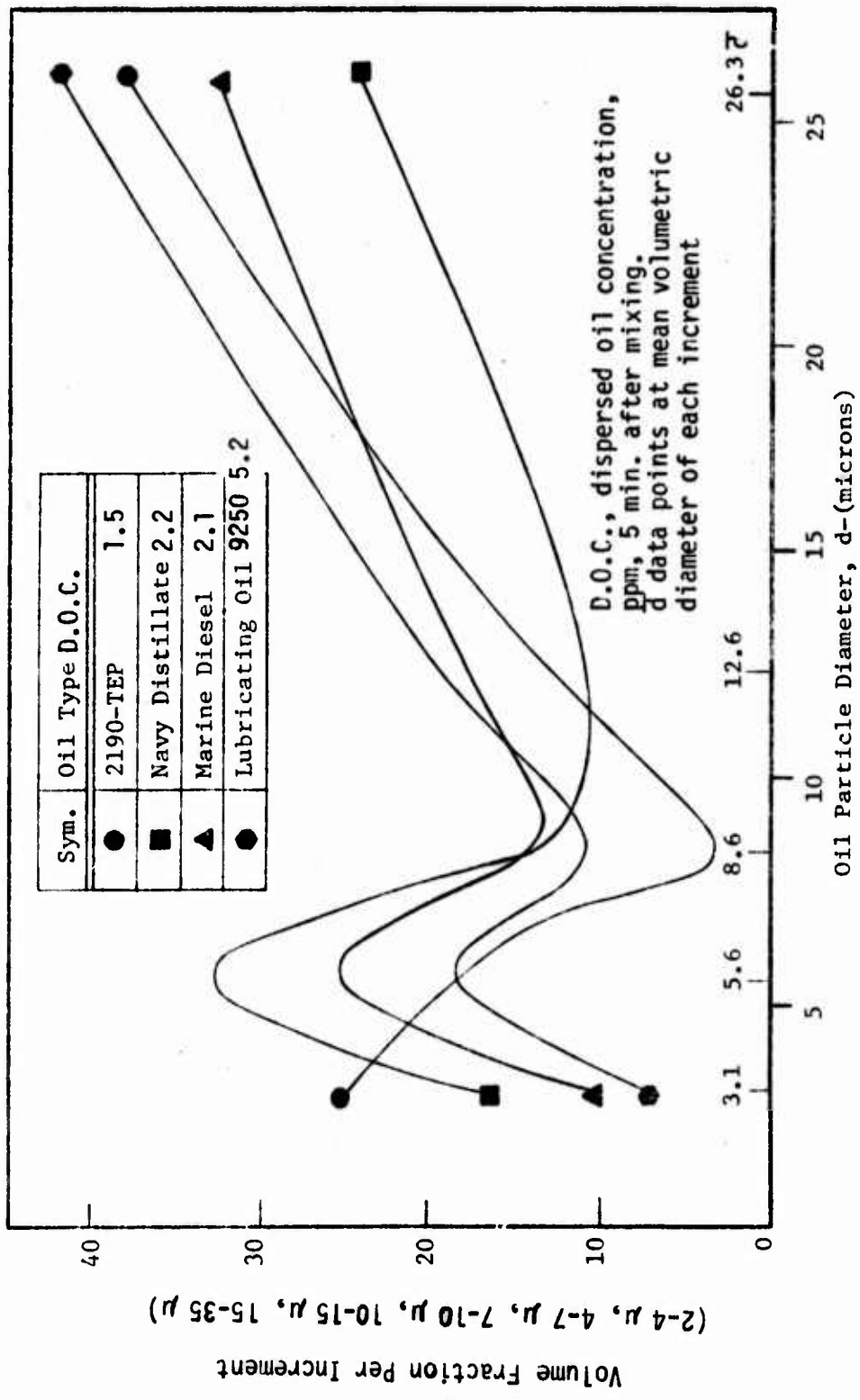
All of the experimental data presented in Section 4.0 Experimental Results were obtained by oil volume calculations based on particle counts of dispersed oil particles in the test mixtures of oil, water and surfactant. The term "dispersed" represents oil droplets in the 2-35 micron range. The basic data used for this oil volume calculation are presented in Appendix A. The data are presented as counts per 5 milliliters of a 1 : 60 dilution of the original sample less background and taken five minutes after time zero. Time zero is the instant when agitation of the mixture was completed. The exact time sequence, sample handling and counting procedures were described earlier in Section 3.0 Experimental Procedure.

To evaluate the emulsifying effects of synthetic detergents, high molecular weight polymers and commercial products on oily-water mixtures, the simple oil/water mixtures were considered as the baselines. The emulsifying effects under study were (1) amount of dispersed oil in the mixture, and (2) stability of this mixture. The amount of dispersed oil was found by calculations of volume from particle count data, and stability of emulsions was judged by the particle size distribution which indicated the volume fraction present in small particles. These small particles, of diameter less than ten microns, represented a nearly permanent emulsion since they tend to remain dispersed unaffected by gravity; in addition, the presence of sufficient surface active agent tends to prevent flocculation and coalescence of these small oil droplets.

### 5.1 Particle Size Distribution of Baseline Oil/Water Mixtures

The percentage distribution and concentration of dispersed oil in the baseline oil/water mixtures is tabulated in Table 4.1 and 4.2. These are dispersed oil concentrations (D.O.C) and particle size distributions for the simple oil/water mixtures generated with no detergent using the technique outlined in Section 3.0. This data is plotted in Figures 5.1 and 5.2 as volume fraction per counting increment versus volumetric mean diameter of each increment.

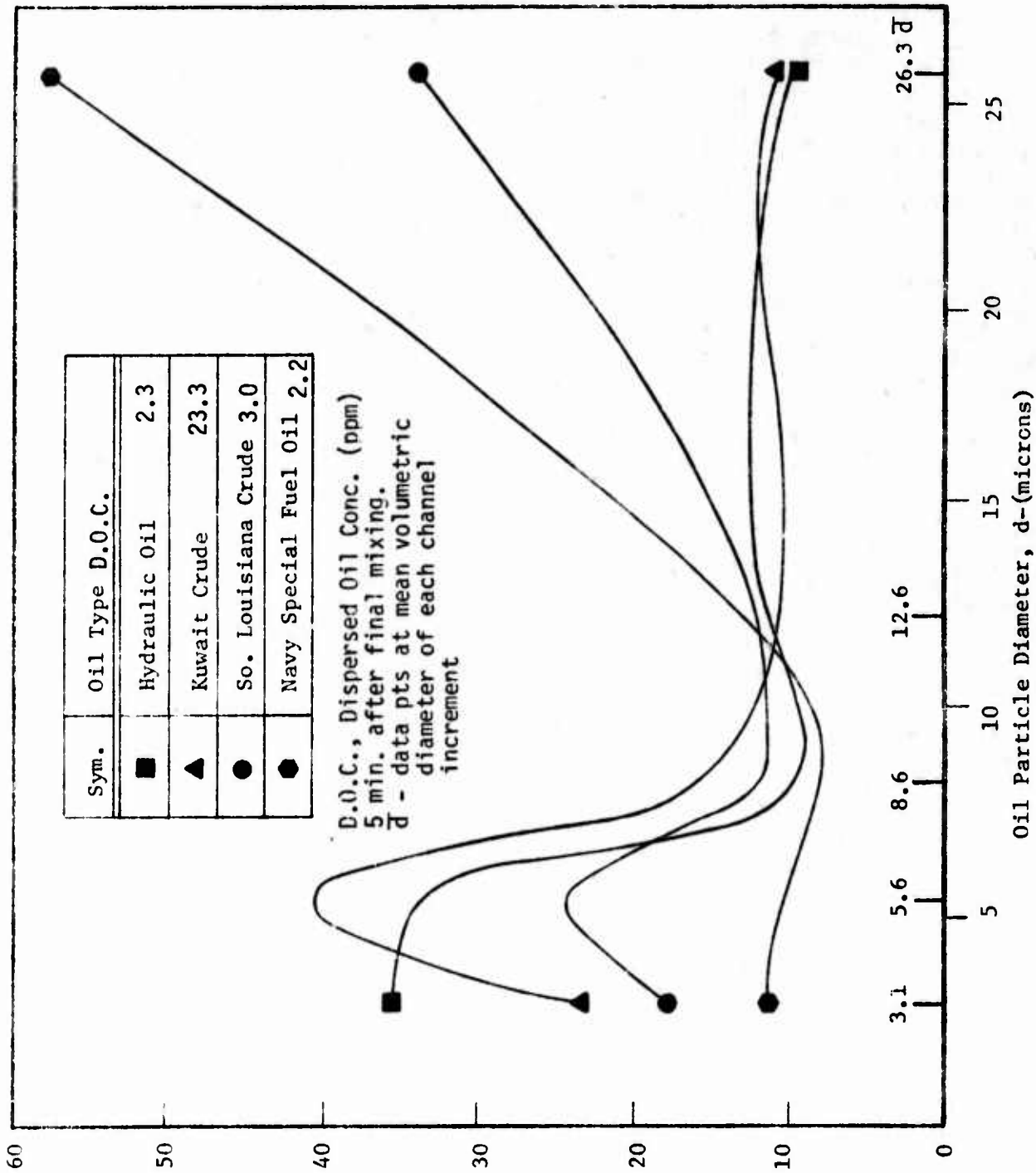
Although the dispersed concentration of each oil is quite similar for all test oils (except Kuwait Crude which will be discussed later), their size distributions show differences depending on the type of oil, e.g. 2190-TEP and Lubricating Oil 9250 show smaller volume fractions in the small size ranges than do the lighter oils (Marine Diesel, Navy Distillate) indicating that lubricating oils are emulsified less readily. This could be accounted for by physical properties such as density and viscosity. These differences in particle size distribution of an O/W mixture between types was expected to cause concomitant differences whenever detergent was added.



Distribution of Oil Droplet Size In Disperse Phase of Test Oil/Water Mixtures (Ref. Table 4.2)

Figure 5.1

Volume Fraction Per Increment  
 (2-4  $\mu$ , 4-7  $\mu$ , 7-10  $\mu$ , 10-15  $\mu$ , 15-35  $\mu$ )



Distribution of Oil Droplet Size  
 In Disperse Phase of Test Oil/Water Mixtures (Ref. Table 4.2)

Figure 5.2

## 5.2 General Trends of Oil/Water/Detergent Mixtures

Although emulsified oil concentration with a given detergent seemed to vary substantially with each oil, the concentrations of emulsified oil were more directly comparable between the groups of individual oil types. That is, for a given detergent sample, emulsified oil concentrations were generally similar for lubricating oils (2190 TEP, 9250), light fuel oils (marine diesel, Navy Distillate Fuel) and crude oils (Kuwait crude, South Louisiana crude) as groups. With all classes of detergents tested, dispersed oil concentration was usually highest for fuel oils, with the crude oils emulsified only slightly less. The lubricating oils were far less susceptible to emulsification as evidenced by substantially lower dispersed oil concentration than either crudes or the fuels with any detergent type. Hydraulic oil was not considered in any of the three above mentioned categories, as it is a unique oil type due to its constituents and use. It generally fell closest to the crude oils in concentration of emulsified oil with most detergent samples.

Table 5.1 is presented below as a simple, broad over-view of all the tests. The data presented in this table are average concentrations of dispersed oil for the test oil types with surfactant of a given chemical type present. The eight test oils were classified according to type; the dispersed oil concentrations of oils within that group, with any detergent of a given type, at all concentrations; were averaged together. (Dispersed oil concentrations for the test oils with respect to the individual detergent types and concentrations are tabulated in Tables 4.3 to 4.7 inclusive.) The dispersed oil concentrations of the base line oil-water mixtures were also averaged, and are also presented in Table 5.1.

From the data shown in Table 5.1, the following broad conclusions can be drawn:

- (1) Syndets of cationic type produced the highest concentration of dispersed (or emulsified) oil with all of the oil types tested.
- (2) Of the three detergent types, anionic syndets generated least emulsified oil with fuel oils.
- (3) For crude oils and lubricating oils, addition of both anionic or non-ionic syndets produced similar amounts of emulsification.
- (4) Hydraulic oil dispersability falls between the lubricating oils (low dispersability and the other groups).

TABLE 5.1

AVERAGE DISPERSED<sup>1</sup> OIL CONCENTRATION  
FOR FOUR OIL TYPE GROUPS  
IN PRESENCE OF DETERGENT<sup>2</sup>

Data at 5 minutes after final  
mixing; all input oil concen-  
tration - 500 ppm.

(n = number of data points averaged for that value)

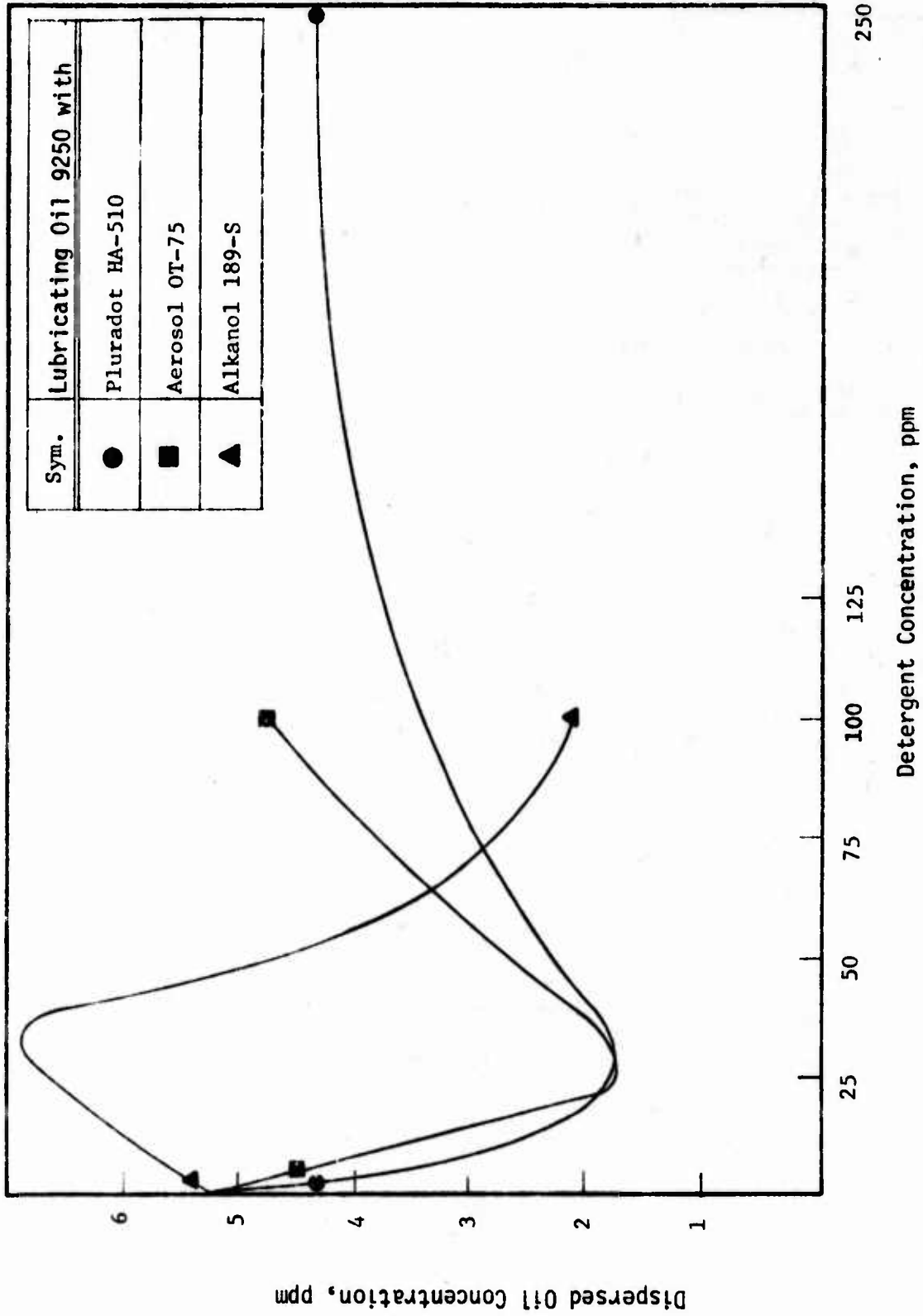
Detergent Type	Anionic	Cationic	Non-Ionic	No Detergent
OIL TYPE:				
Fuel Oils: (marine diesel, navy distillate)	12.1 n=5	35.8 n=9	27.3 n=15	2.2 n=2
Lubricating Oils: (2190-TEP, Lub- ricating Oil 9250)	4.2 n=12	6.1 n=14	4.6 n=15	3.3 n=2
Crude Oils: Kuwait Crude, S. Louisiana Crude, Navy Special Fuel Oil	18.0 n=9	32.2 n=5	16.1 n=1	9.5 n=3
Hydraulic Oil	7.1 n=4	20.2 n=2	12.3 n=9	2.3 n=1

- Notes: 1. Oil dispersed as droplets with diameters  
between 2 to 35 microns.
2. Detergent concentrations 25, 50, 100 ppm

Although these general observations are probably indicative of the emulsifying effect of the various synthetic detergent types on oil/water mixtures, a more in-depth analysis relating to the purpose of this study was made.

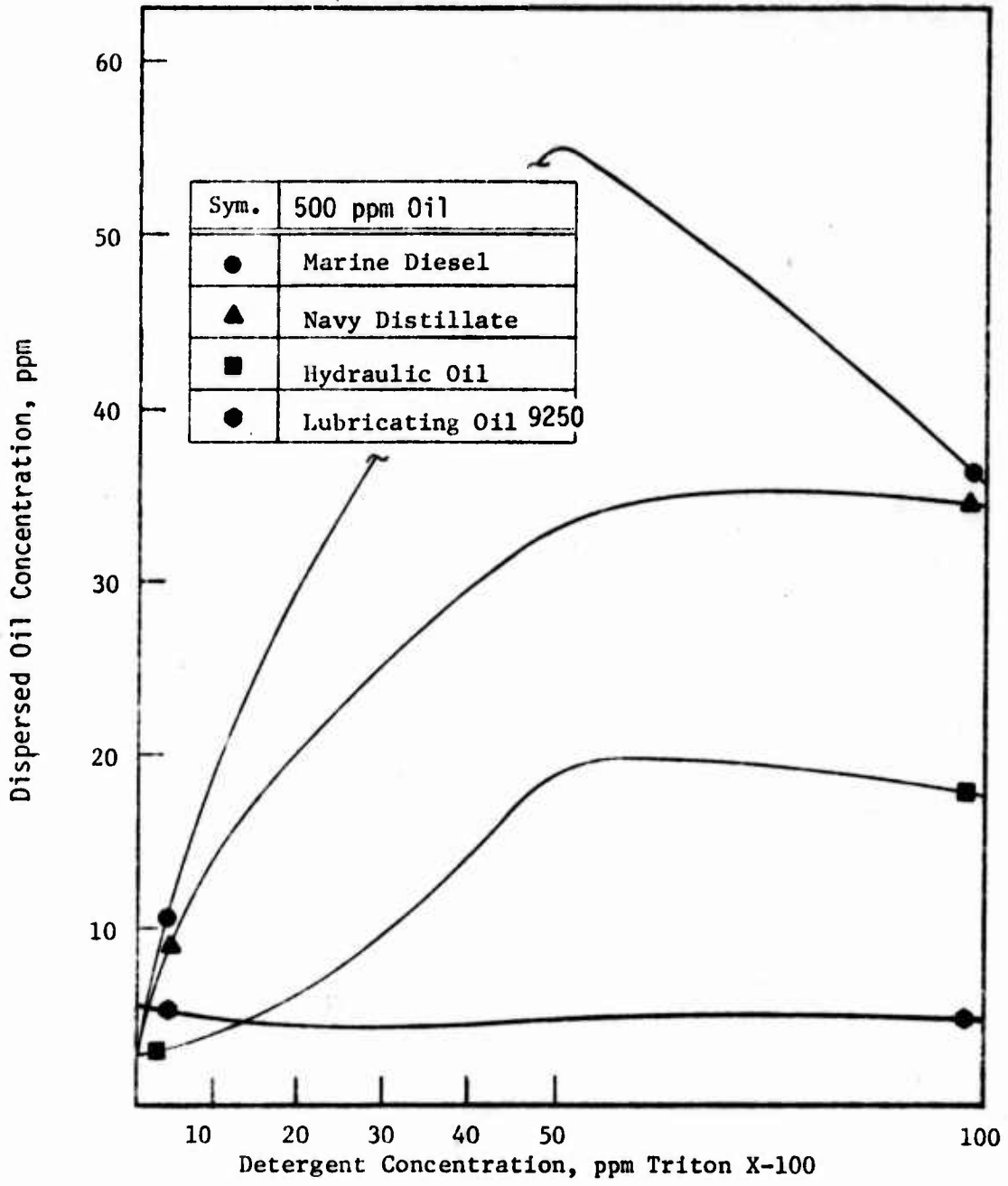
Low detergent concentrations (less than 100 ppm) of anionic and non-ionic detergents and high molecular weight polymers seem to exert a demulsifying effect on lubricating and crude oils, as evidenced by higher dispersed oil concentrations in the oil/water only mixtures relative to the oil/water plus detergent emulsions (Tables 4.3, 4.5, and 4.7). The "demulsification" probably occurred during the two minute settling period during which time the freshly generated emulsion is unstable and flocculation and coalescence took place. Detergent concentrations less than 100 ppm were insufficient to provide a complete monomolecular film over each oil droplet, and hence did not stabilize the emulsion. Also, small concentrations of surfactants lower the surface tension of water, and consequently the interfacial tension between dispersed oil and water is similarly lowered. This reduction in interfacial tension would also enhance flocculation and coalescence. For example, a mixture of lubricating oil 9250 and distilled water showed a dispersed oil concentration of 5.2 ppm; with the addition of 25 ppm Aerosol OT-75 (anionic) the dispersed oil concentration in the mixture had dropped to 1.9 ppm (Table 4.5, Figure 5.3). Similar demulsification effects on this lubricating oil were evidenced with low concentrations of commercial products All and Rinse (Table 4.6).

However, the presence of detergents in most of the oily water mixtures studied usually increased the amount of dispersed oil. The amount of emulsification was studied as a function of increasing detergent concentration. It was found that increases in dispersed oil concentration were not directly proportional to increases in detergent concentration. The general trend of emulsification in presence of detergent indicated an initial increase of dispersed oil with addition of detergent, followed by a leveling off of dispersed oil concentration with increasing detergent concentration. In some cases dispersed oil content decreased upon further addition of detergent. These phenomena are illustrated in Figures 5.4, 5.5, 5.6, and 5.7, where dispersed oil concentrations to detergent concentration for the three non-ionic detergents are plotted. (The curves for Kuwait Crude with Span 80 and Intravon SO - Figures 5.5 and 5.7 - show the demulsifying effect of low concentrations of detergents which was discussed previously.) An effect such as this "leveling off" of emulsification may be explained by the micro processes which were occurring in the mixtures. The addition of small amounts of detergent reduced interfacial tension which favored emulsification of the oil. At a higher concentration level, enough detergent adsorbed onto the dispersed oil droplets, to form a complete interfacial film impeding flocculation and coalescence. At this point a substantial amount of oil was dispersed, but was then stabilized by the presence of sufficient detergent. If the dispersed oil drops are completely covered by adsorbed detergent



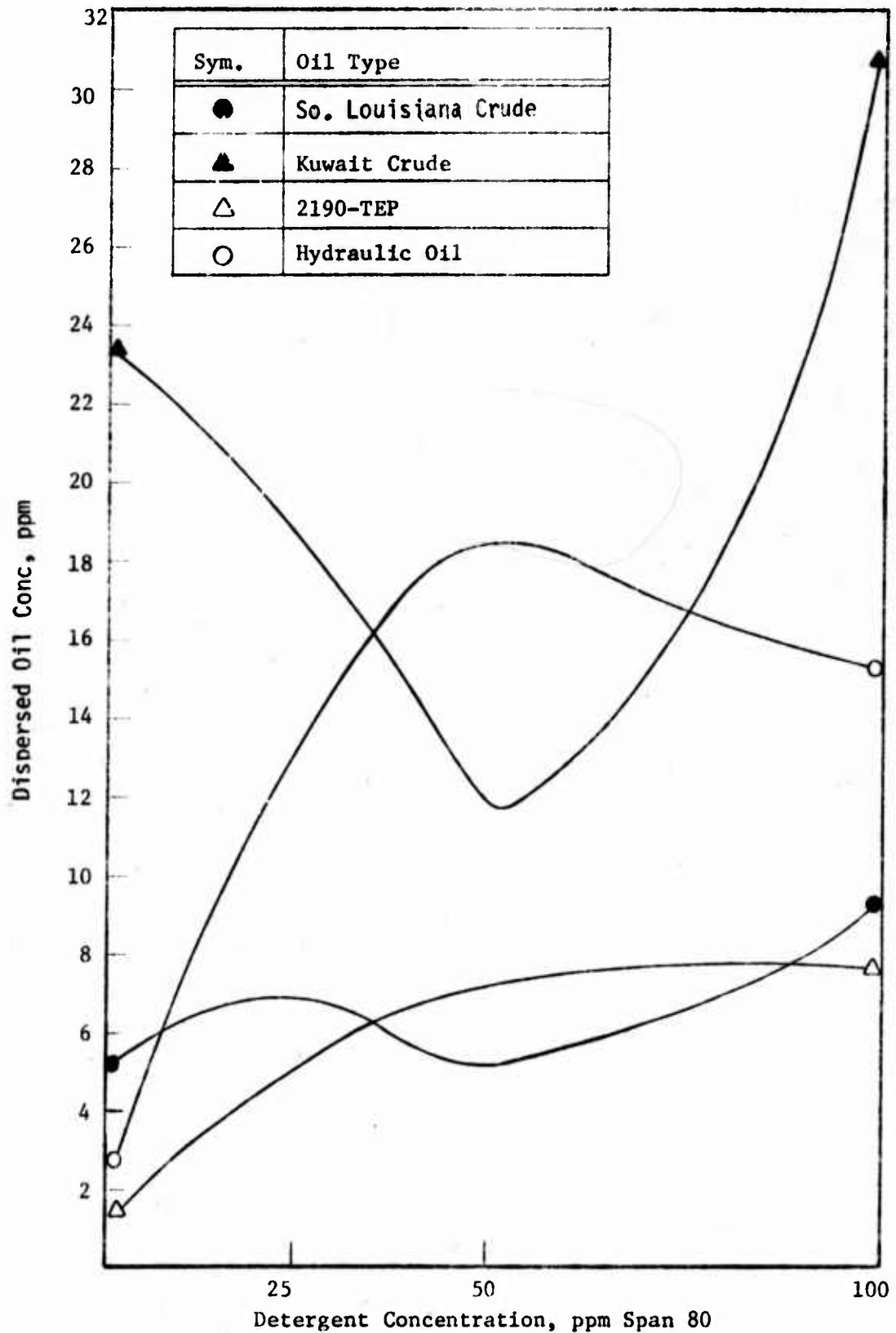
Dispersed Oil Concentration vs. Concentration of 3 Detergents  
(Ref. Tables 4.5, 4.7)

Figure 5.3



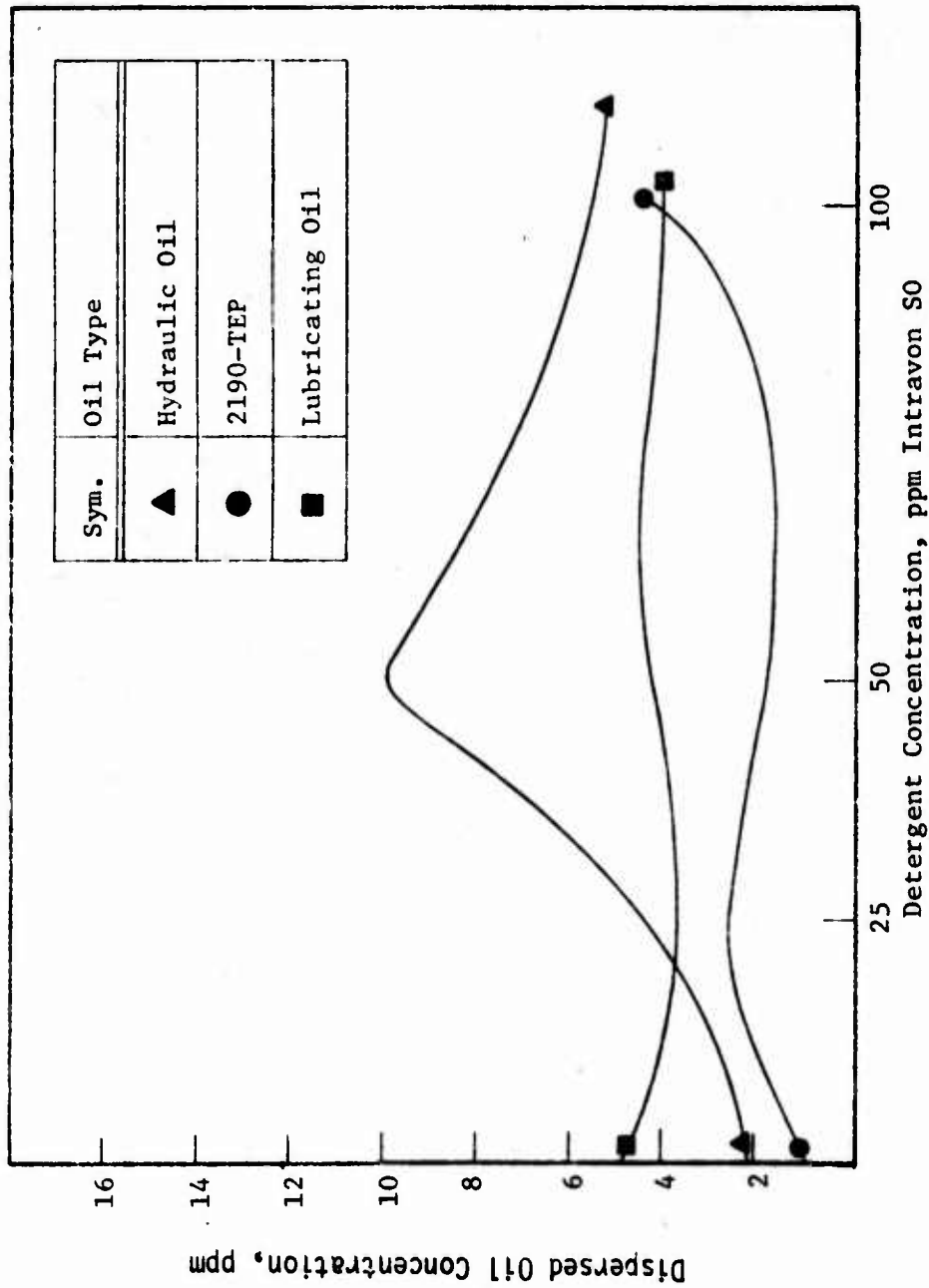
Dispersed Oil Concentration Vs. Non-ionic Detergent Concentration (Triton X-100) (Ref. Table 4.3)

Figure 5.4



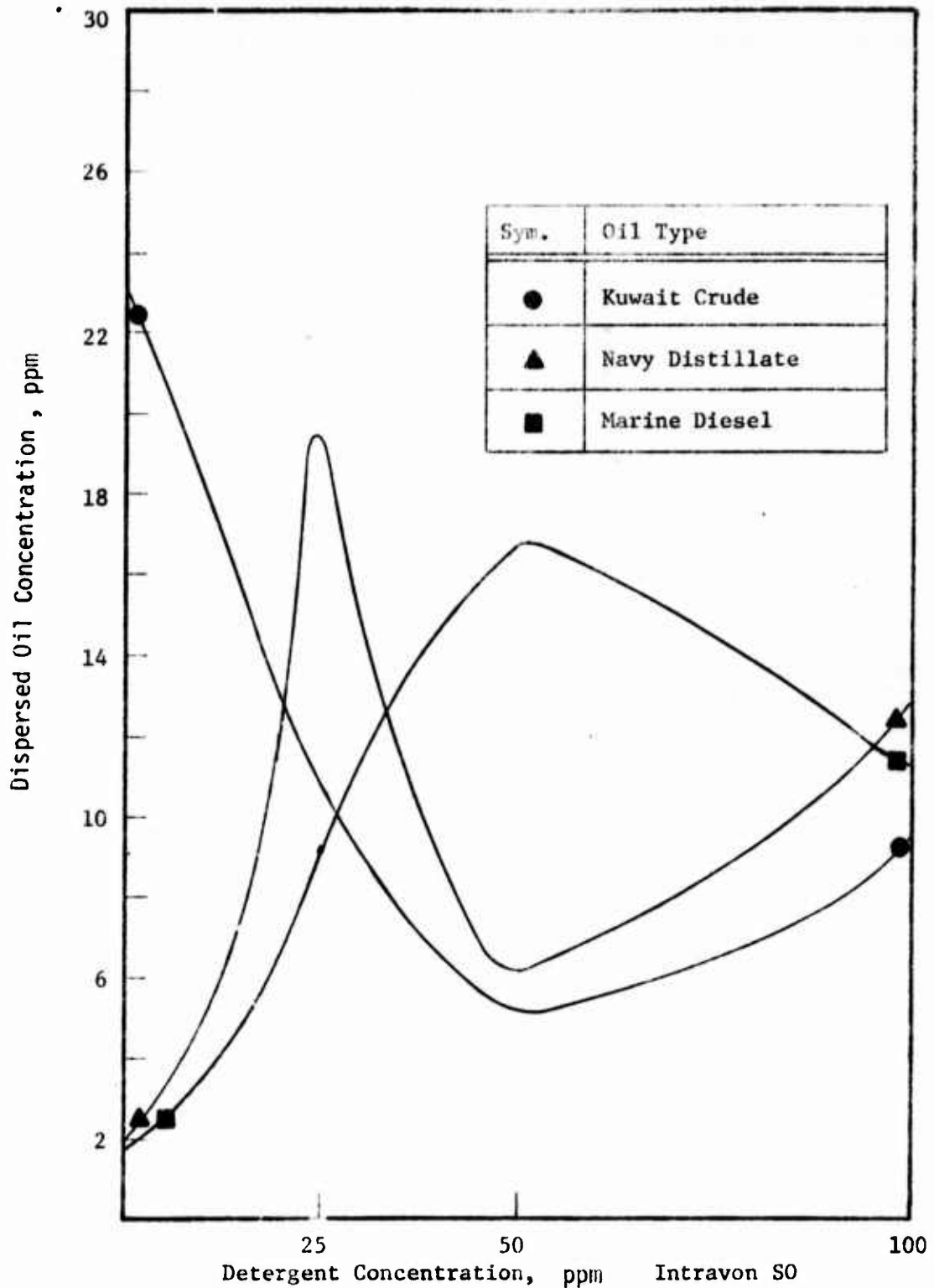
Dispersed Oil Concentration Vs Non-ionic Detergent Concentration (Span 80) (Ref. Table 4.3)

Figure 5.5



Dispersed Oil Concentration Vs Non-Ionic Detergent (Intravon S0) Concentration  
(Ref. Table 4.3)

Figure 5.6



Dispersed Oil Concentration vs Non-Ionic Detergent (Intravon S0). (Ref. Table 4.3)

Figure 5.7

further addition of detergent (e.g. higher detergent concentration) caused only small changes in emulsifying effect (i.e. 34.6 ppm dispersed Navy distillate with 100 ppm Triton X-100. Figure 5.4, Table 4.3). This was not true in all cases, since with both Triton X-100 and Intravon S0 dispersed oil content of marine diesel decreased with increasing surfactant concentration. (Figures 5.4, 5.7, Table 4.3).

The emulsifying effects of the three pure detergent types (cationics, anionics and non-ionic) were compared in Table 5.1, as an over-view of all the test emulsions generated. The emulsifying effect, or the amount of dispersed oil of the detergents of each chemical type on each oil (input concentration of 500 ppm) is presented in Tables 4.3 - 4.5, inclusive. By comparing the data presented in these tables, one can again see that the cationic type detergents generated emulsions with the highest dispersed oil concentrations. This was also physically evident by the cloudy or milky appearance of the mixtures which persisted hours after mixing.

Table 4.3 presents the dispersed oil concentrations in the presence of non-ionic type surfactants. The readily emulsifiable fuel and crude oils showed relatively high concentrations of dispersed oil, ranging from 8.9 ppm (marine diesel/25 ppm Intravon S0) to 55.1 ppm (marine diesel 50 ppm Triton X-100). The hydraulic oil/non-ionic detergent mixtures had dispersed oil content ranging from 4.2 ppm (with 25 ppm Intravon S0) to 19.7 ppm (with 50 ppm Triton X-100). The lubricating oils were only minimally emulsified, as dispersed oil content was less than 10 ppm in the fifteen cases tested.

As can also be noted from Table 4.3, Triton X-100 and Span 80 generated similar amounts of dispersed oil, which was substantially higher than that produced by Intravon S0. (Mixtures with Intravon S0 had less than 20 ppm total dispersed oil). However emulsions with Triton X-100 and Span 80 differed considerably in dispersed oil present as small (<10 microns) droplets. Those with Span 80 showed less dispersed oil in the 2-10 micron range than mixtures with Triton X-100, which was indicative of less stable emulsions. Of the non-ionic surfactants, mixtures with Intravon S0 had the least oil content (less than 10 ppm) dispersed in particles between 2-10 microns. McCutcheon's Detergents and Emulsifiers Annual 1972 classifies Intravon S0 as a non-ionic type and describes it as a mixture of surfactants. Based on its similarity to the anionic types in emulsifying tendency it seems likely that a slightly anionic-type surfactant may be present in the formulation.

Of these three types of pure detergent-actives, the anionic type promoted the least emulsification (e.g., maximum dispersed oil concentration was 36.3 ppm with Kuwait crude oil and 50 ppm Alkanol 189-S). Of the thirty eight tests conducted with anionic type detergents, thirty showed less than 15 ppm total dispersed oil, and none exceeded 15 ppm oil present as droplets between two and ten microns diameter (see Tables 4.5, 4.10).

The commercial products tested also produced mixtures low in dispersed oil content, e.g. maximum dispersed oil concentration was 16.3 ppm Navy Distillate with 25 ppm Rinso (Table 4.6). However, addition of the test concentrations of these detergents actually represent less surfactant than the nominal concentration, since these products are diluted with inert ingredients. If one assumes that these products contain 20% surfactant, the maximum concentration of detergent present in these test mixtures was 20 ppm. Even this amount of detergent doubled the amount of dispersed oil present in most cases; therefore from this standpoint, it would seem that commercial products have a substantial emulsifying effect.

The presence of high molecular weight polymers in bilge water even at high concentrations (125 ppm), had a demulsifying effect on two test oils (Kuwait crude and Lubricating Oil 9250) (Figure 5.3). This may be due to the presence of natural surface active agents in crude oils and various constituents in the lubricating oil whose effects are minimized or even counteracted by the polymers. Dispersed oil content in the mixture of the third test oil (2190-TEP) with the polymer Mersol SH was higher than the simple Oil/Water mixture, but only approached 10 ppm at a polymer concentration of 125 ppm (Figure 5.8).

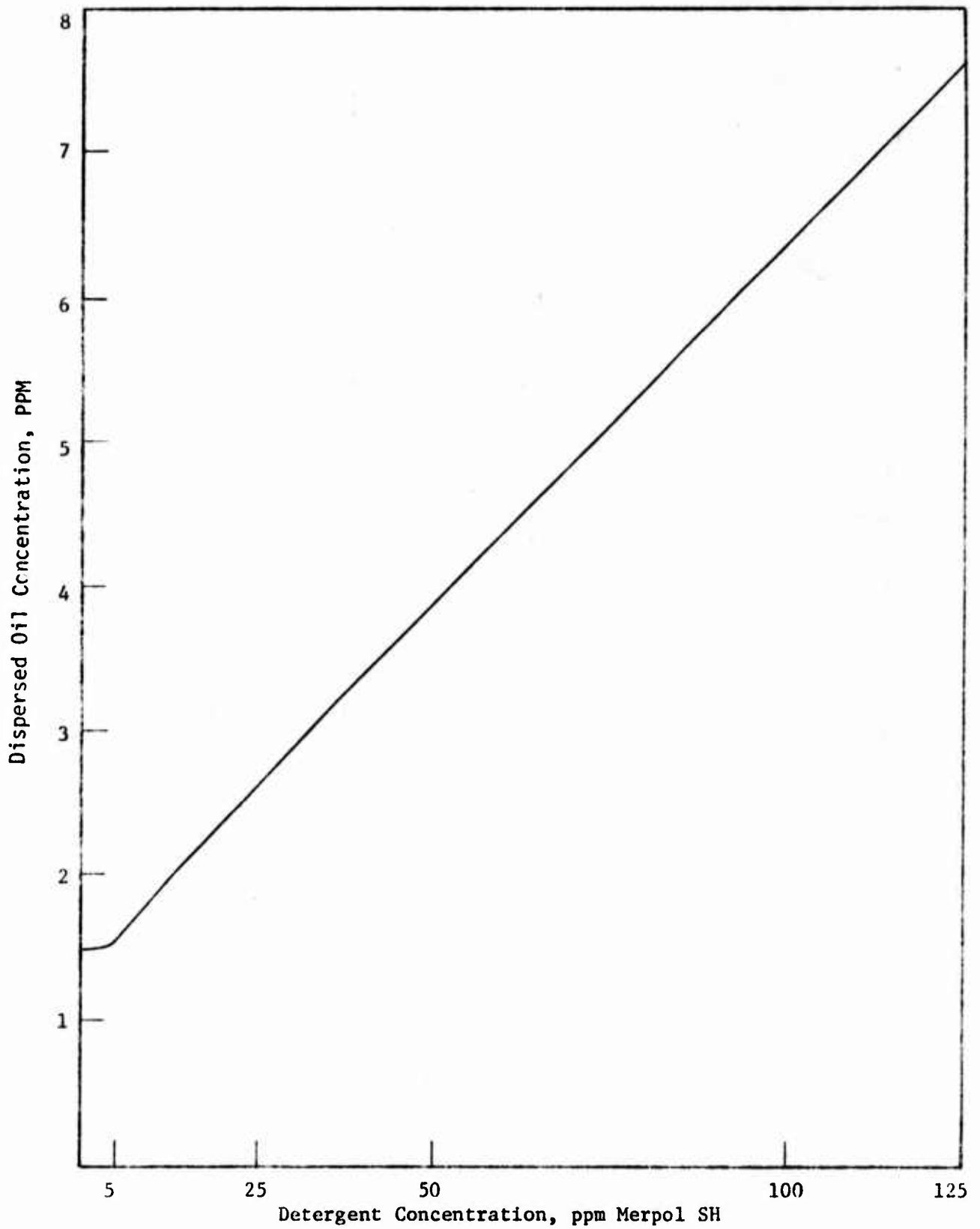
Although dispersed oil concentration was used as the measure of emulsifying effects of detergents, particle size distribution of the dispersed oil is important and necessary. The distributions can be used to determine the fraction of the total dispersed oil concentration present in any selected size range. Such percentage distributions are shown in Figure 5.9 where the test results with Navy Distillate and Triton X-100 (non-ionic) are shown. From Table 4.8 it can be seen that more oil in diameters <10 microns is present with detergent than with no detergent, but the percentage distribution indicates an opposite trend. Or, in a more illustrative fashion:

NAVY DISTILLATE: TRITON X-100

		<u>0</u>	<u>25</u>	<u>50</u>	<u>100</u> PPM Detergent
	Particles 10 $\mu$				
Table 4.8	Actual Concentration (ppm)	1.4	8.4	11.7	18.2
Figure 5.9	Volume Fraction (%)	70	50	40	62

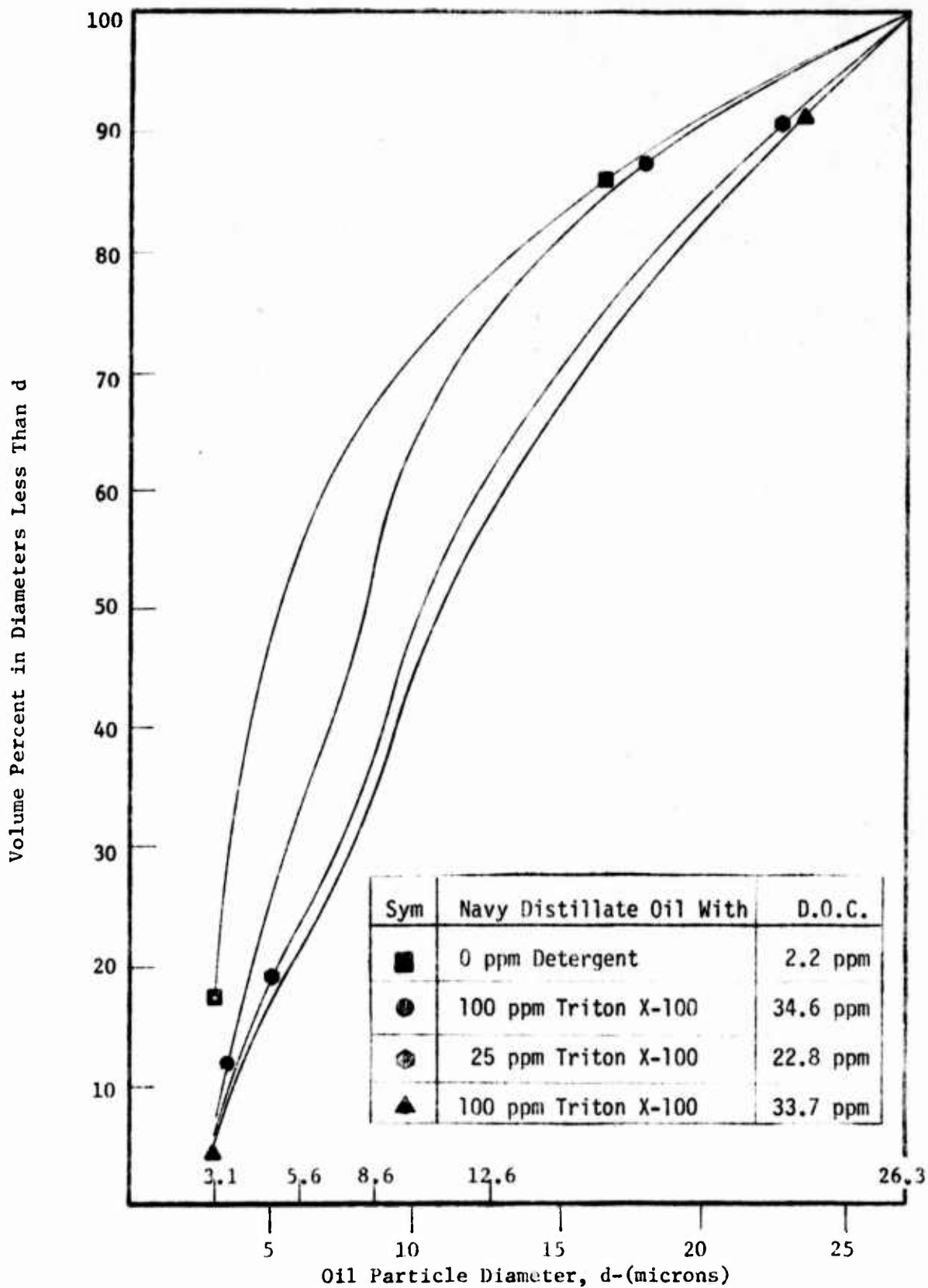
Therefore, in evaluations of this type, it was deemed more important to determine concentration levels than to obtain statistical distributions. That is, does more detergent of a type produce more highly dispersed oil in bilge water mixtures?

Additional discussion of this effect on particle size distribution of oil by various detergents is seen in Figure 5.10 where distributions of Navy Distillate with 25 ppm of cationic (Aerosol C-61), anionic (Klearfac AB-270) and non-ionic (Span 80) detergent are presented. The volume per cent of dispersed oil in small particles (less than ten microns) was quite similar for the simple oil/water mixture (63.7%), and the cationic detergent mixture (61.3%) (See Table 4.9). The mixture with non-ionic Span 80 showed the smallest fraction of volume (34.5%) in the small size range. Comparison of the total concentration (2-35  $\mu$ ) of dispersed oil to the concentration (2-10  $\mu$ ) indicates the stability



Dispersed Oil Concentration (2190-TEP) Vs Polymer Concentration (Merpol SH)

Figure 5.8



Effect of Non-Ionic Detergent Concentration on Oil Drop Size Distribution.

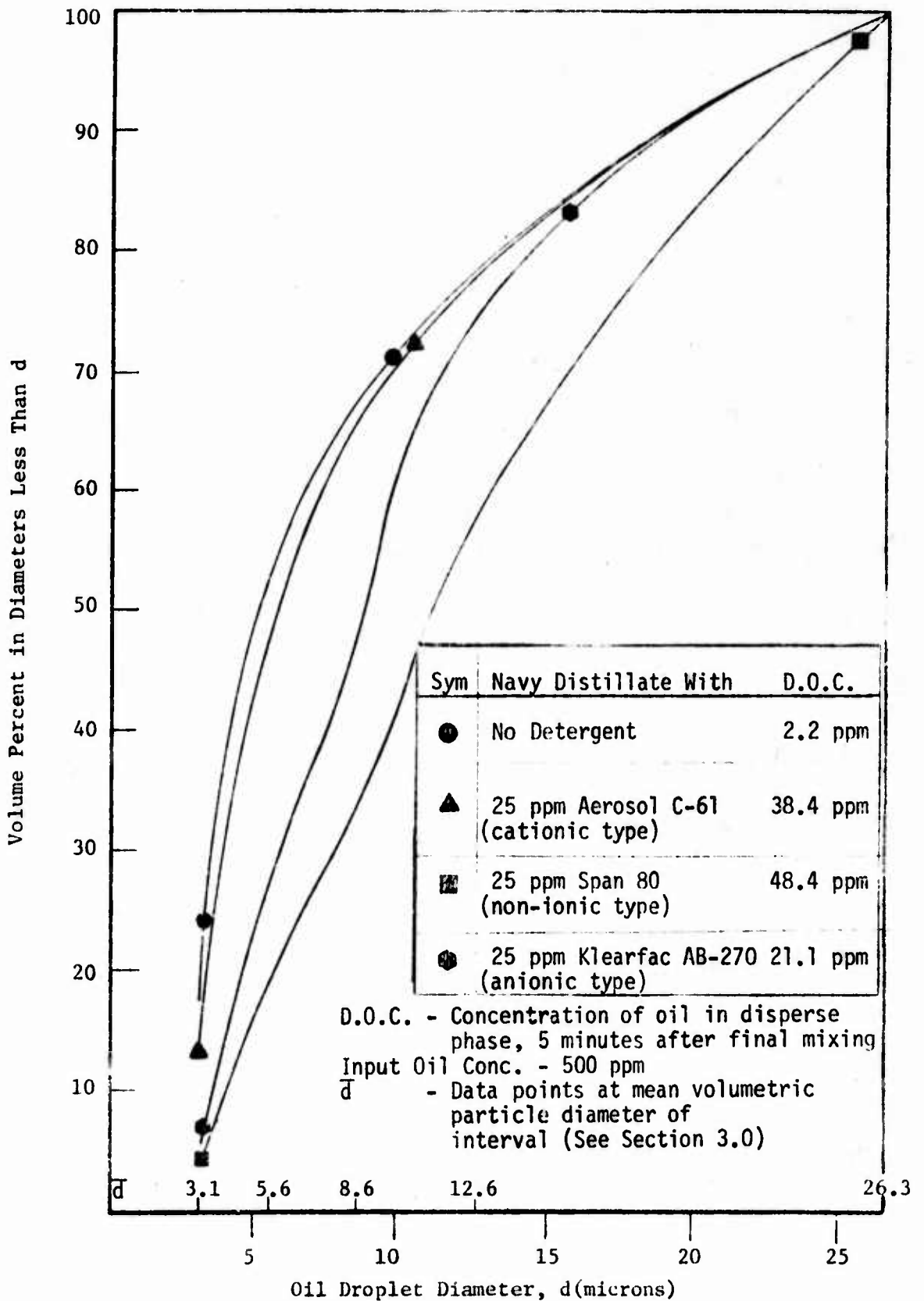
Figure 5.9

PARTICLE SIZE DISTRIBUTION (AS CUMULATIVE PER CENT)  
OF NAVY DISTILLATE OIL/DETERGENT MIXTURES IN FIGURE 5.9

All Oil Input Conc. - 500 PPM  
 Data at 5 Minutes After Mixing

	d (microns)					D.O.C.* In PPM
	3.1	5.6	8.6	12.6	26.3	
500 ppm Navy Distillate	17.6	52.6	67.3	79.4	100.0	2.2
500 ppm Navy Distillate with 25 ppm Triton X-100	4.8	22.2	38.0	62.4	100.0	22.8
500 ppm Navy Distillate with 50 ppm Triton X-100	4.6	19.7	34.9	58.2	100.0	33.7
500 ppm Navy Distillate with 100 ppm Triton X-100	6.1	29.6	52.6	77.1	100.0	34.6

\*D.O.C. - Dispersed Oil Concentration (2-35  $\mu$ )



Effect of Detergent Type on Oil Drop Size Distribution

Figure 5.10

PARTICLE SIZE DISTRIBUTION (AS CUMULATIVE VOLUME PERCENT) OF NAVY DISTILLATE  
OIL/DETERGENT MIXTURES PLOTTED IN FIGURE 5.10

ALL OIL INPUT CONC. - 500 ppm  
 DATA AT 5 MINUTES AFTER MIXING

	d (microns)					D.O.C.* IN ppm
	3.1	5.6	8.6	12.6	26.3	
500 ppm Navy Distillate	17.5	52.6	67.3	79.4	100.0	2.2
500 ppm Navy Distillate' with 25 ppm Aerosol C-61	13.6	47.4	67.0	79.1	100.0	38.4
500 ppm Navy Distillate with 25 ppm Span 80	3.7	19.4	34.5	58.6	100.0	48.4
500 ppm Navy Distillate with 25 ppm Klearfac AB-270	4.7	27.5	49.4	75.1	100.0	21.1

\* D.O.C. - DISPERSED OIL CONCENTRATION (2-35 $\mu$ )

of the mixture. One can see that although Span 80 generated the highest total dispersed oil concentration (48.4 ppm), it had a relatively low concentration of oil dispersed as droplets  $<10\ \mu$  (16.7 ppm). The cationic detergent Aerosol C-61 generated 38.4 ppm dispersed oil, but 21.2 ppm was present as droplets  $<10\ \mu$ . The anionic surfactant Klearfac AB-270, showed a larger fraction distribution in the small size range than Span 80 (49.2% compared to 34.5%), but a lower dispersed oil concentration in this same size range (10.4 ppm compared to 16.7 ppm). This was, of course, due to the fact that the presence of Klearfac AB-270 emulsified the least amount of oil (21.1 ppm) (in 2-35  $\mu$  range) of these three detergents.

The foregoing discussion illustrates the necessity of reviewing more than one factor in judging detergent effect on an oily-water emulsion, especially when comparing detergent types. It should be emphasized that both particle size distribution and dispersed oil concentration must be used in conjunction to determine the extent of emulsification. This was done in Tables 4.8 - 4.13 which tabulate the volume per cent and dispersed oil in small size ranges and total dispersed oil content for each oil-detergent mixture. The following conclusions can be made when considering dispersed oil content in size range two to ten microns only:

- (1) All cationic type detergents produced mixtures with the highest dispersed oil concentration (fuel and crude oil averaged around 25 ppm; lubricating oils averaged approximately 7 ppm).
- (2) The non-ionic types generated mixtures with substantially lower dispersed oil content: Triton X-100 generated approximately 15 ppm dispersed oil with fuel oils, 2 ppm with lubricating oil 9250. Span 80 generated approximately 10 ppm dispersed oil with fuel and crude oils, 4 ppm with the lubricating oils. Intravon S0 (non-ionic) produced mixtures with only 5 ppm dispersed oil for fuel and crude oils, 2 ppm dispersed oil with lubricating oils.
- (3) Two anionic types, Klearfac AB-270 and Aerosol OT-75 were similar in emulsifying ability, dispersing approximately 8 ppm with fuel and crude oils, approximately 3 ppm with lubricating oils.
- (4) Of the pure detergent types, Alkanol 189-S, also anionic, emulsified the least oil since 14 out of 16 test mixtures showed less than 5 ppm dispersed oil.
- (5) All three commercial products and all three high molecular weight polymers generated mixtures with dispersed oil content less than 10 ppm in all thirty tests.

### 5.3 Effect of Temperature on Oil/Water/Detergent Emulsions

Emulsions of any type, including oil in water, may be unstable with respect to various external perturbations, e.g., temperature, electrical fields, etc. For bilge applications, temperature would probably be one

dominant external influence. For this reason, surfactant activity of mixtures prepared in water of 120°F, 73°F (ambient) and 40°F was compared. At the elevated temperature, the amount of emulsified oil was generally less than in mixtures prepared at ambient temperature. For example, at 73°F a mixture of hydraulic oil and 100 ppm Aerosol OT-75 showed 6.7 ppm dispersed oil; at 120°F, a mixture of the same components showed only 3.2 ppm dispersed oil (See Table 4.13). This trend can be explained by the fact that interfacial viscosity is temperature dependent, falling rapidly to low values at even slightly elevated temperatures. Interfacial viscosity is the viscosity of the interfacial film of adsorbed emulsifier which influences flocculation and coalescing rates. Therefore, even though higher temperatures tend to produce more emulsification (lower oil viscosity) the lower interfacial viscosity increases flocculation and coalescing rates. Also, the higher temperature reduces the surface tension of the adsorbed layer of surfactant on the dispersed oil droplets. This layer is more likely to rupture, providing more contact points between the individual oil droplets, hence enhancing flocculation and coalescence.

One oil, South Louisiana Crude, showed virtually the same amounts of emulsified oil at the three temperatures, but with striking differences in oil drop size distribution (Figure 5.11). The emulsion generated at high temperature had a substantially larger percentage of small droplets than emulsions generated at ambient or low temperature. This apparent contradiction of the above postulation meant that the presence of natural surface-active agents in the crude oil produced a set of emulsifying conditions which were enhanced by temperature.

The overall effect of low temperature on oil/water detergent mixture was strictly a viscosity and surface tension effect. At low temperature the viscosity of the oil increases and substantial oil remains unemulsified after agitation.

#### 5.4 Effect of Salinity

Sea water in varying amounts was expected to influence type and stability of oily water mixtures generated in bilge water. Bilge water is considered to be generally fresh or brackish water, but introduction of dissolved salts from sea water should show substantial effects on stability of emulsions.

As has been described earlier the presence of an electrolyte contributes to emulsion instability due to the behavior of the charged double layer which arises around the dispersed droplets. Oil droplets tend to exhibit a slight negative charge, which attract a monolayer of positive charges at the oil/water interface. These charges in turn attract ions from the solution of opposite charge forming a second, more diffuse layer. This charged double layer keeps the oil dispersed due to repulsion of like charges. When additional ions are introduced from a source such as salt water, discharge of double layer charges may be involved, leading to emulsion inversion or demulsification. From



Effect of Temperature on Oil Drop Size Distributions of South Louisiana Crude Oil

Figure 5.11

PARTICLE SIZE DISTRIBUTIONS (AS CUMULATIVE VOLUME PERCENT) OF  
SOUTH LOUISIANA CRUDE OIL/DETERGENT MIXTURES AT THREE TEMPERATURES PLOTTED  
IN FIGURE 5.11

	d (microns)				
	3.1	5.6	8.6	12.6	26.3
	%				
500 ppm So. Louisiana Crude with 25 ppm Klearfac AB-270 73°F	8.2	28.1	39.7	55.5	100.0
500 ppm So. Louisiana Crude with 25 ppm Klearfac AB-270 40°F	12.0	34.0	45.1	61.6	100.0
500 ppm So. Louisiana Crude with 25 ppm Klearfac AB-270 120°F	19.3	67.1	84.6	94.8	100.0

the data generated and the trends indicated (Table 4.15) emulsions generated in a medium of 50% salinity are less stable than those generated in distilled water, as indicated by lower concentrations of emulsified oil in these samples. Demulsification was probably occurring during the two-minute settling period due to enhancement of flocculation and coalescence by the high electrolyte concentration.

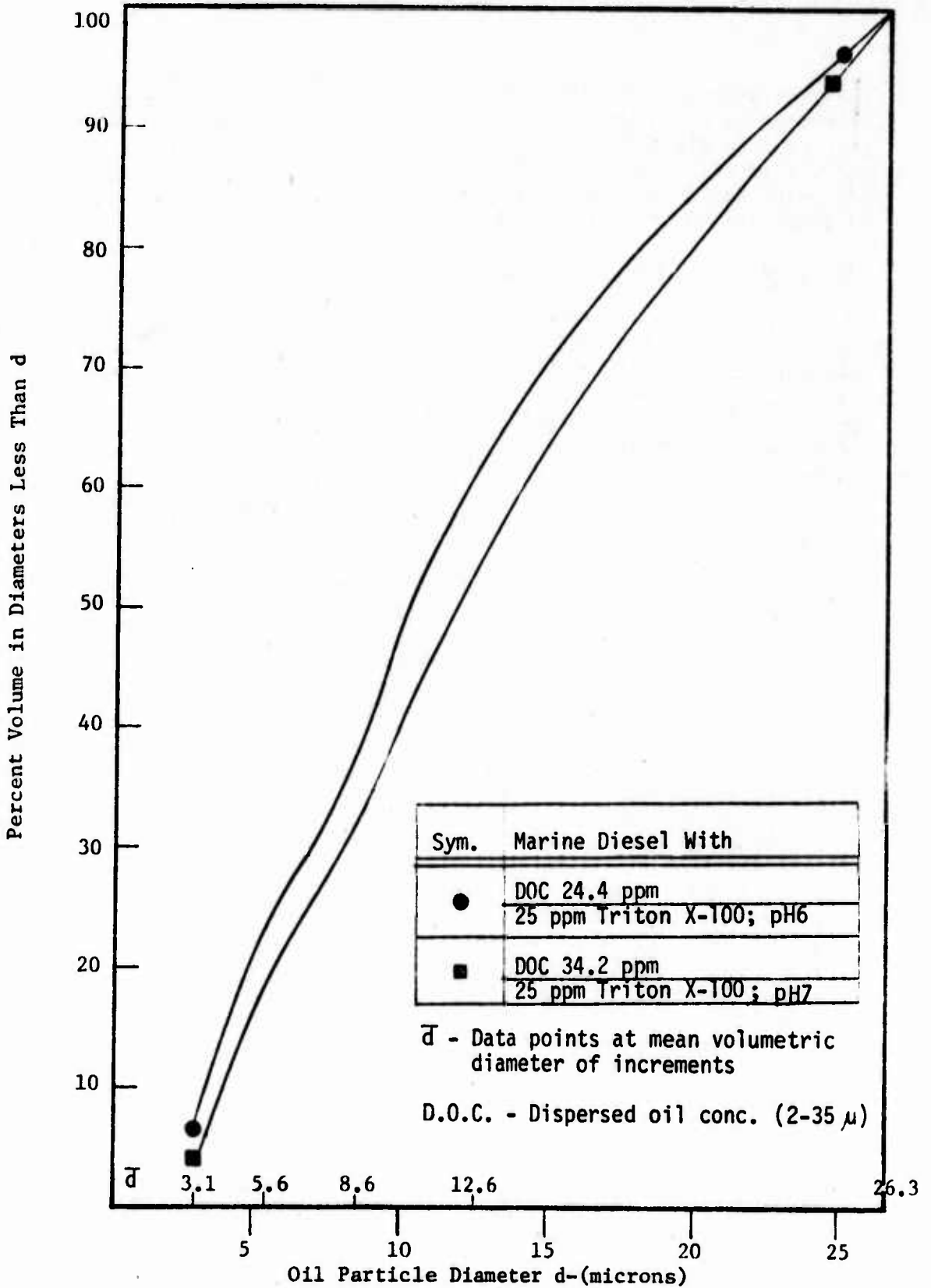
#### 5.5 Effect of pH on Oil/Water-Detergent Emulsions

The presence of extraneous or additional ions present in sea water or in acidic or alkaline media may affect the amount of emulsification and the stability of the emulsion generated. The effect of pH on these test emulsions seems relatively small, perhaps due to the fact that many aqueous solutions of surfactants are slightly acidic originally. The range of pH investigated (6-8) may have only encompassed the pH range of surfactant solutions. In addition, some of the surfactants have amphoteric properties in that it acts as a cationic detergent in acid conditions and as an anionic type in alkaline conditions. The similarity in oil drop size distribution of emulsions of marine diesel and Triton X-100 generated at pH 6 and 7 can be seen in Figure 5.12. This similarity in drop-size distribution accounts for the fact that oil concentration in the small droplet size range (two- ten microns) was virtually the same at both pH's (8.8 ppm at pH 6, 10.6 ppm at pH 7) although total dispersed oil concentration was 10 ppm higher at pH 7.

#### 5.6 Effect of High Detergent Concentration

In the tests discussed up to this point, maximum detergent concentration was 100 ppm, with input oil concentration of 500 ppm. This is a detergent-oil ratio of 1:5; it is possible that detergent concentration could equal or even exceed oil concentration in bilge water. For this reason the emulsifying effect of higher concentrations of detergents was also investigated. A pure detergent of each chemical type (Product BCO-cationic, Alkanol 189-S - anionic, and Intravon SO - non-ionic) was tested at concentrations of 500, 1000 and 5000 ppm with marine diesel oil and 2190-TEP (500 ppm input oil concentration). All other experimental parameters and experimental techniques were held constant.

The emulsifying activity of these detergents in high concentration is presented in Figures 5.13, 5.14, and 5.15. As can be seen from these figures, increasing the detergent concentration beyond 100 ppm also increased the amount of dispersed oil in the mixture. In concentrations of 500, 1000 and 5000 ppm the non-ionic detergent Intravon SO produced mixtures with the highest dispersed oil concentration for both test oils, 2190-TEP and Marine diesel (Table 4.16). At 5000 ppm Intravon SO, 54.1 ppm marine diesel, and 14.9 ppm 2190-TEP appeared as dispersed oil (with 500 ppm input oil concentration). 5000 ppm of the cationic detergent, Product BCO, emulsified nearly the same amount (as the Intervon SO) of marine diesel (52.5 ppm) and slightly less 2190-TEP (9.7 ppm). Of these three detergents, the anionic detergent, Alkanol 189-S, produced the least emulsification of these test oils with a maximum of only 5.3 ppm 2190-TEP and 23.8 ppm marine diesel as dispersed oil.



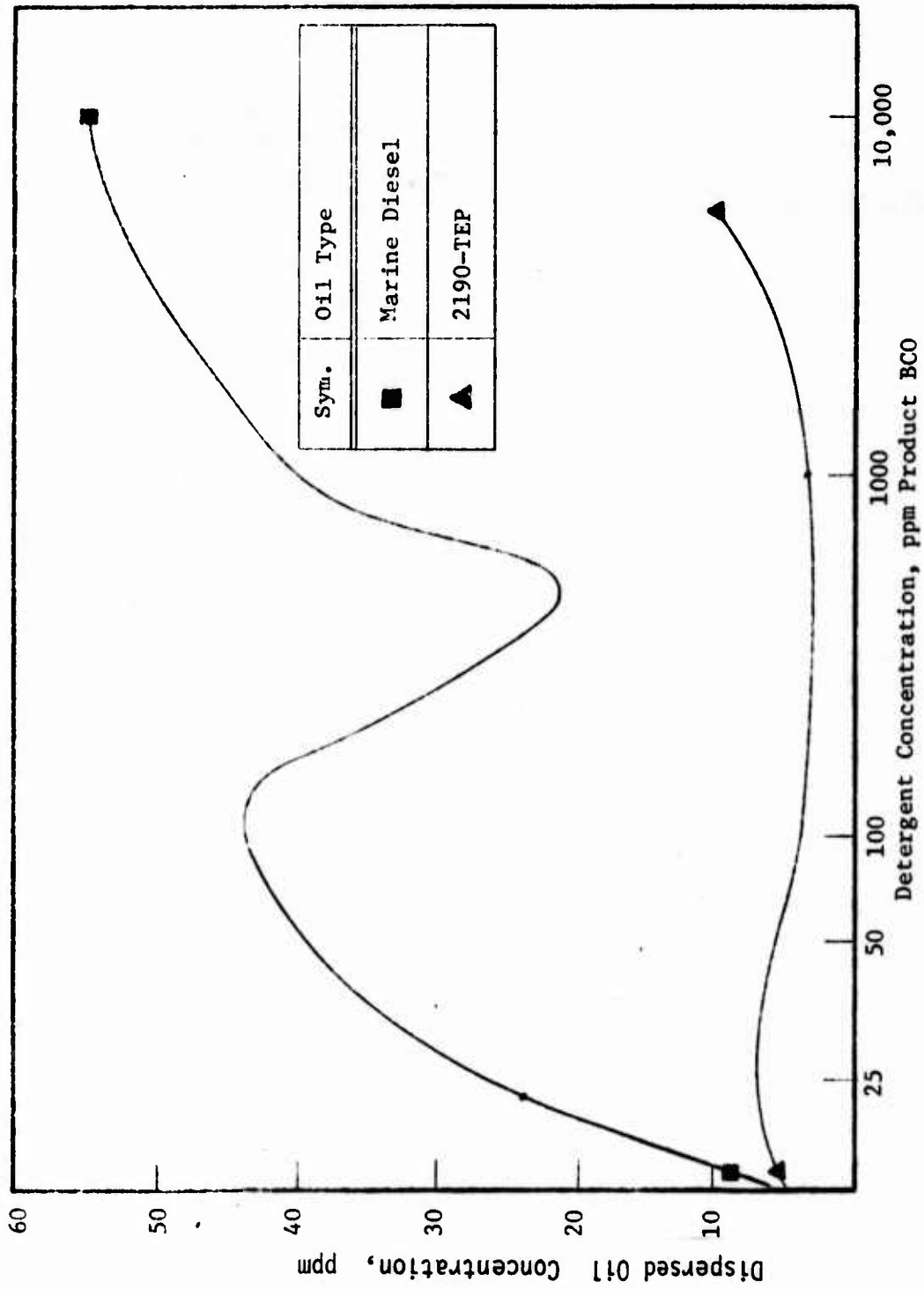
Effect of pH on Oil Drop Size Distributions of Marine Diesel  
(5 Minutes After Final Mixing)

Figure 5.12

PARTICLE SIZE DISTRIBUTIONS (AS CUMULATIVE VOLUME PERCENT) OF  
MARINE DIESEL/DETERGENT MIXTURES PLOTTED IN FIGURE 5.12

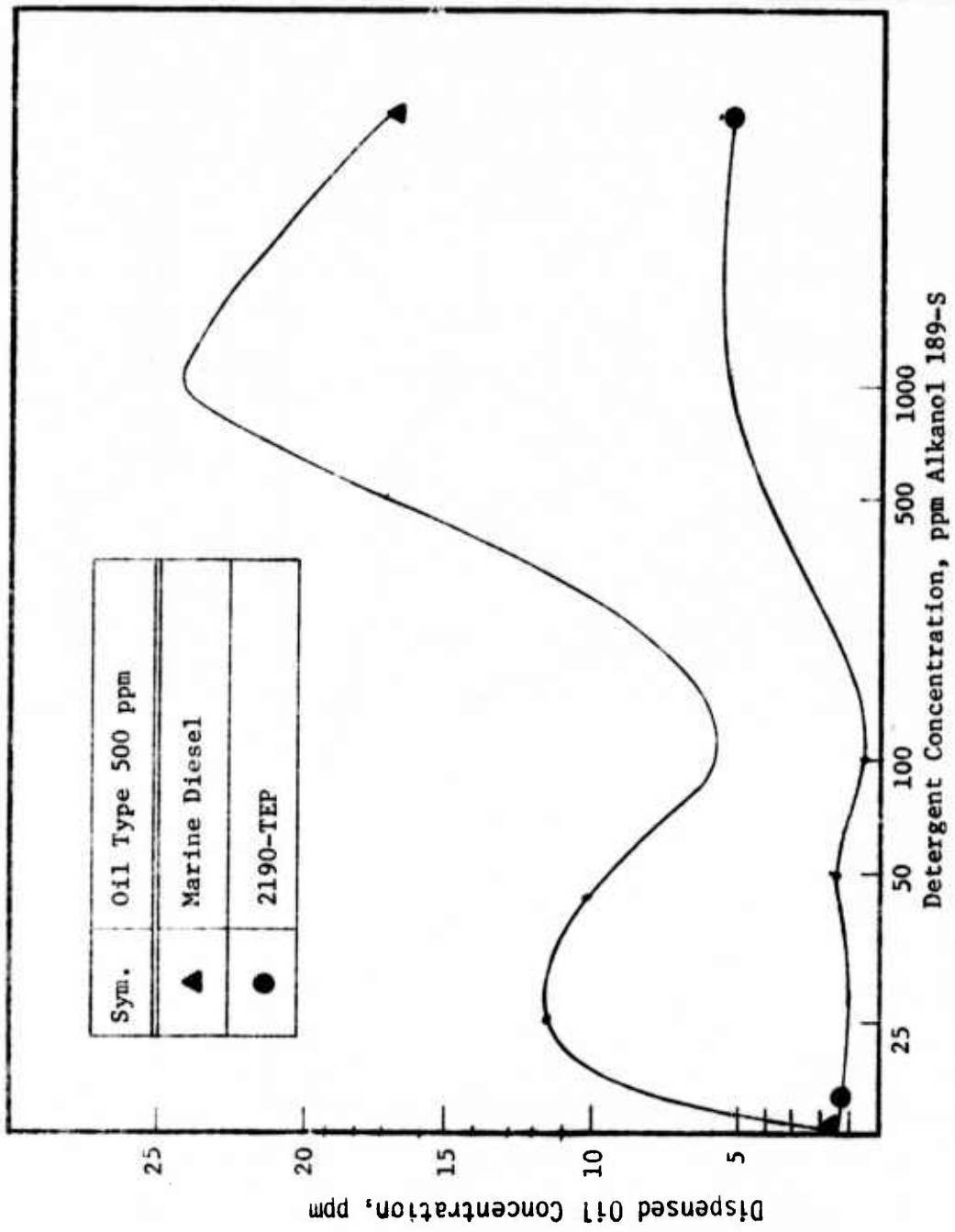
	$\bar{d}$ (microns)					D.O.C.* In ppm
	3.1	5.6	8.6	12.6	26.3	
500 ppm Marine Diesel with 25 ppm Triton X-100 pH 7	3.6	18.3	32.2	54.1	100.0	34.2
500 ppm Marine Diesel with 25 ppm Triton X-100 pH 6	5.2	23.4	37.7	62.5	100.0	24.4

\* D.O.C. - DISPERSED OIL CONCENTRATION (2-35  $\mu$ )



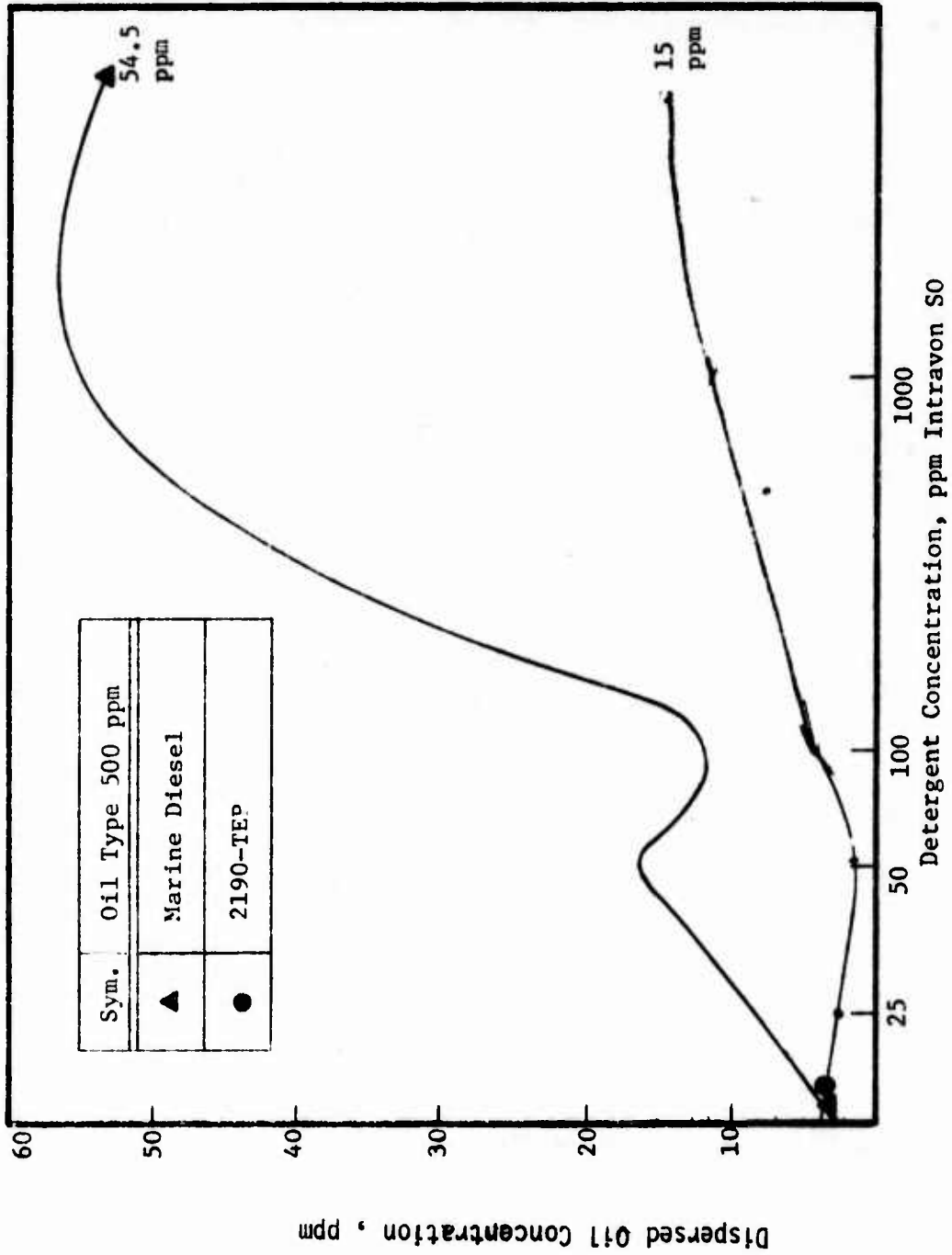
Dispersed Oil Concentration vs. Cationic Detergent Concentration (Ref. Table 4.16)

Figure 5.13



Dispersed Oil Concentration vs. Anionic Detergent Concentration (Ref. Table 4.16)

Figure 5.14

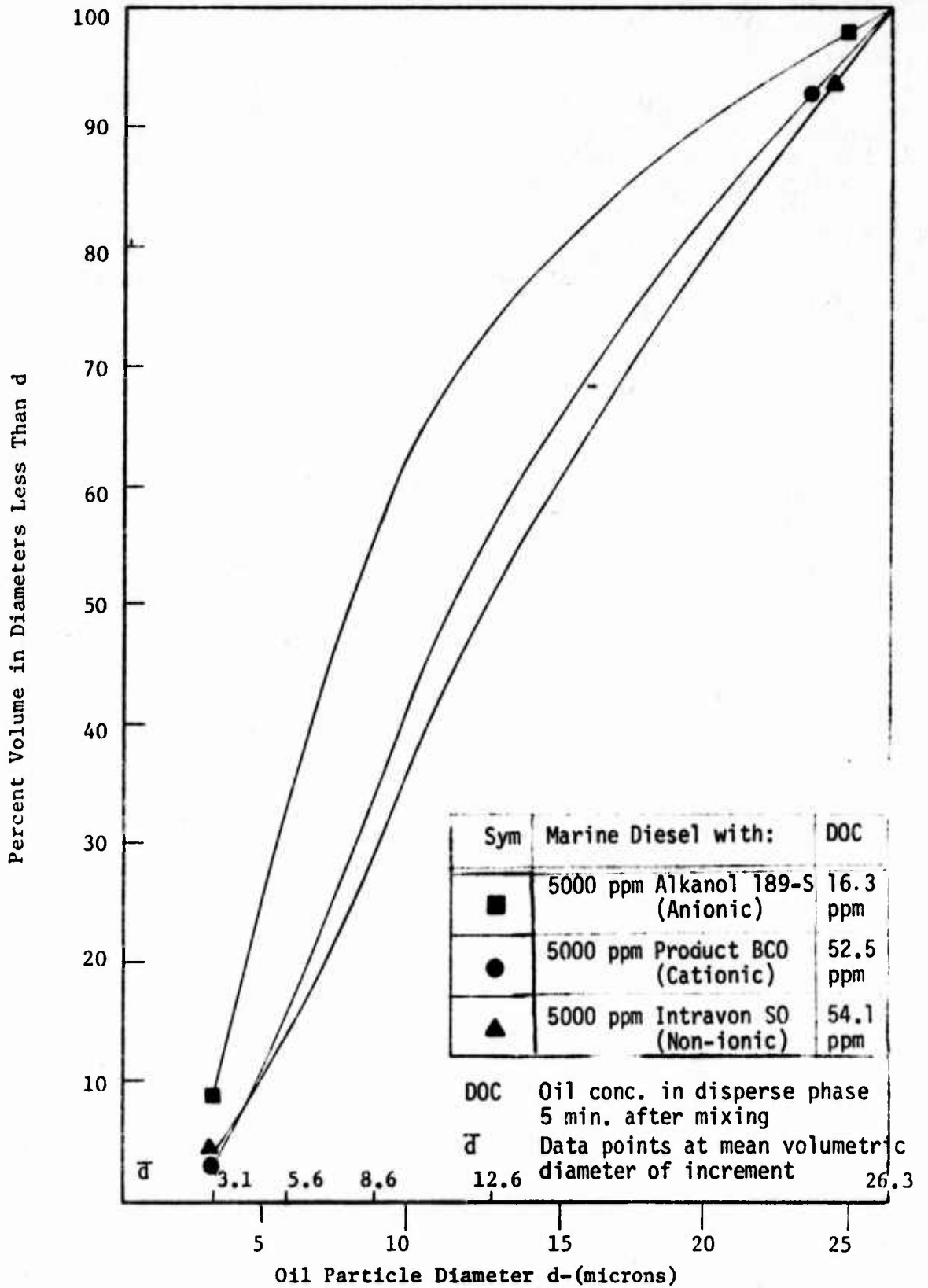


Dispersed Oil Concentration vs. Non-Ionic Detergent Concentration  
(Ref. Table 4.16)

Figure 5.15

Although the amount of dispersed oil increased substantially with detergent concentrations equal or greater than input oil concentration, the amount of emulsification did not increase proportionally. In fact, a levelling off of emulsifying activity with increased detergent concentration was indicated by all three detergent types. This finding was of interest for bilge water applications, since it implies that for given agitation rate and intensity, emulsification produced with 5000 ppm detergent was not much more severe than an emulsion produced with 1000 ppm detergent.

The severity of emulsions generated with high detergent concentrations can be also judged from the volume percentage distributions Figures 5.16, 5.17, and 5.18 and total dispersed oil concentration (Table 4.16). Although the Intravon SO showed the smallest volume fraction present as small droplets (between two and ten), it produced mixtures of these test oils with the highest concentration of oil dispersed as small droplets (Table 4.16). Product BCO cationic showed an emulsifying effect similar to the Intravon SO, dispersing 4.4 ppm of 2190 -TEP and 17.0 ppm marine diesel as small droplets (between two and ten microns). Although mixtures with Alkanol 189-S had a comparatively large fraction of volume present as small droplets, actual dispersed oil concentration in the 2-10 micron size range was only 10.5 ppm marine diesel and 2.2 ppm of 2190-TEP (Table 4.16). That anionic detergent caused the least emulsification of these two test oils was consistent with the trends evidenced in previous tests performed with detergents up to 100 ppm in concentration.



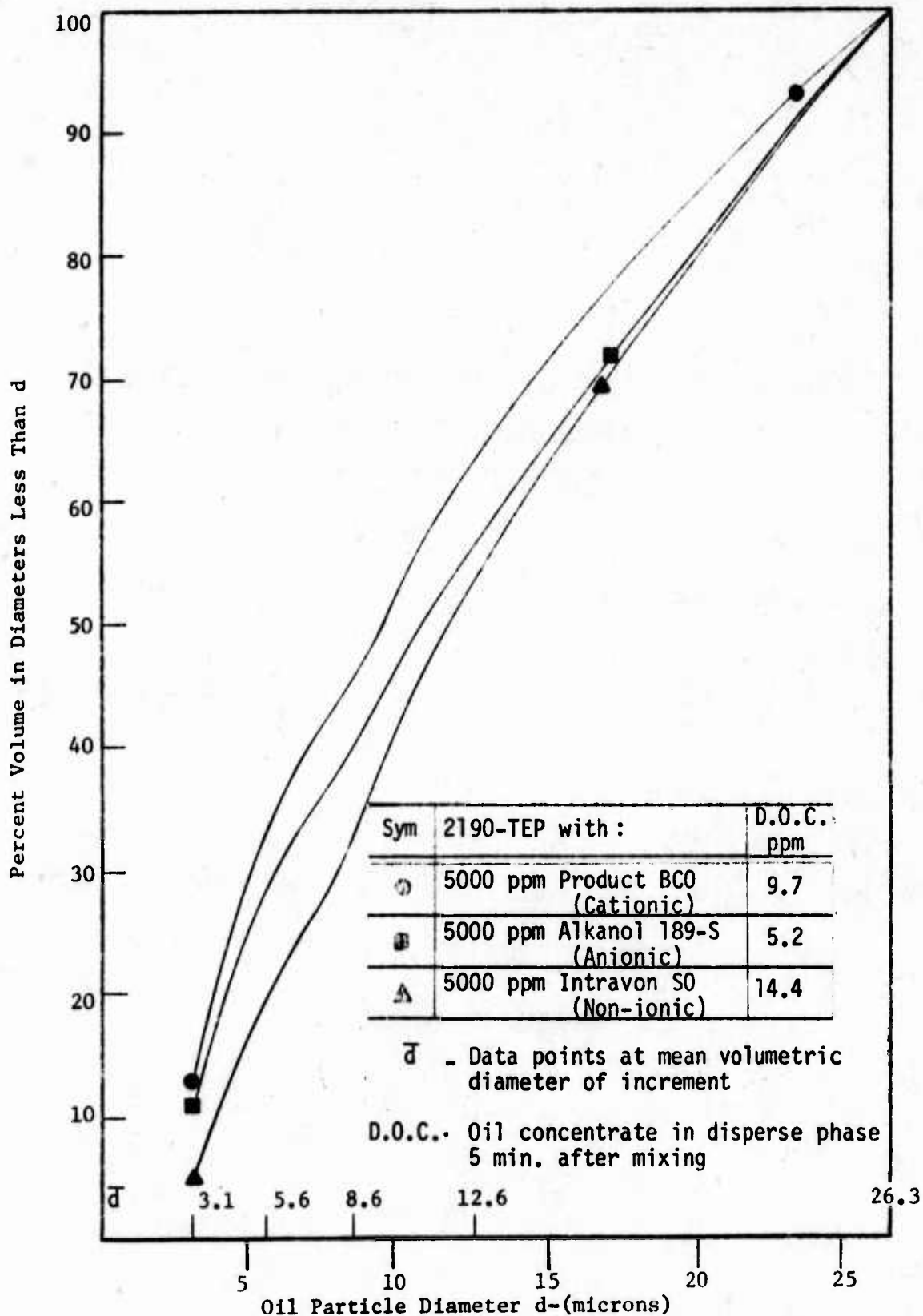
Effect of Detergent Type (5000 ppm) on Oil Drop Size Distribution of Marine Diesel

Figure 5.16

PARTICLE SIZE DISTRIBUTIONS (AS CUMULATIVE VOLUME PERCENT) OF  
MARINE DIESEL/DETERGENT MIXTURES  
PLOTTED IN FIGURE 5.16

	$\bar{d}$ (microns)					D.O.C.*
	3.1	5.6	8.6	12.6	26.3	IN ppm
500 ppm Marine Diesel with						
5000 ppm Aikanol 189-S	8.9	33.1	54.6	74.0	100.0	16.3
5000 ppm Intravon SO	2.8	14.2	29.6	51.3	100.0	54.1
5000 ppm Product BCO	2.6	15.6	32.4	58.1	100.0	52.5

\* D.O.C. - DISPERSED OIL CONCENTRATION (2-35 $\mu$ )



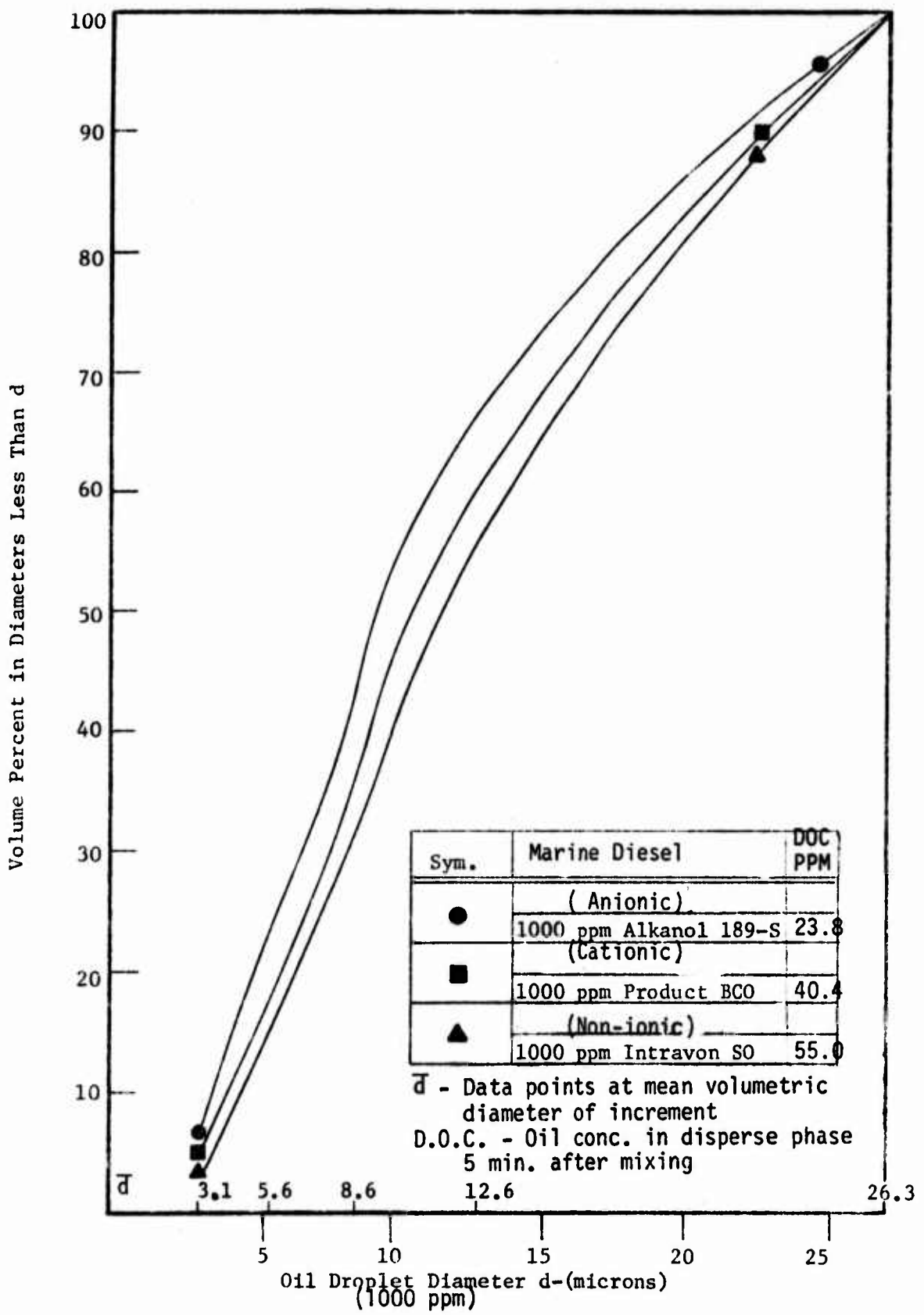
Effect of Detergent Type (5000 ppm) on Oil Drop Size Distribution of 2190-TEP

Figure 5.17

✓

PARTICLE SIZE DISTRIBUTIONS (AS CUMULATIVE VOLUME PERCENT)  
OF 2190-TEP/DETERGENT MIXTURES  
PLOTTED IN FIGURE 5.17

	d (microns)				
	3.1	5.6	8.6	12.6	26.3
<u>FIGURE 5.17</u>					%
500 ppm 2190-TEP with					
5000 ppm Alkanol 189-S	10.2	28.3	40.4	56.3	100.0
5000 ppm Intravon SO	4.8	19.6	33.6	54.7	100.0
5000 ppm Product BCO	11.9	33.0	45.6	64.7	100.0



Effect of Detergent Type on Oil Drop Size Distribution  
 Figure 5.18

''  
PARTICLE SIZE DISTRIBUTIONS (AS CUMULATIVE VOLUME PERCENT) OF  
MARINE DIESEL/DETERGENT MIXTURES PLOTTED IN FIGURE 5.18

	d (microns)					
	3.1	5.6	8.6	12.6	26.3	D.O.C.* IN ppm
500 ppm Marine Diesel with						
1000 ppm Alkanol 189-S	4.4	22.9	44.2	67.7	100.0	23.8
1000 ppm Intravon SO	2.6	15.2	31.0	56.3	100.0	55.0
1000 ppm Product BCO	4.1	19.6	35.5	61.4	100.0	40.4

\*D.O.C. - Dispersed Oil Concentration (2-35 $\mu$ )

## 6.0 Conclusions and Recommendations

Based on the data obtained in this study the following conclusions and observations were made:

- a. Cationic surfactants consistently produced the greatest amount of dispersed oil of all the test mixtures studied under the various parameters and conditions used.
- b. Non-ionic surfactants ranked next in emulsifying ability but with greater variations in particle size distribution between the three non-ionic surfactants tested.
- c. Anionic surfactants produced the lowest dispersed oil concentration of the three types of surfactants tested.
- d. High molecular weight polymers showed only small effects on emulsification and in some cases, produced less dispersed oil than the base-line oil/water mixtures.
- e. Commercial detergents caused marginal changes in emulsification of all oil samples tested. However, these selected detergents should not be directly compared with the pure, detergent "actives" mentioned above, since these commercial formulations contain varying, lesser fractions of true surfactant.
- f. Temperature (40 to 120°F) and pH (6-8) effects did not appreciably change the dispersion of the oils tested. However, increasing salinity produced lesser amounts of dispersed oil.
- g. Increasing detergent concentrations did not produce corresponding linear increasing dispersed oil concentrations. Upon reaching the critical micelle concentration there appeared to be a levelling off of the amount of oil dispersed.
- h. Conversely, small amounts ( $< 100$  ppm) of various surfactants of all three types seemed to exert a de-mulsifying effect on the oil dispersed, especially lubricating and crude oils.
- i. Any oil detector/monitor whose operating principle depends on oil particle size distribution will be grossly affected by the presence of any detergents.
- j. For oil/water emulsions, experimental sampling and analytical techniques need to be scrutinized for applicability to liquid-liquid mixtures since oil droplet sizing and counting by conductance (Coulter) or by optical (HIAC, Microscope) means each have advantages and disadvantages. A combination of the two techniques would solve some of the problems in droplet size analysis in the presence of solids and gas bubbles.

Based on the limited, survey-type experimental effort encompassed in this report, the following recommendations are offered:

1. Commercial detergents for shipboard use should not produce a deleterious effect on the bilge water unless used in quantities greater than 5-10 times the oil content. Commercial detergents containing non-ionic and/or anionic surfactant ingredients would be more desirable than those containing cationic surfactants.
2. Specifications for shipboard detergents and cleansers should call out anionic/non-ionic formulations and the type of chemical nomenclature should be more exactly described.
3. New formulations should be prepared and tested in a more comprehensive study to develop a shipboard cleaner with satisfactory cleaning properties and with minimum or short-term effect on bilge waters.

Finally, the study reported herein represented a brief, once through examination of detergent behavior under a limited and rather fixed set of data. However, for the purpose of the study, the stated conclusions are based on sufficient evidence to warrant making these conclusions. The chemistry and experimental technique is complicated and much more can and should be done to thoroughly understand and control what happens in a ship's bilge and thereby better control any pollution which may emanate from the ship.

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## APPENDIX I

### Compilation of Oil/Water Particle Size Data

The data summarized in this section have been abstracted from various sources pertaining to the production, processing, treatment, and analysis of oil/water mixtures. The objective is to bring together information on the subject for the purposes of comparison and interpretation. For example, the data on the effects of detergent addition may be used in conjunction with the findings of this report to obtain a more comprehensive view of the phenomena involved.

Each set of data is presented in graphical form under the title of the report from which it was obtained. Following each title there is a brief statement of the objective of the study, the types of oil used, a description of the dispersing methods employed, and the techniques used for particle size analysis.

For consistency, all data are presented in the form of cumulative percent of the volume (or number) contained in all particles less (or greater) than a stated size 1-4. As a practical example, consider Figure I which appears later in this section (as Figure 30). Here two cumulative volume curves (1C and 2C) are given along with the two corresponding size distributions, 1f and 2f, respectively. With some counting devices (e.g., the Coulter Counter) both the size distribution and cumulative curves can be obtained automatically. In Figure I, curves 1f and 2f give the volume fraction per micron increment in diameter as a function of diameter. Such curves are also referred to as Fractional Volumetric Distribution. In some cases, mainly depending on the method of measurement, the distributions are expressed in terms of number (population) fraction per micron size increment (e.g., Figure 7g). These can be converted to volume fraction by a straightforward, but often tedious, numerical procedure. It is common practice to normalize the distribution to unity and the cumulative curves to 100% for the entire size range.

It is often useful in a particular application to plot the cumulative curves on a special type of grid paper. For instance, when plotted on log-probability paper, a system of coordinates based on the probability integral, additional information may be extracted from the data. If the data were transformed to a straight line by this change of coordinates, the distribution is log-normal in form and is thus defined mathematically. In this case the entire distribution can be characterized by two parameters; namely, the mean diameter and standard deviation. By way of illustration, the transfer of curves 1c and 2c (Figure I) to the log-normal grid in Figure 2 resulted in nearly straight lines; hence, the distributions can be considered as log-normal to a good approximation. From these lines one can immediately obtain the mean volume diameter,  $d_v$ , and the standard deviation,  $\sigma$ . Here  $d_v$  corresponds to the 50% size, or 3.45 and 8.8 microns for lines 1c and 2c, respectively. Physically, this means that the total volume is divided equally above and below the size  $d_v$ . Also, it turns out that  $\sigma$  can be calculated from either of the diameter ratios:

$$\sigma = \frac{84.13\% \text{ diameter}}{50\% \text{ diameter } (d_v)} = \frac{50\% \text{ diameter } (d_v)}{15.87\% \text{ diameter}}$$

Having determined  $d_v$  and  $\sigma$ , the following relationship may be used to transpose Figure 2 from a volume to a number distribution; i.e.,

$$\ln d_v = \ln d_g + 1.5 \ln^2 \sigma \quad (1)$$

where  $d_g$  is the geometric mean diameter on a number basis. It can be shown that  $\sigma$  is unchanged by this transformation; thus, the volume and size plots will be parallel on the log-normal grid as indicated by the broken lines in Figure 2. Conversely, a log-normal size distribution may be transposed to a volume distribution by the same procedure. Again, references 1-4 are recommended for detailed discussions of particle size data presentation and the mathematical properties of various distributions.

The following curves are grouped according to source. Within the limits of practicality, each graph will be self explanatory.

#### 1. Vortex Concept For Separating Oil From Water <sup>5</sup>

The following data relate to an investigation of the feasibility of using a vortex separator for shipboard applications.

A 1 inch square Lucite channel was installed in the inlet duct to the vortex separator for observing and photographing the oil particles. Microflash photographs were taken of the oil particles. These were then enlarged approximately 17 times to facilitate the particle size - frequency measurements.

As described in the report, six types of oil were used in this study, namely: a naphthene-base crude oil, SAE 40 lube oil, No. 6 fuel oil, a diesel fuel, Navy Distillate, and SAE 10W-20W-30HD (high detergent) lube oil. The authors considered that the latter two were of special interest because they tend to be easily emulsified.

Two methods of dispersion were used. In the first oil was injected into the main flow by a probe situated downstream of a centrifugal pump (the pump type is not specified). For additional dispersion, screens were mounted midway in the Lucite channel perpendicular to the flow. The screens were Dutch weave-rectangular mesh with 4 to 6 percent open area. Both 12X64 and 14X176 mesh were used. Figures 3 and 4 relate to this method of dispersion. In the second method the oil was dispersed by injection upstream of the centrifugal pump. Figure 5 shows the effect of pump speed on the particle size distribution for crude oil. These results are compared (see Note I) with the distribution which was obtained when the oil was injected downstream as in the previous method. The distribution resulting from flow through the 14X176 mesh is also presented (see Note 2) for comparison. According to this reference, these results tend to confirm that oil-water mixtures can be pumped with a centrifugal pump without significant break up of the oil particles, provided the pump is operated well under its design speed.

The effects of oil type and concentration on size distribution are given in Figure 6 for a centrifugal pump operating at 1800 ppm. Here again the oil was injected upstream of the pump.

All the graphs are presented as they appear in the original report except that the data points have been deleted for convenience of reproduction. The symbols serve only as a means of identification.

## 2. Evaluation of Pump Emulsification Characteristics<sup>6</sup>

This study examined the emulsification characteristics of a rotary, sliding vane pump (Blackmer, Model BXL 1/4 NAF-NHROV) and a centrifugal pump (Gould, 1750 rpm, type 3755) under various conditions of oil feed and discharge pressures. All tests were conducted at a flow rate of 10 gpm. A limited parametric investigation emulsion formation by an ultrasonic generator (Branson Sonic Power Co., Model W140 Sonifier) operating at 140 watts and 20,000 Hz was also carried out to complement the pump emulsification data.

Both a Coulter Counter (Model TA) and photomicrography were used to determine droplet sizes. In-line photomicrographic analysis gave rough information on the break-up of the oil while the Coulter Counter was mainly applied to the size-frequency analysis of the finely dispersed phase. The latter technique was used to obtain the cumulative concentration curves presented in this section. Samples were drawn off through a 1/4" O.D. copper tube. The Coulter Counter analysis was performed after allowing the sample to stand for one minute. The sampling procedure is treated in considerable detail in this report. The test oil was introduced at the center line of the pump inlet pipe. In all cases the test oil was made up of a mixture of 70% lube oil and 30% Navy Distillate. No additional characteristics of these oils are given.

All of the curves of cumulative oil concentration are presented as they appear in the original report except that the individual data points have been deleted for convenience of reproduction. These curves, which give the actual concentration in ppm, may be normalized to a percentage basis by the application of the conversion factor appended to each curve. Thus in Figure 7 the curve designated by the open circle is associated with the factor .0255. This is just the reciprocal of the total concentration in the dispersed phase for this particular set of data multiplied by one hundred i.e.  $1/3920 \times 100$ . As a numerical example we see from this particular curve that the cumulative oil concentration for all particles up to 3 microns in diameter is approx 100 ppm. Therefore, in terms of percent of the total concentration we have  $100 \times .0255$  or 2.55% for the cumulative percentage of oil contained in all sizes less than 3 microns. Similarly, for the next curve designated by the open triangles we find the cumulative percentage of oil contained in all particles below 3 microns is about  $30 \times .050$  or 1.5% of the total.

The conclusions drawn by the authors of this report are summarized as follows:

- a) The emulsification characteristics of a sliding vane pump are somewhat more favorable than those of a centrifugal pump.
- b) Operating the pump below rated capacity is an effective way of decreasing emulsification.
- c) The emulsion characteristics are less severe for a salty than for a fresh water continuous phase. Also the addition of surfactants enhance the formation of small droplets.
- d) Concentrations of 10 ppm in the dispersed phase are accounted for by droplets with diameters up to 2 microns and 4.5 microns for feed concentrations of 10,000 and 1,000 ppm respectively.

### 3. Centrifuge Coalescer Concept for Separating Oil From Water Discharged From Ships

The following data were obtained under a program for the development and testing of the proposed Foster-Miller concept of an axial flow, centrifuge separator to separate oil-water emulsions for shipboard applications. Since the performance of the separator was expected to depend strongly on particle size distribution an experimental program was undertaken to measure size distribution produced by emulsifying mechanisms to be encountered aboard ship. These are, 1) the "sloshing mode" of mixing for ballast and bilge water due to the ships motion and 2) shear and turbulence induced emulsification caused by passing the oil-water mixture through a centrifugal pump. A Burrell Wrist action shaker operating at the highest speed (Fisher, Catalog No. 14-260) was used to simulate sloshing. A 10 gpm, 150 head, Ingersoll-Rand centrifugal pump (Model N 3/4 X 5 HK -1/2 Unit 3 graph 1) and a Sears Blender (Catalog No. 34P82652) were used to simulate shearing due to passage through a typical centrifugal pump. Performance tests were run on the test model separator using oil water mixtures of No.2, No.4, and Nigerian crude oils (light) and detergent additives, such as Gamlen D, Lubrizol Corp. OS No. 29817A and Ajax liquid cleaner.

Drop size distributions and total oil content were measured using a Coulter Counter (Model Z<sub>p</sub>). Although no specific times were specified, the authors infer that the size analysis was initiated as soon after (i.e. "immediately") sample withdrawal and preparation as possible. In the case of the centrifugal pump, samples were drawn off through a pitot tube arrangement. After preparation, i.e. dilution of the sample in an electrolytic solution (as required in the use of the Coulter Counter) counting was started at once. It took about four minutes to complete a size-frequency count over 17 diameter ranges. Drops were counted in each range for about 8 seconds, starting with the largest drop size and working downwards. The total volume of oil and the cumulative volumetric distribution was determined by numerical integration.

All of the following curves are presented in essentially the same form as they appear in the original text except that the data points have been deleted for convenience of reproduction. In some cases, e.g. in Figure 30 both the size distribution (expressed as volume fraction/micron) and the corresponding cumulative volume plot are given. As mentioned in the Introduction, the cumulative curve can be obtained directly from the distribution curve by integration. This was done automatically during the counting process.

### 4. Laboratory Evaluation of the Emulsifying Characteristics of Pumps<sup>8</sup>

This study examines the emulsifying characteristics of different pumps suitable for shipboard pumping of bilge and ballast water oily wastes. The tests were designed to investigate the effect of oil type, input oil concentration, detergent additions, pump operating characteristics (pressure and flow rate), and salt versus fresh water, on emulsification. The oils used are identified as No 2 fuel oil, no 6 fuel oil and a "typical" diesel lubricating (Lube) oil. Detailed physical properties are given in the subject report. The oils were tested with and without the addition of 10 percent (relative to the oil concentration on a volume basis) Gamlen D surfactant (Lubrizol Corp. OS No. 29817A).

With respect to the effects of detergents, the results of these tests show that detergent addition (Gamlen D) increased both the total and finely

dispersed oil fractions for all oils, though the effect is more significant on refined than on residuals. It appeared that the heavy viscous oils like No. 6 are dispersed to the same extent as a light thin oils such as No.2.

The pumps used are described as follows:

- a) Sliding Vane Pump, Blackmer Pump Div. of Diver Corp. Grand Rapids, Mich, Model BXL2 1/2 N.F. rated 100 gpm at 500 rpm maximum
- b) Centrifugal Pump, Ingersoll-Rand, Aldrich Div. Model 3x2x8HC. rated 150 gpm, 150 head at 3550 rpm.
- c) Centrifugal Pump, Crane-Deming Pumps, Chicago, Ill., Model 4021, Size 1.5L rated 150 gpm, 150 ft. head at 1750 rpm.
- d) Diaphragm Pump, Parker Systems, Inc., Norfolk, Va., Model M15P double diaphragm, air operated, rated 100 gpm at 100 psi air and 90 scfm, 1.38 gal per stroke (1/2 cycle)

Emulsification was accomplished by injection of oil upstream of the pump inlet. The authors state that dispersion due to the injection process was negligible compared to the pump dispersion. Both influent and effluent samples for size analysis were withdrawn through pitot probes located in the center of the main flow. Each sample was allowed to settle in a beaker for one minute prior to transferring a small quantity to a dilution beaker as required for the Coulter Counter (Model ZB) size analysis.

All of the following curves are presented as they appear in the original text. The symbols serve only to identify the curves. No data points were shown on the original curves.

#### 5. Development Program of a Continuous Regenerating Moving Bed to Remove Oil From Oil-Water Suspensions<sup>9</sup>

The ultimate objective of this program was to develop a device for scavenging oil from oily ballast discharges. This report, by nature of the investigation, contains relatively little experimental data on particle size distributions per se.

A variable aperture dispersing orifice was designed to simulate particle size distributions encountered in actual deballasting operations. The size distribution was controlled by varying the area, and hence the pressure drop across the orifice. The Kuwait crude test oil was injected into the salt water feed at the upstream side of the orifice which was situated at the inlet to the filter bed being evaluated.

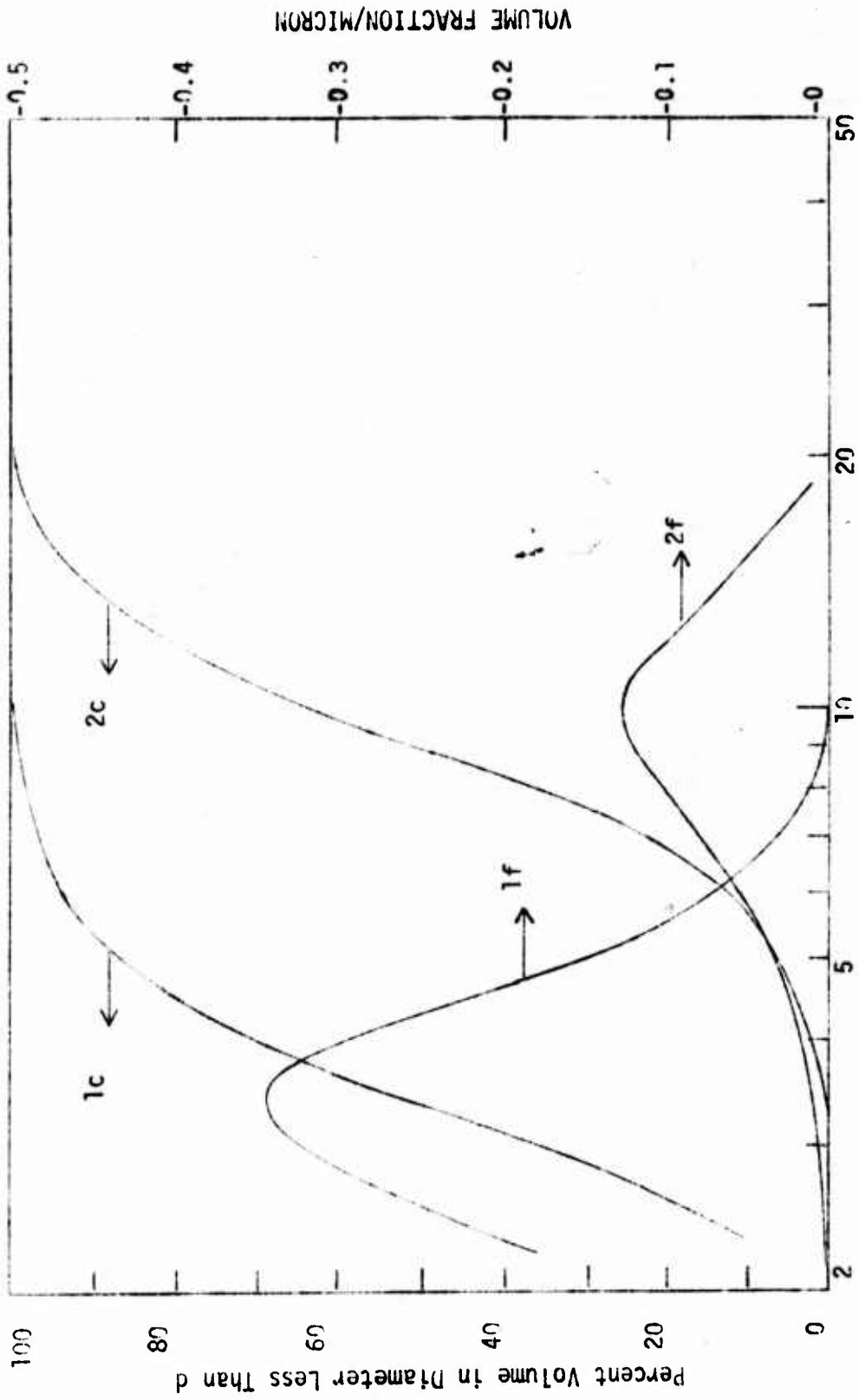
Samples were obtained by drawing off the oil-water mixtures through a 1/4" probe at a point downstream of the dispersing orifice. The samples then passed through a transparent flow cell 1/4" wide mounted on a microscope

stage/ Photographs were taken of the sample stream as it flowed through the cell. In practice, sufficient numbers of pictures were taken to develop a statistical basis for the size distribution. Figure 78 depicts representative influent distributions for Kuwait crude plotted in cumulative form on a log-normal grid. The original data were presented in size-frequency form.

Field tests were made to characterize crude oil ballast water during a "typical" tanker deballasting. Figure 79 (presented without transformation) gives an estimate of the cumulative droplet size associated with the discharge of dirty crude oil ballast through a representative tanker plumbing system. Sampling was performed about 100 yards from the tanker near the point of discharge. The microscope photography cell used for these measurements was essentially the same as the laboratory cell. The results indicate that the distribution generated in the laboratory contained a larger fraction of oil in the smaller sizes.

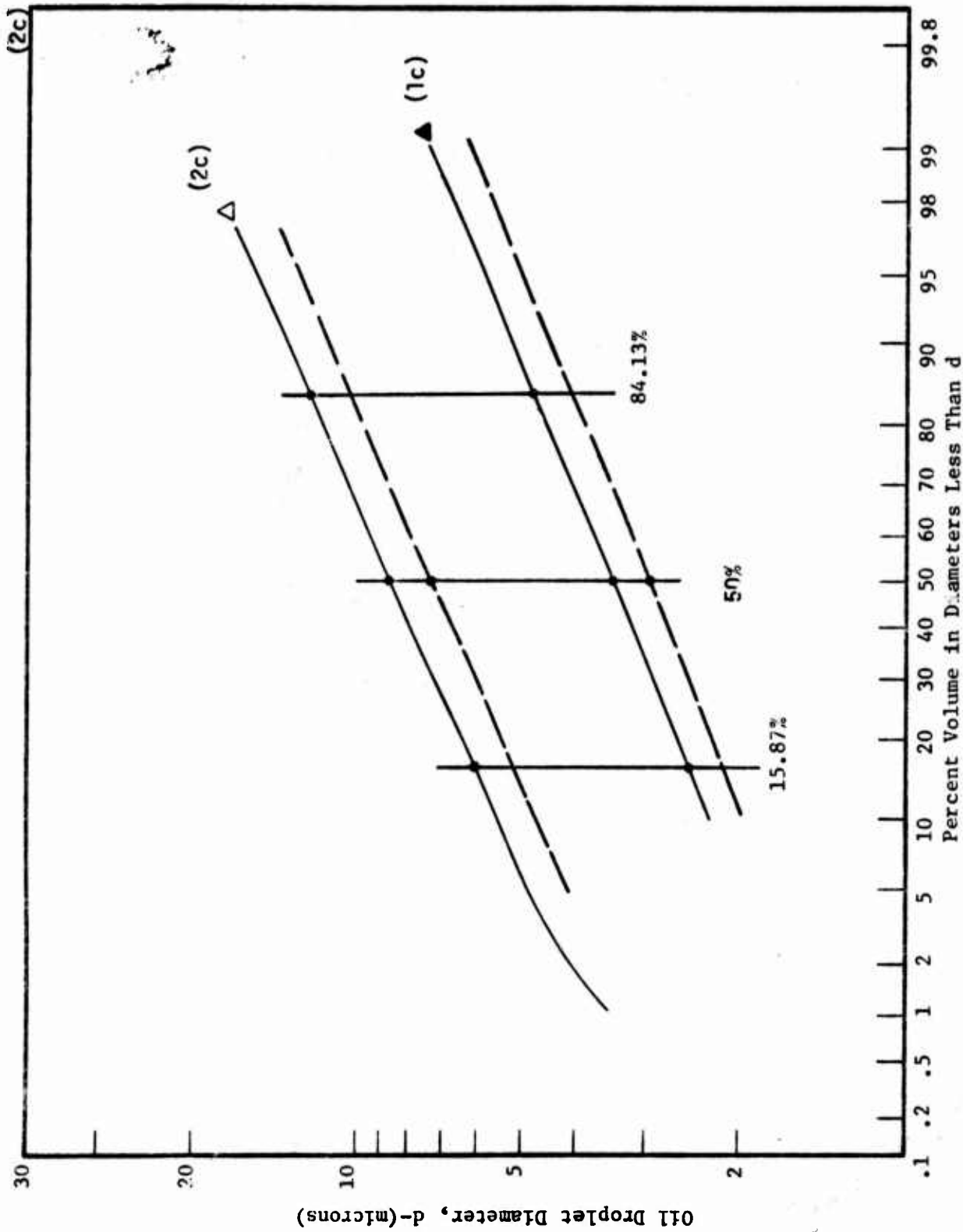
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7. Foster-Miller Associates, U.S. Coast Guard Rep. No. 734305.2/3 - Centrifuge Coalescer Concept for Separating Oil from Water Discharge from Ships, Feb. 1973.
8. Foster-Miller, U.S. Coast Guard Rep. No. G-D-31-74 - Laboratory Evaluation of the Emulsifying Characteristics of Pumps, Oct. 1973.
9. Hydronautics, MARAD Tech. Rep. 7080-1 - Development Program of a Continuous Moving Bed to Remove Oil for Oil-Water Suspensions, Oct. 1971.



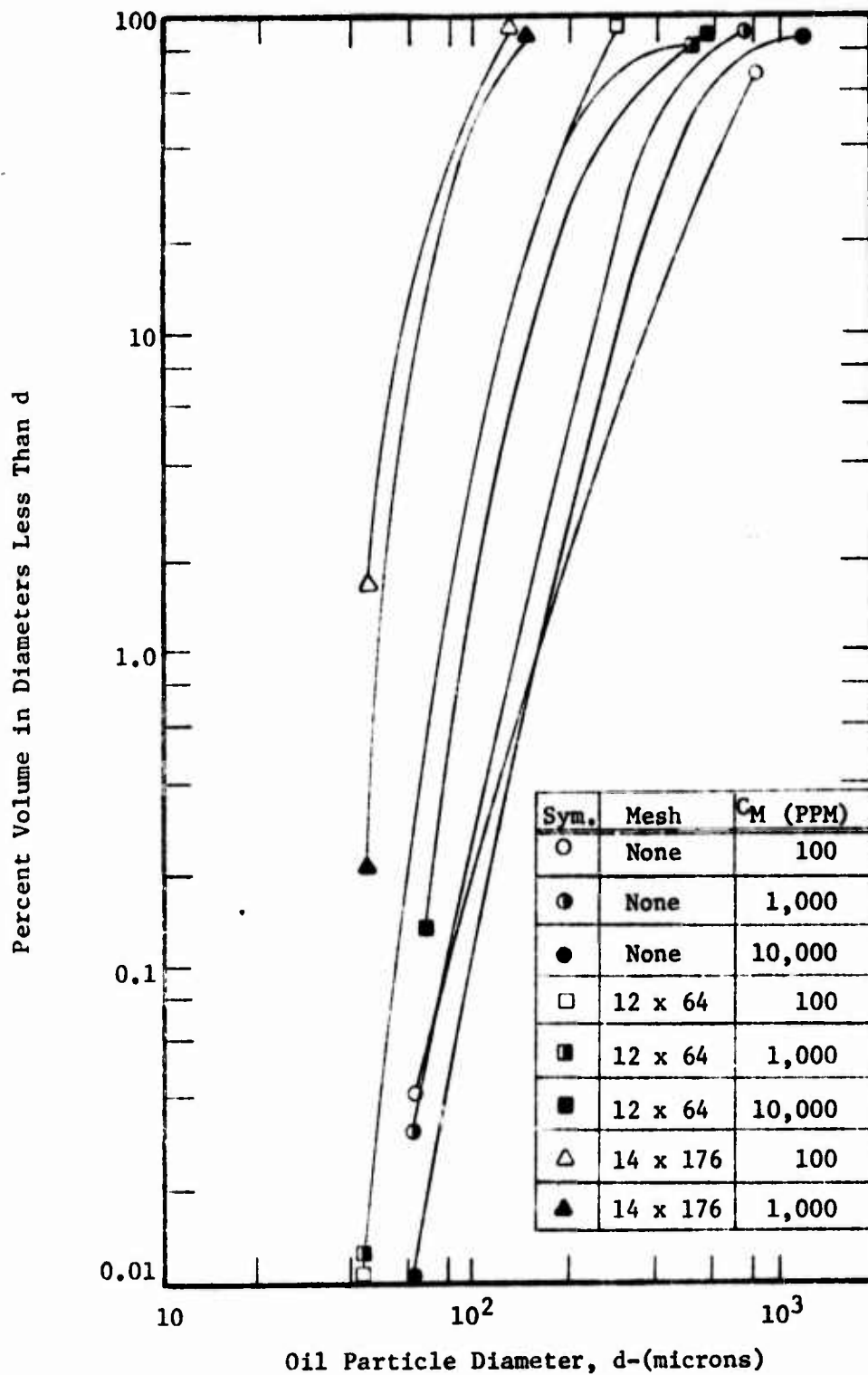
Oil Droplet Diameter,  $d$ -(microns)  
 (Typical Size Distribution and Cumulative Volume Curves)

Figure 1



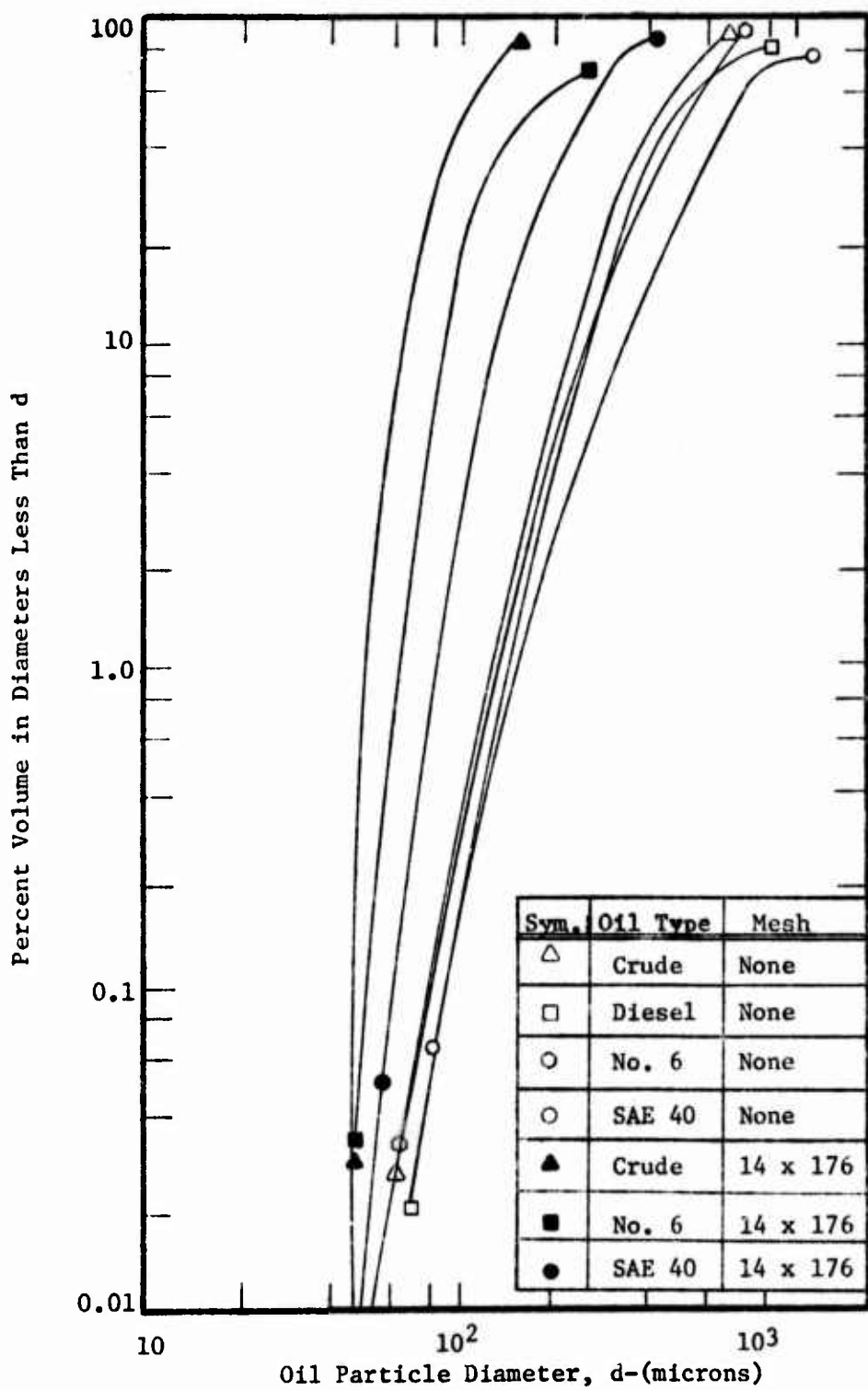
SIZE DISTRIBUTION AS PLOTTED ON LOG PROBABILITY GRID

Figure 2



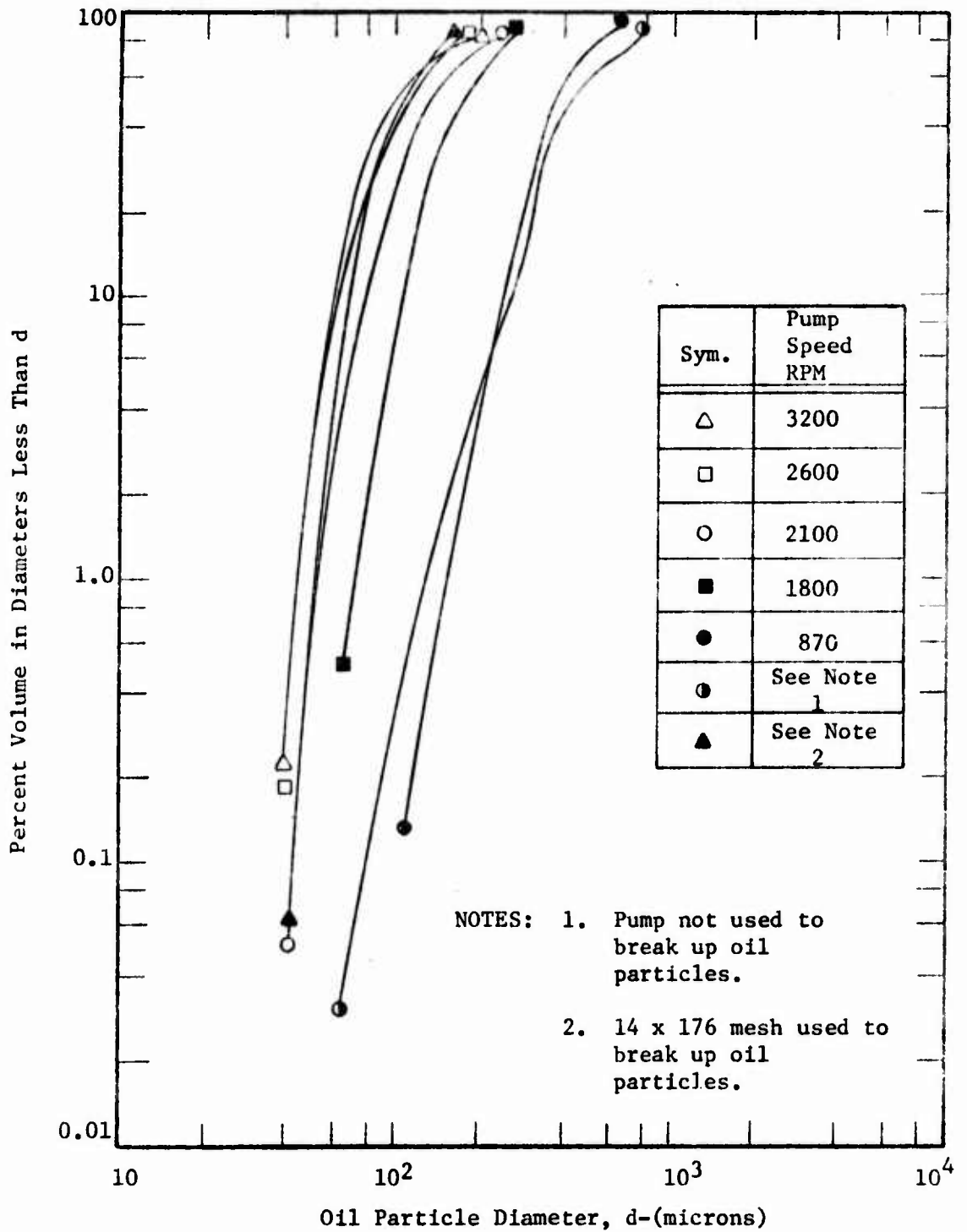
Effects of Oil Concentration ( $C_M$ ) and Screen Mesh Size on Crude Oil Particle Size Distribution

Figure 3



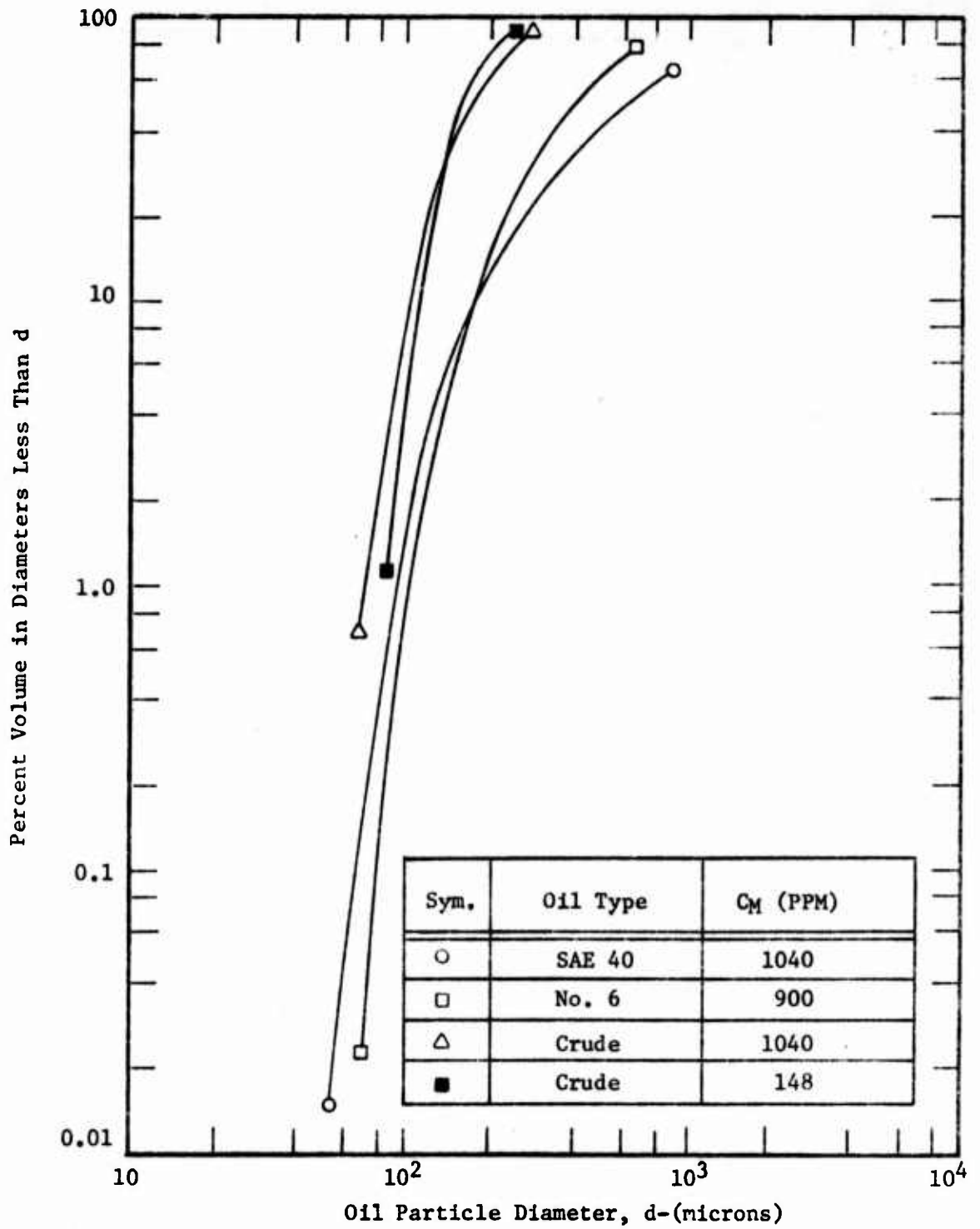
Effects of Oil Type and Screen Mesh Size on Influent Particle Size Distribution to Vortex Separator  
 ( $C_M = 1000$  PPM)

Figure 4



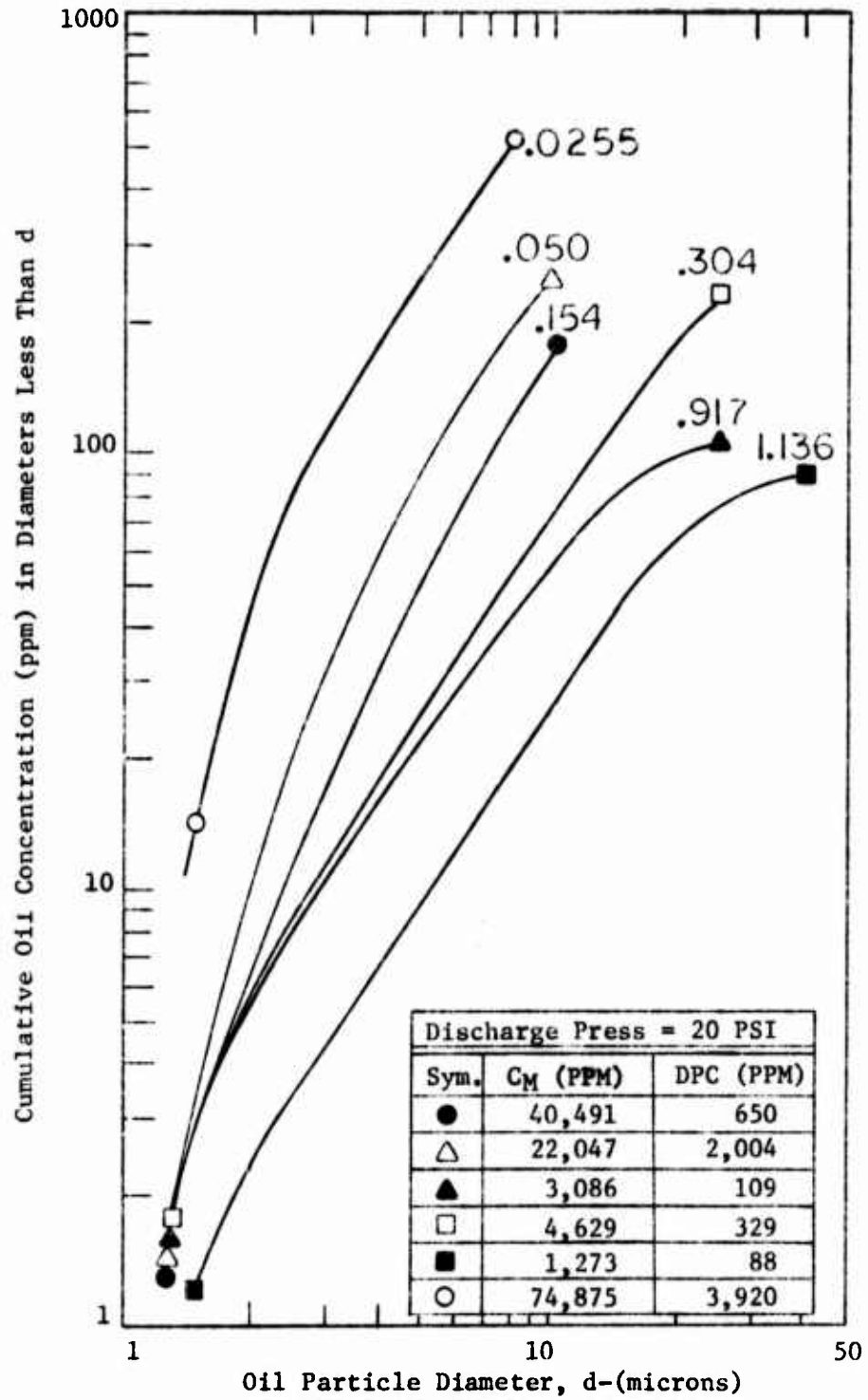
Effects of Centrifugal Pump Speed on Crude Oil Particle Size Distribution for Inlet Oil Concentration ( $C_M = 1,000$  PPM)

Figure 5



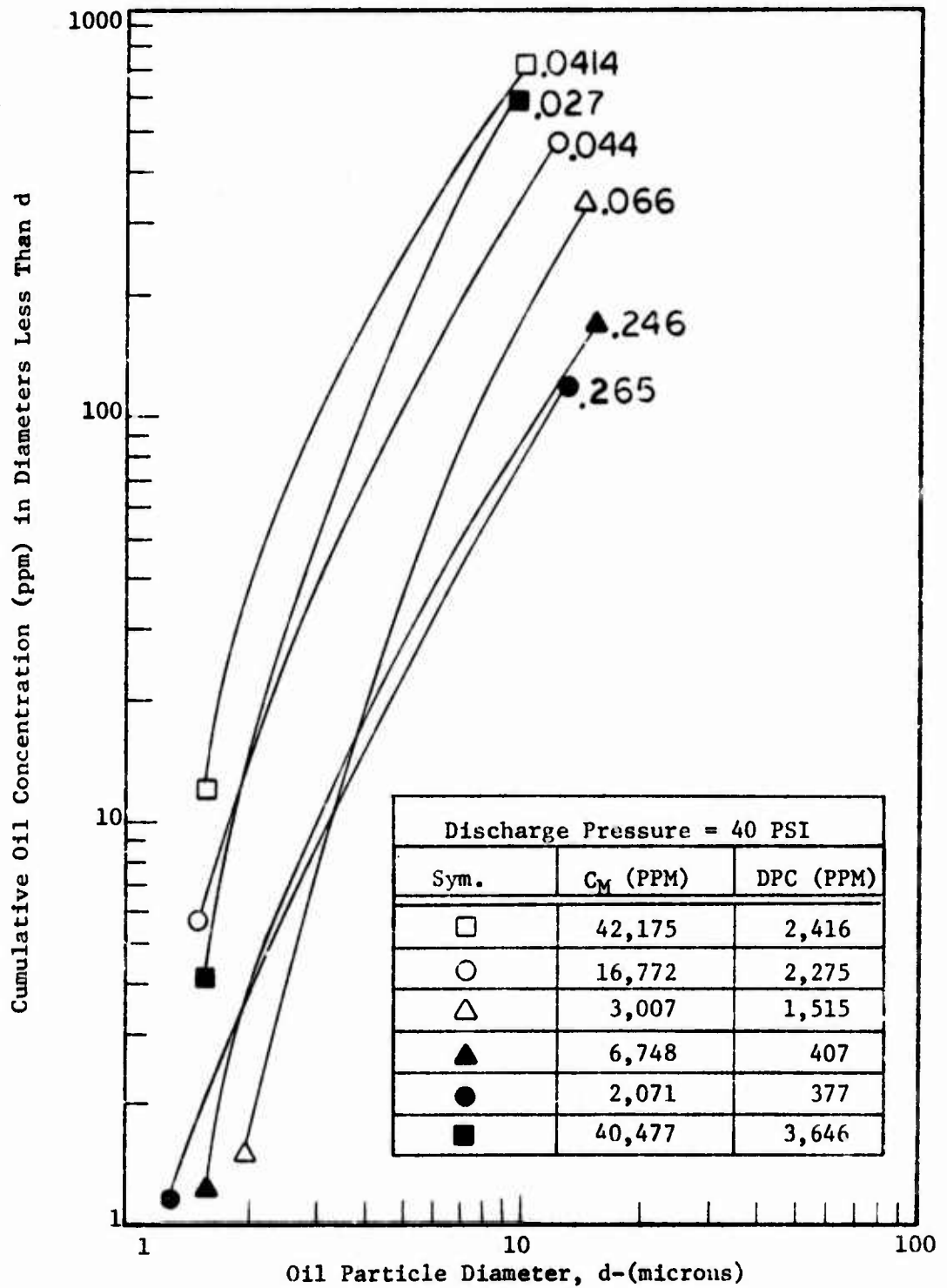
Effects of Oil Type and Concentration on Oil Particle Size Distributions Obtained Using a Centrifugal Pump.  
 Pump Speed = 1800 RPM

Figure 6



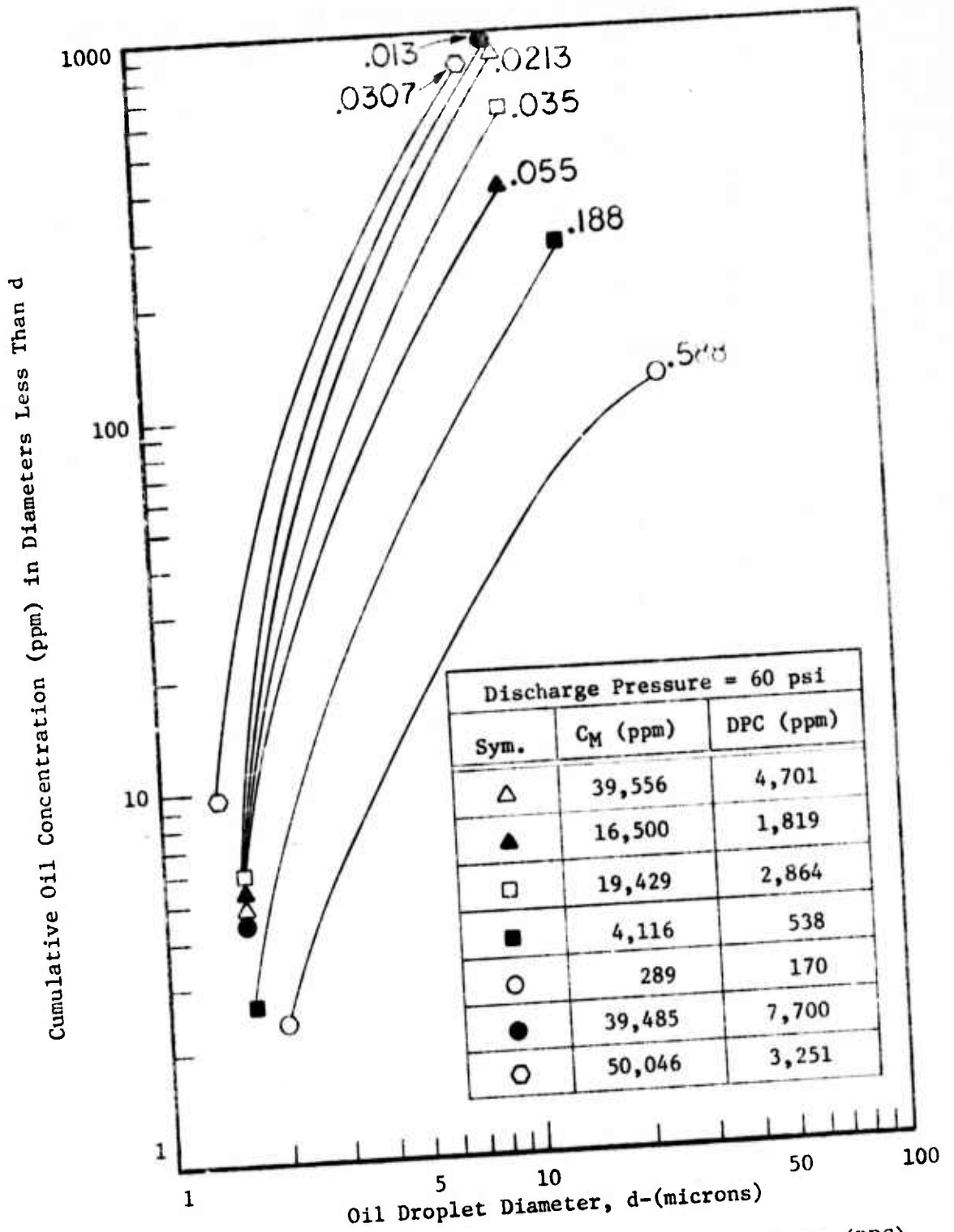
Cumulative Oil Concentration in the Dispersed Phase (DPC) With Rotary Vane Pump, for Specified Feed Concentrations (C<sub>M</sub>) of 70% lube oil + 30% Navy Distillate Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 7



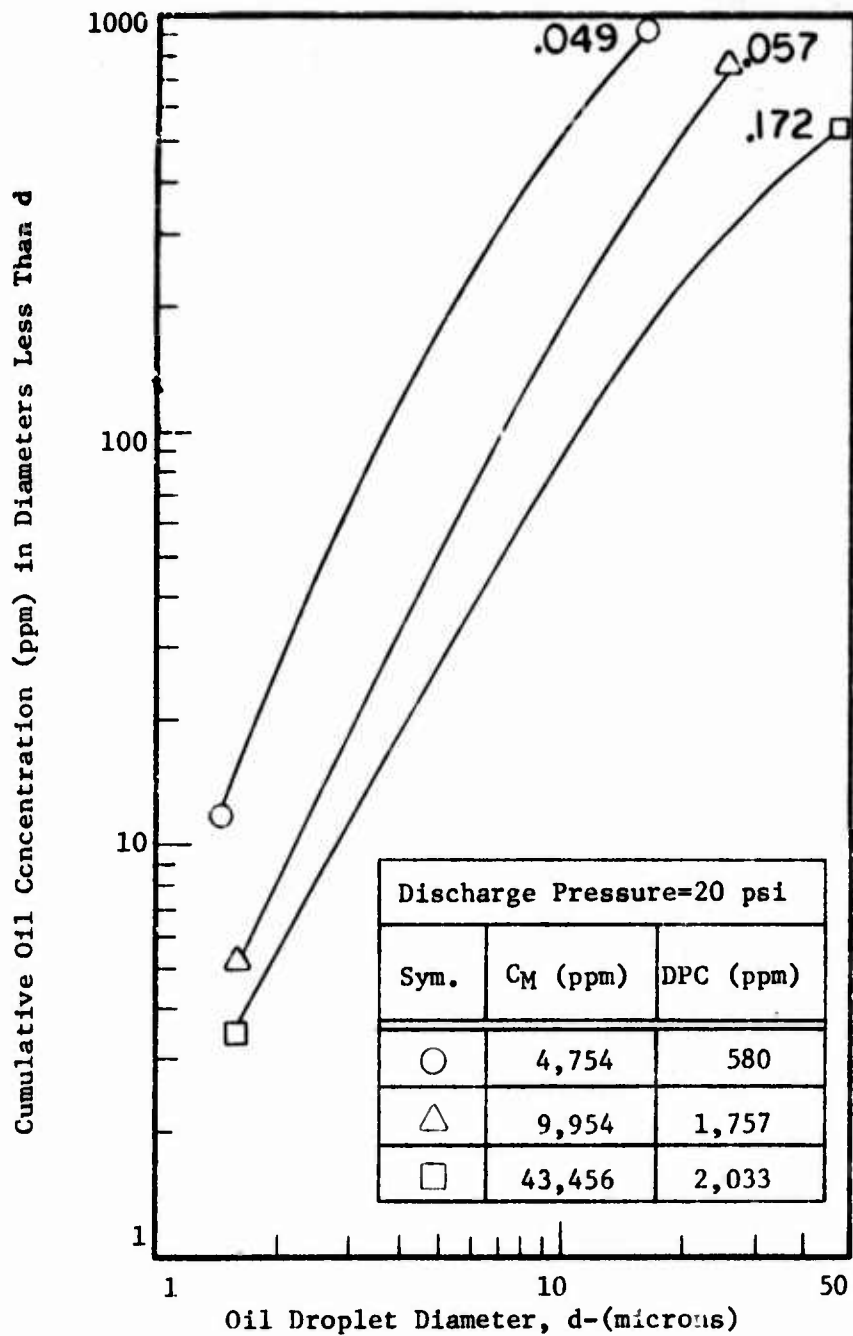
Cumulative Oil Concentration in the Dispersed Phase (DPC) With Rotary Vane Pump, for Specified Feed Concentrations ( $C_M$ ) of 70% lube oil + 30% Navy Distillate Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 8



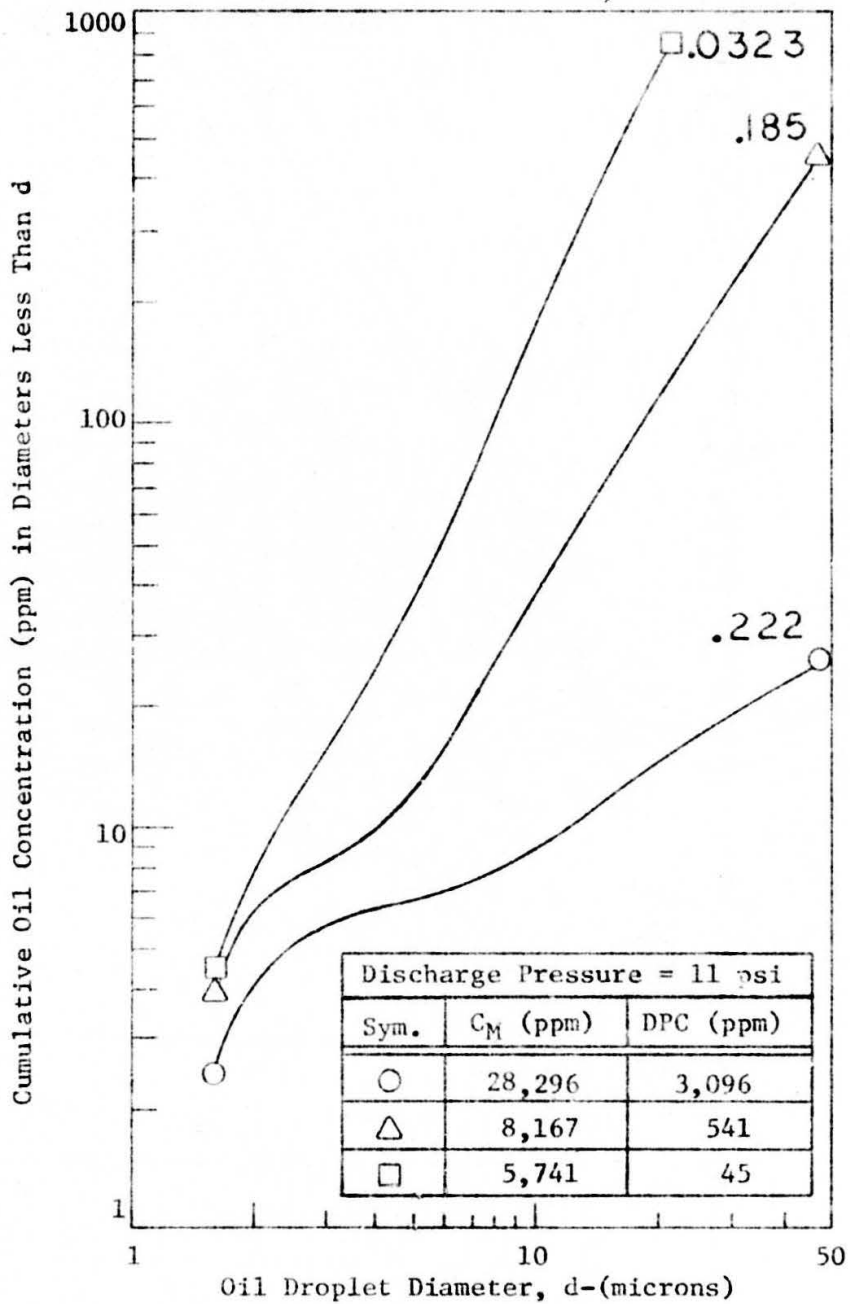
Cumulative Oil Concentration in the Dispersed Phase (DPC)  
 for Rotary Vane Pump for 70% lube oil + 30% Navy Distillate  
 Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 9



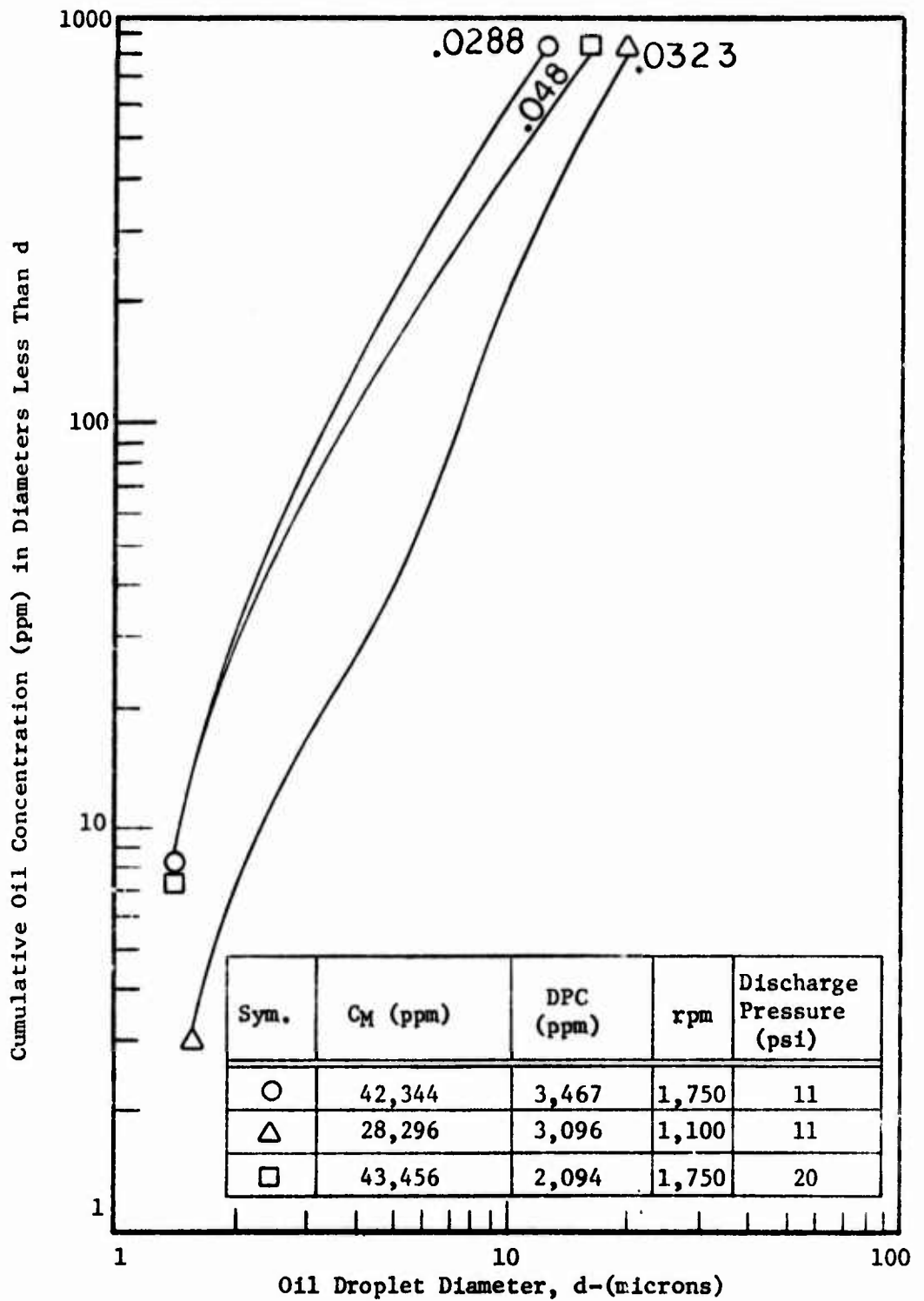
Cumulative Oil Concentration in the Dispersed Phase (DPC) For a Centrifugal Pump, 1750 rpm, with a 70% Lube Oil + 30% Navy Distillate Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 10



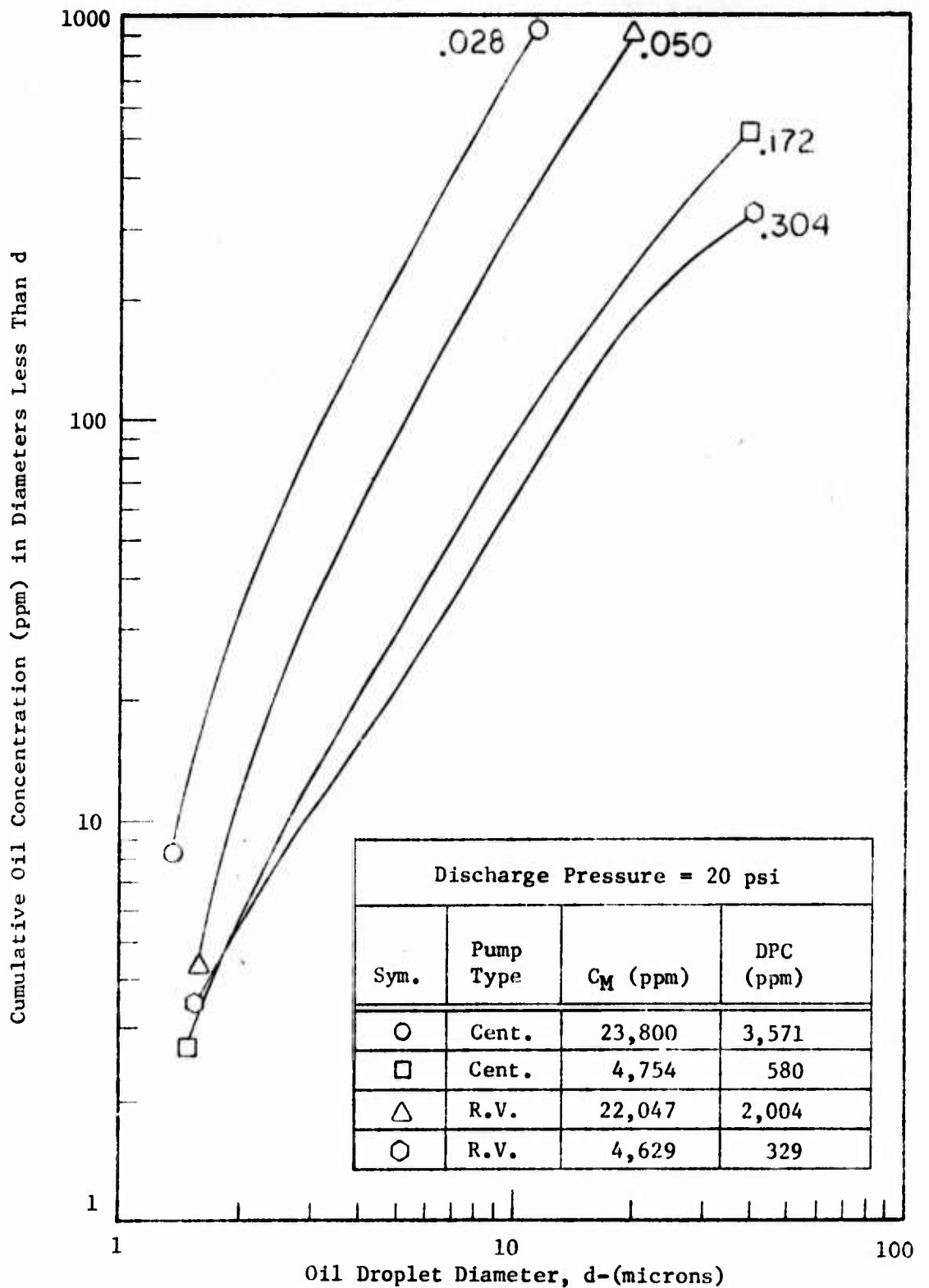
Cumulative Oil Concentration in the Dispersed Phase (DPC) for a Centrifugal Pump, 1100 rpm, with a 70% Lube Oil + 30% Navy Distillate Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 11



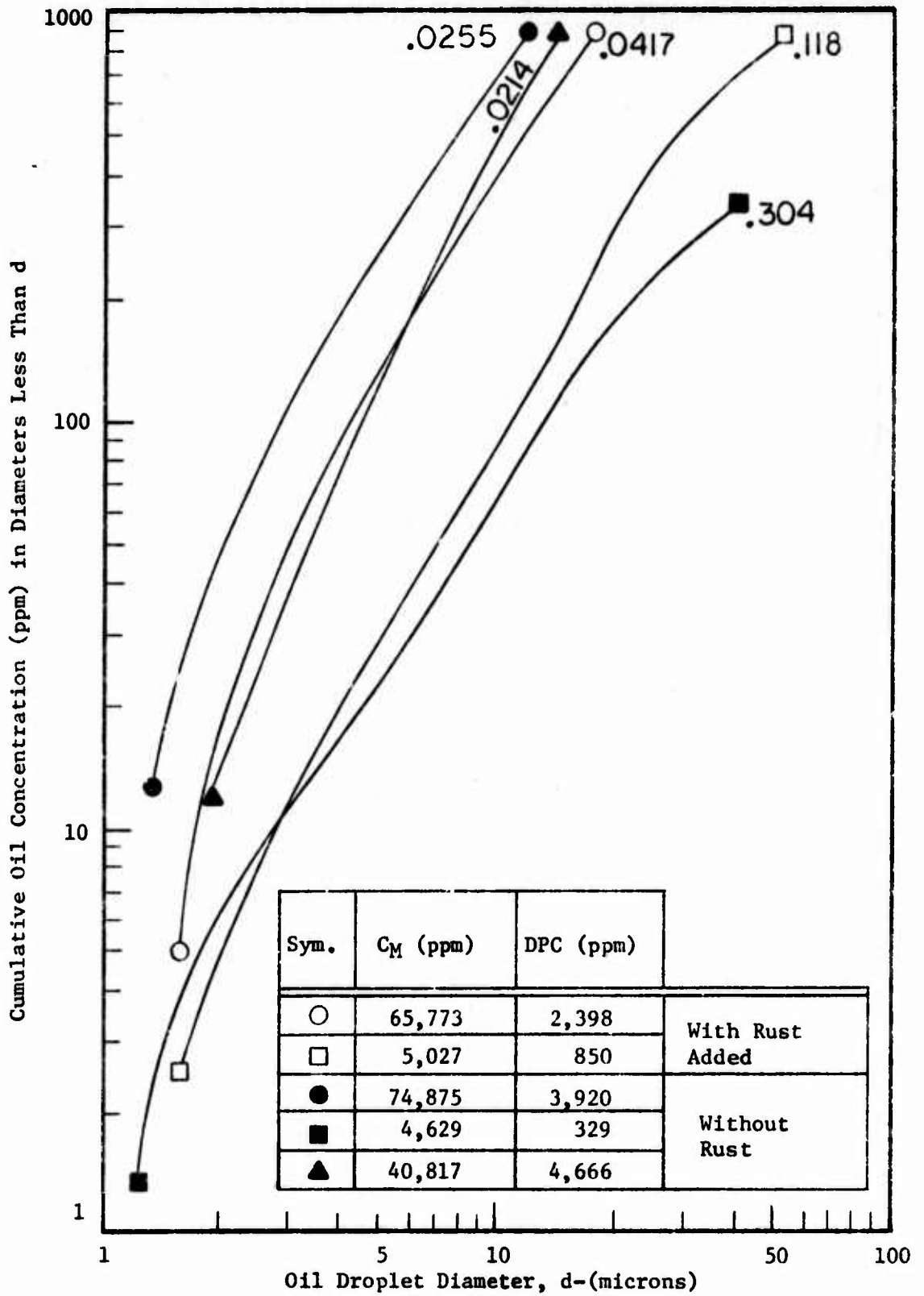
Cumulative Oil Concentration in the Dispersed Phase (DPC) for Three Centrifugal Pump Speeds, with a 70% Lube Oil and 30% Navy Distillate Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 12



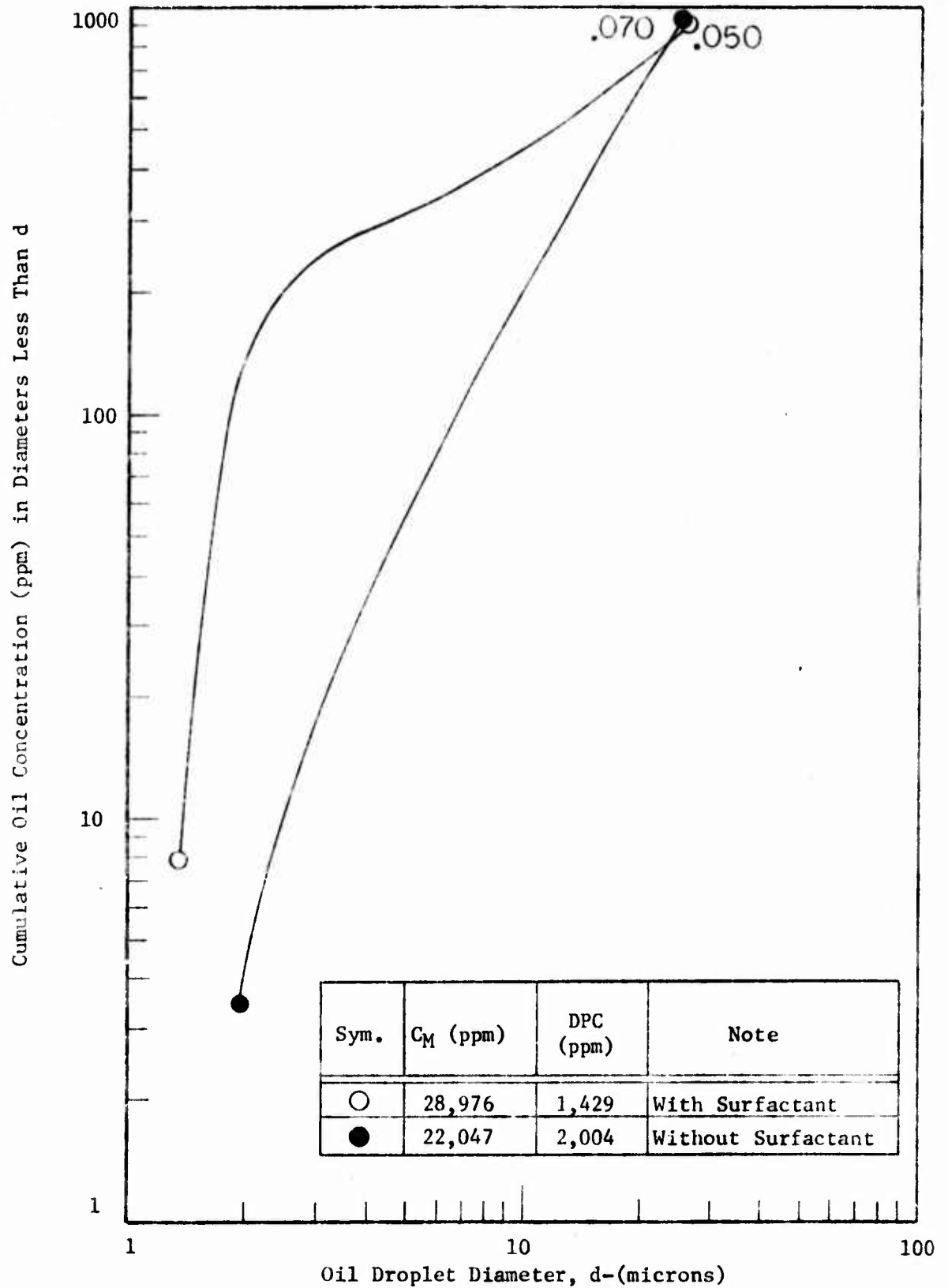
Cumulative Oil Concentration in the Dispersed Phase (DPC), Comparison Between Rotary Vane and Centrifugal Pump (1750 rpm) with a 70% Lube Oil and 30% Navy Distillate Mixture in Salt Water (1.7% salt) at 10 gpm.

Figure 13



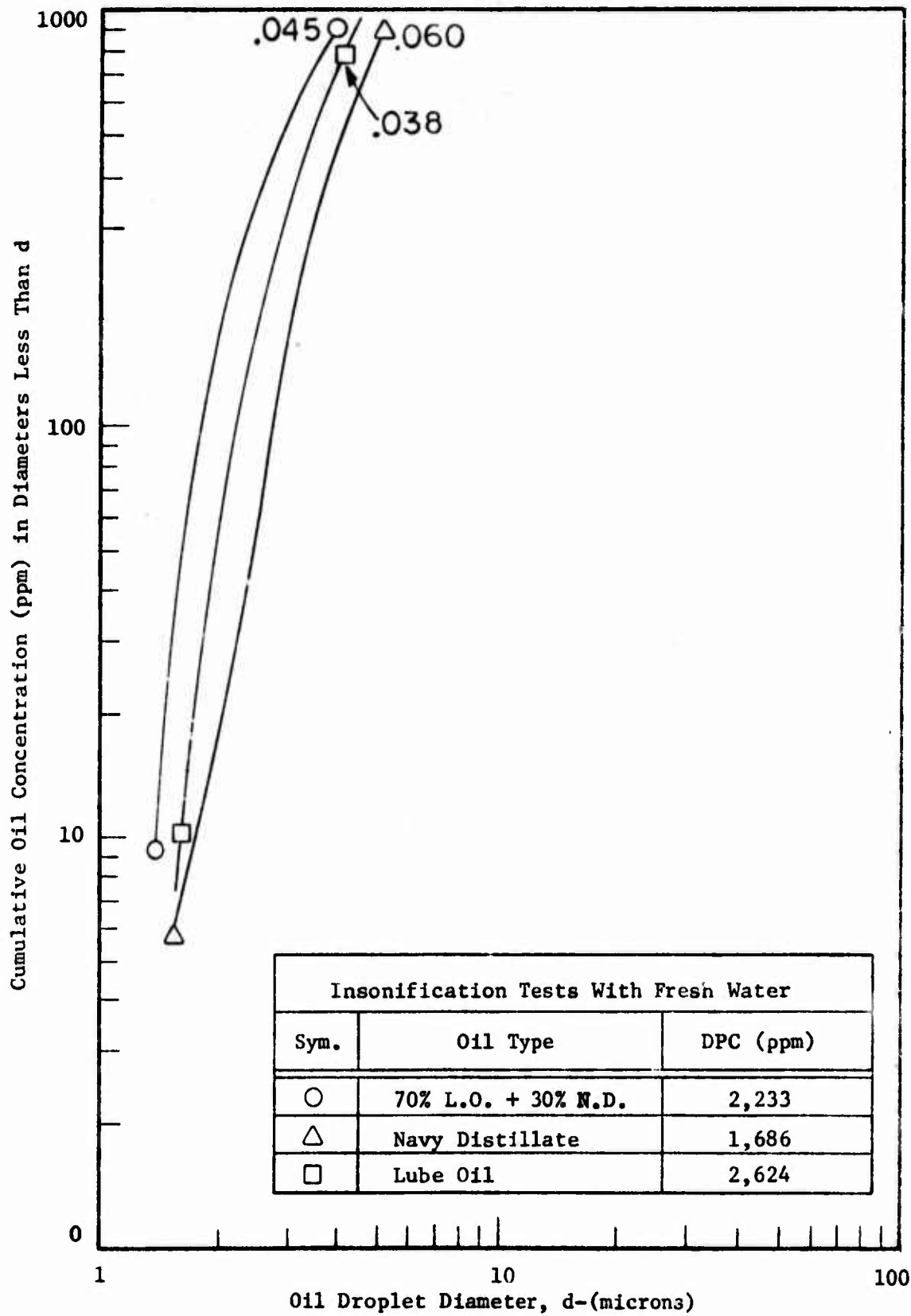
Cumulative Oil Concentration in the Dispersed Phase (DPC), Comparison Between Tests With Rust (1 mg/l of ferric oxide) and Without Rust. Salt Water (1.7% salt), with Mixture of 70% Lube Oil + 30% Navy Distillate, Flowing at 10 gpm.

Figure 14  
110



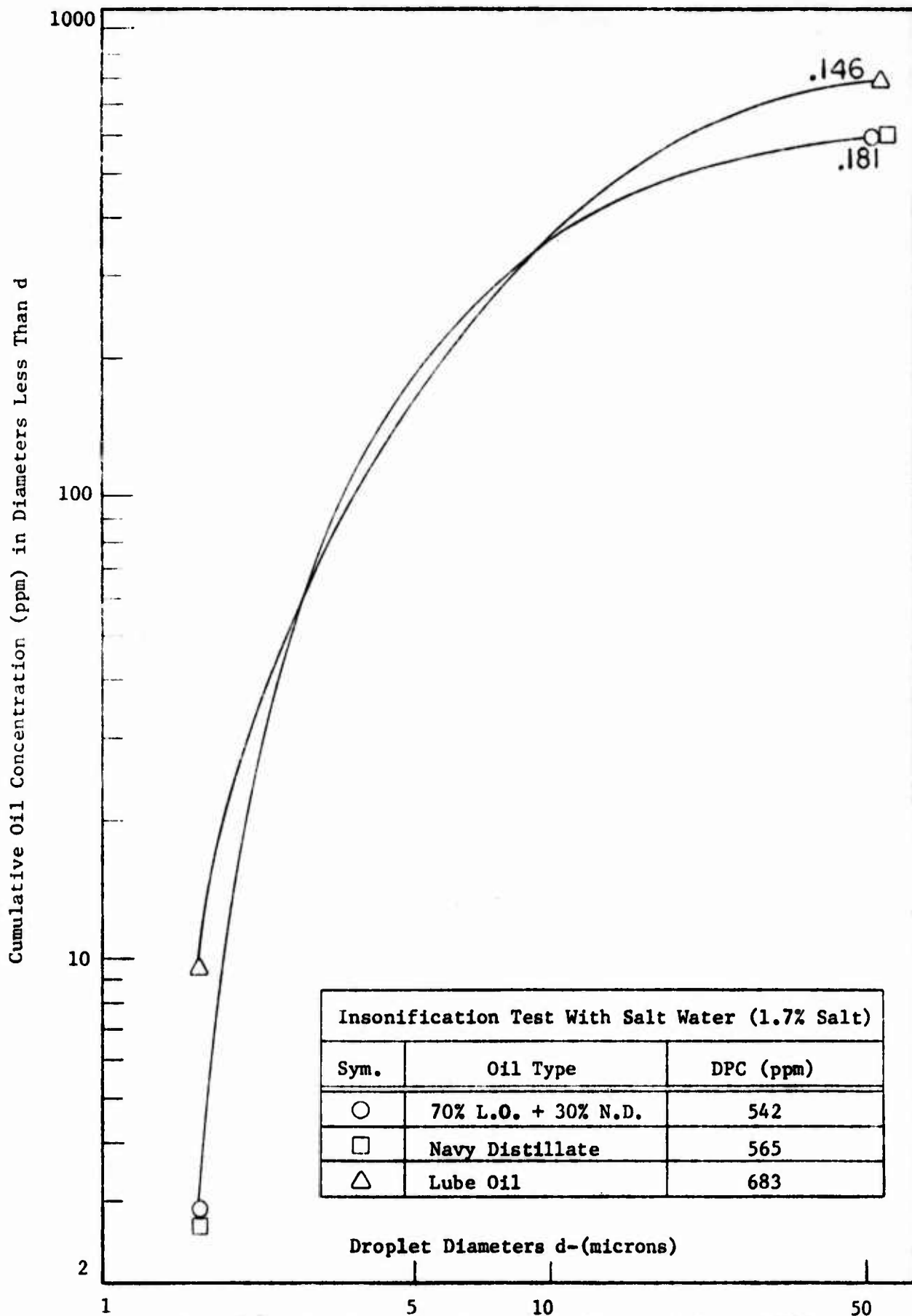
Cumulative Oil Concentration in the Dispersed Phase (DPC), Comparison Between Test With and Without Surfactant. (Phinos, 1% of Oil). Salt Water (1.7% salt), with Mixture of 70% Lube Oil and 30% Navy Distillate, Flowing at 10 gpm.

Figure 15



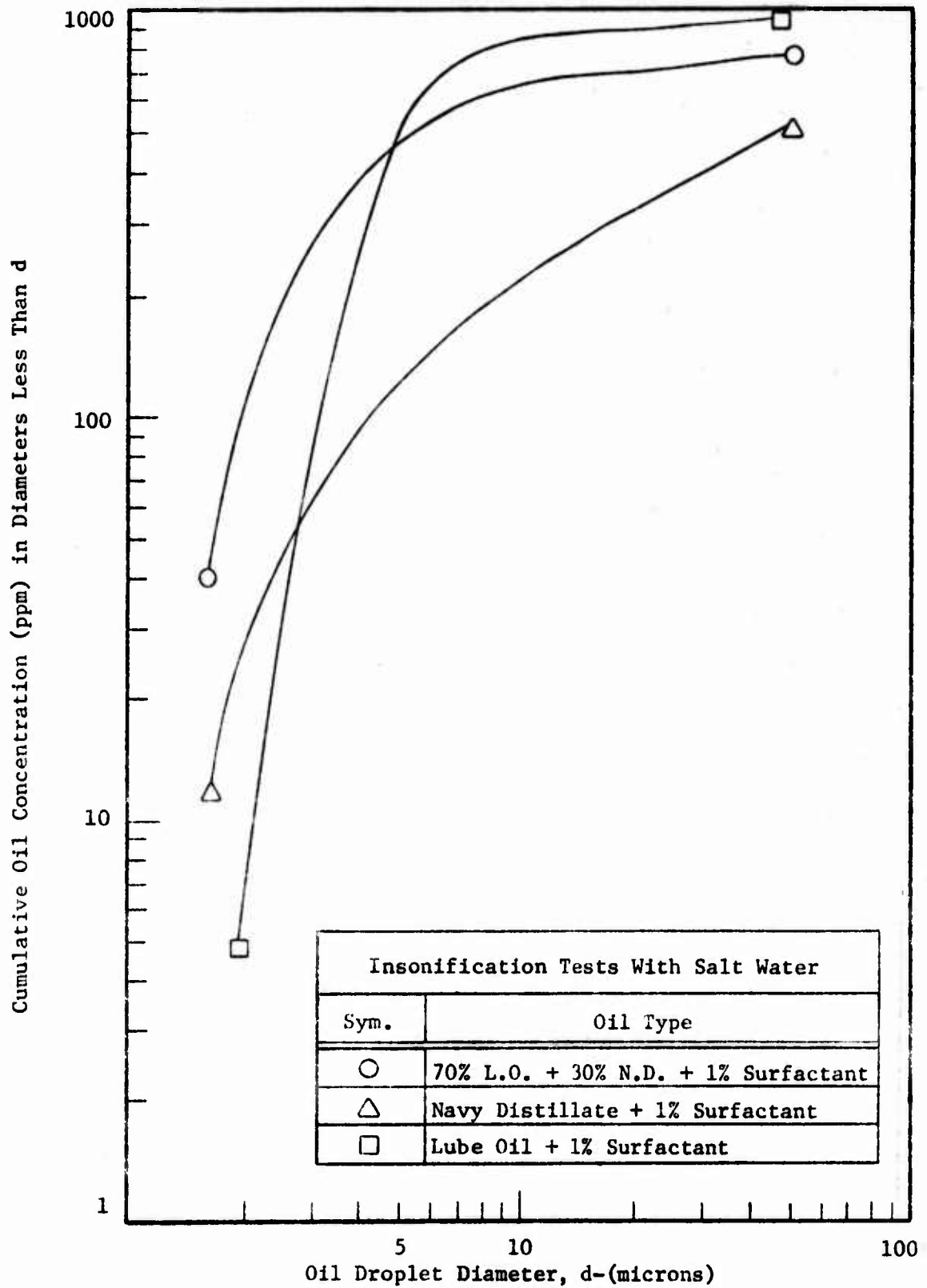
Cumulative Oil Concentration in the Dispersed Phase (DPC),  
with Ultrasonic Emulsification in Fresh Water

Figure 16



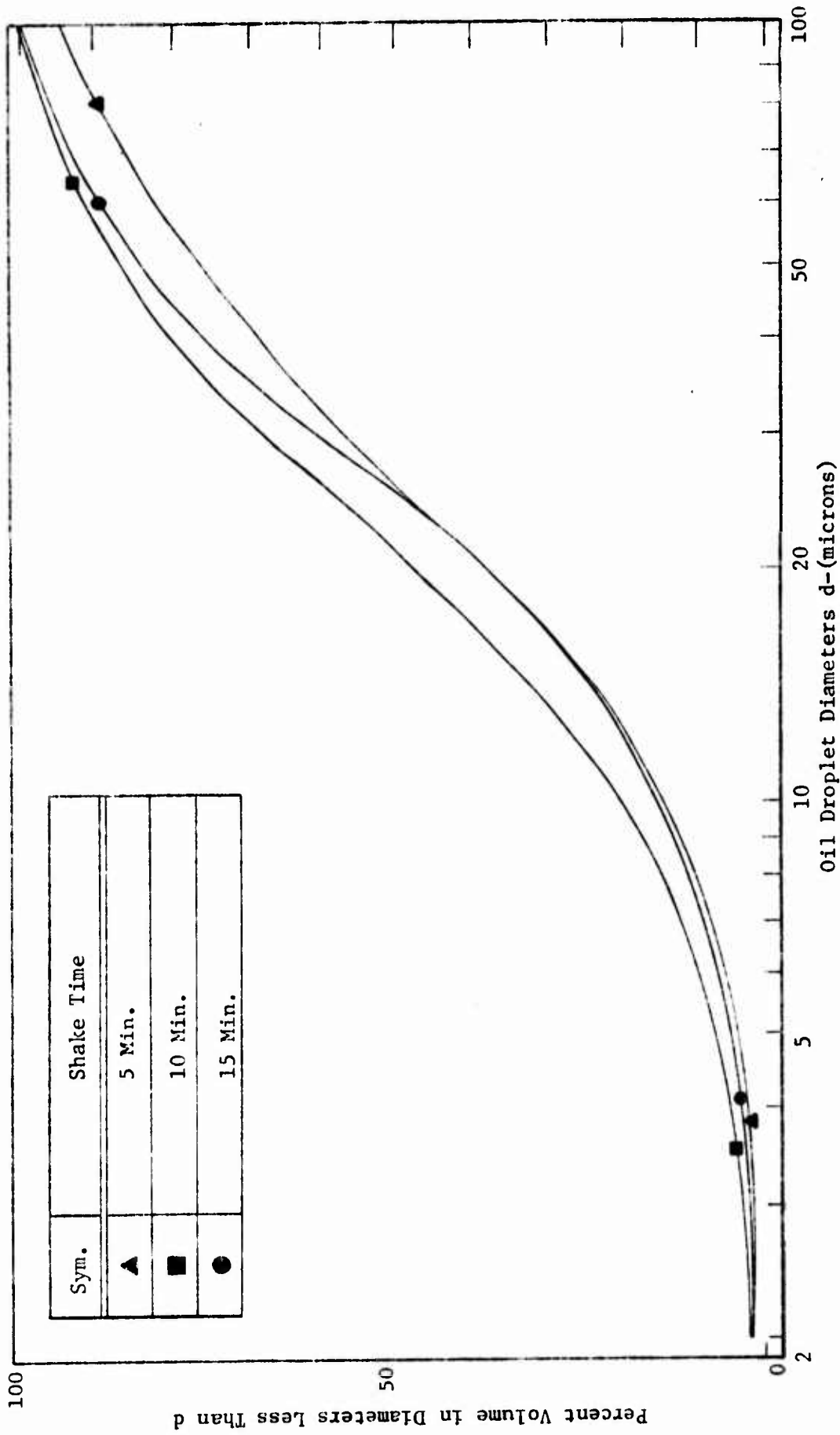
Cumulative Oil Concentration in the Dispersed Phase (DPC) with Ultrasonic Emulsification in Salt Water.

Figure 17



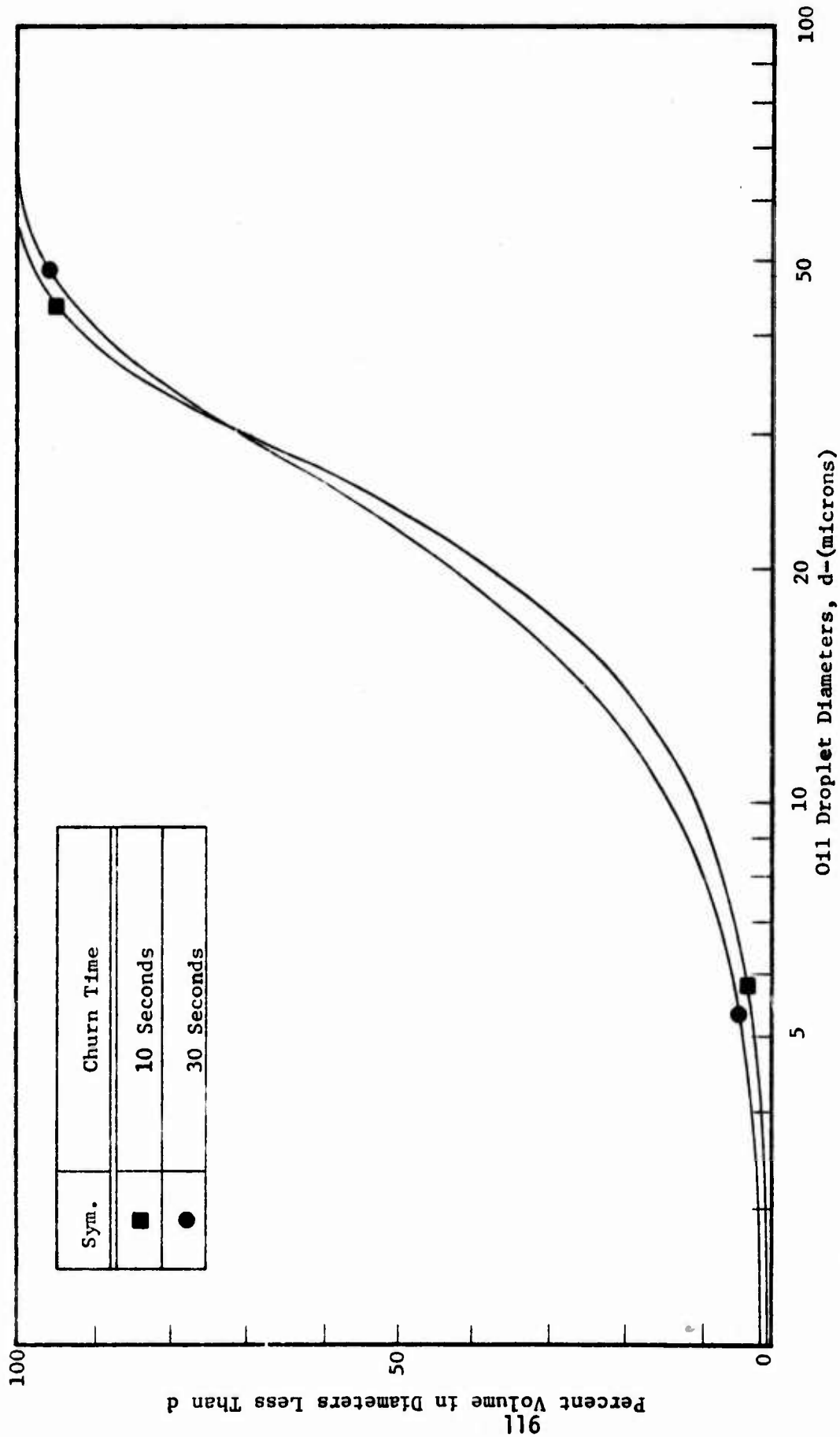
Cumulative Oil Concentration in the Dispersed Phase (DPC) for Salt Water and Surfactant (Phipps, 1% of Oil).

Figure 18



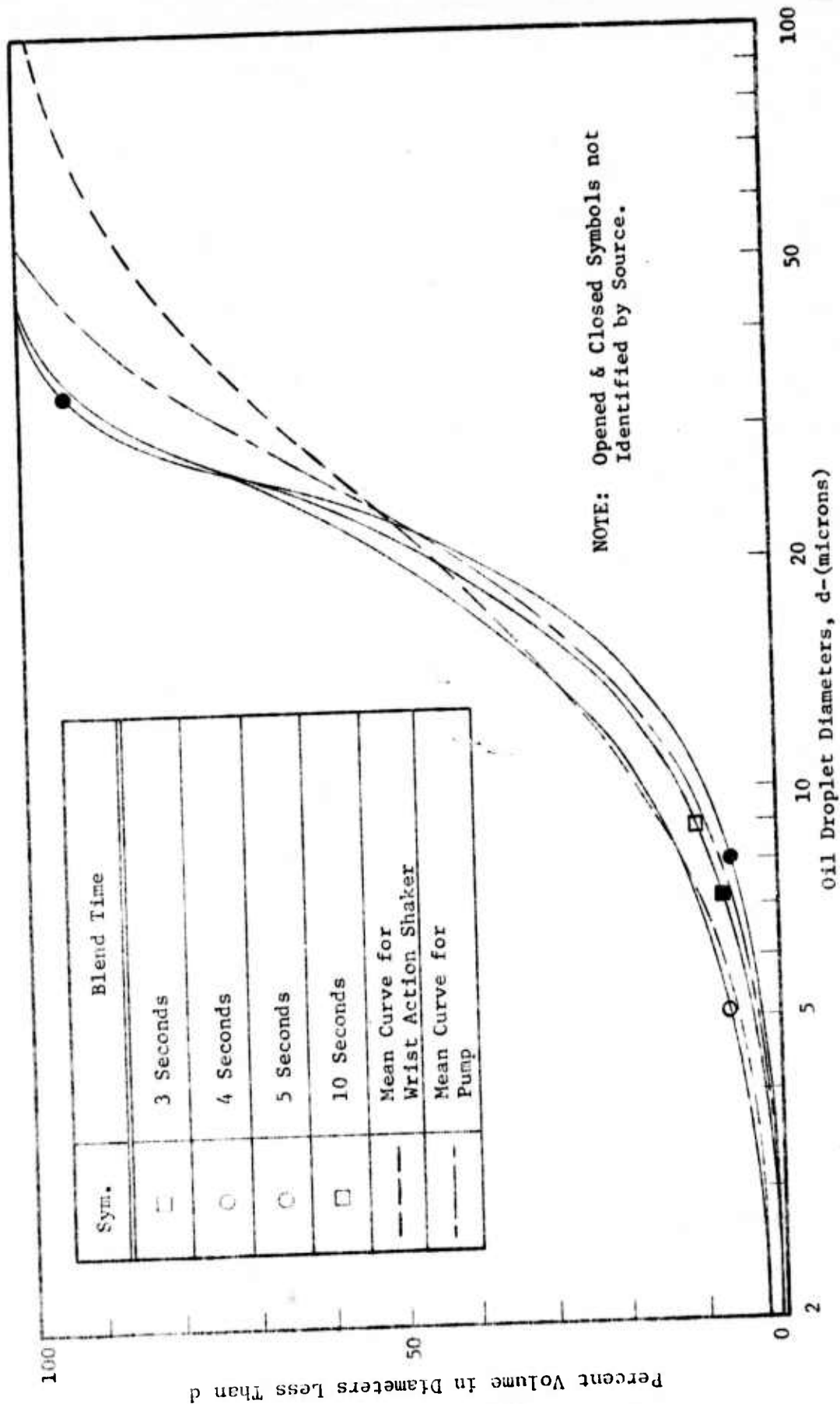
Cumulative Volumetric Drop Size Distributions Produced by Burrell Wrist Action Shaker for 1% #2 Fuel Oil in 2% Saline Solution.

Figure 19



Cumulative Volumetric Drop Size Distributions Produced By an Ingersoll-Rand Centrifugal Pump for 1% #2 Fuel Oil in 2% Saline Solution at 10 gpm. Extended Churn Times Achieved by Recirculation.

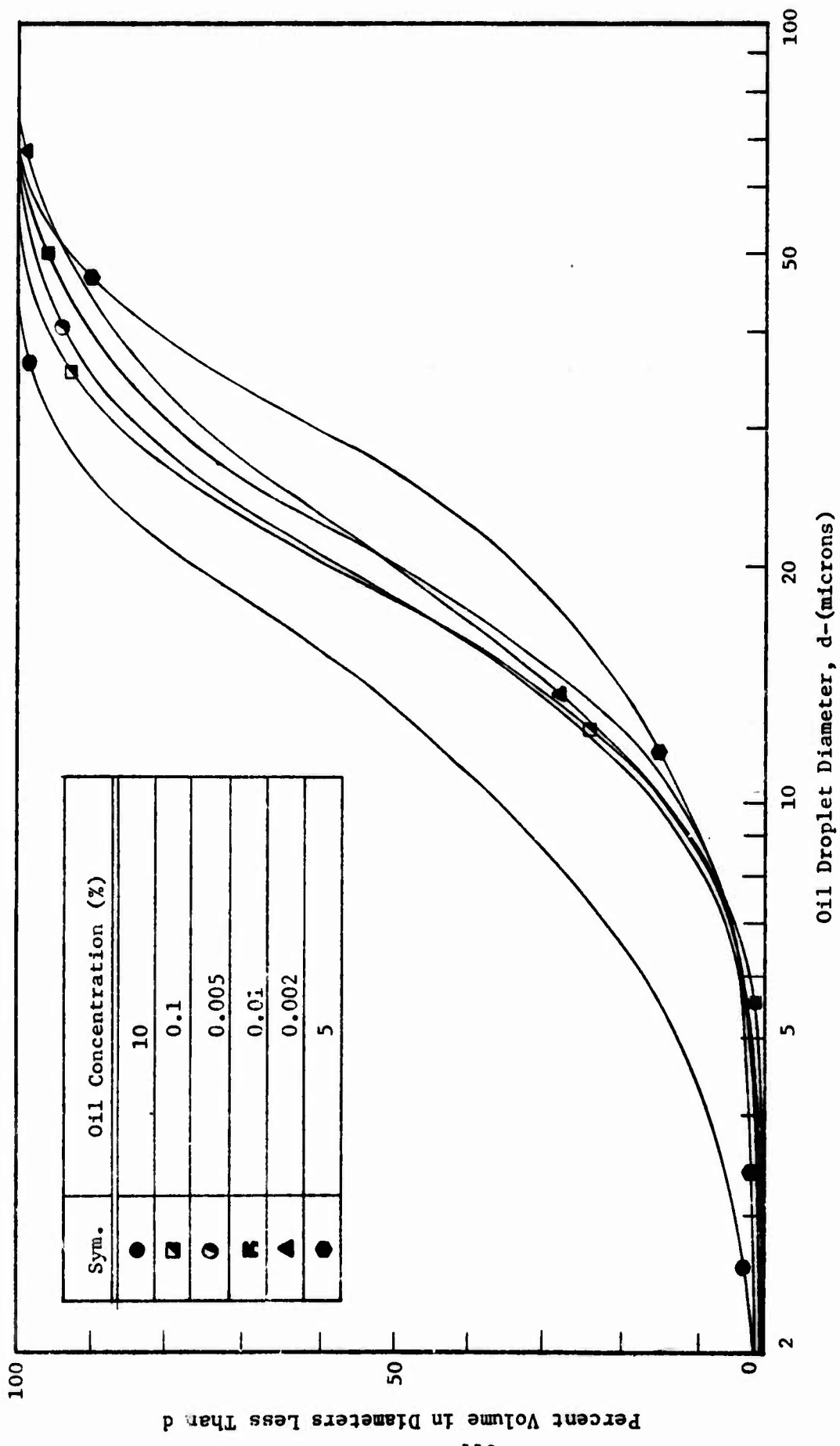
Figure 20



Percent Volume in Diameters Less Than d

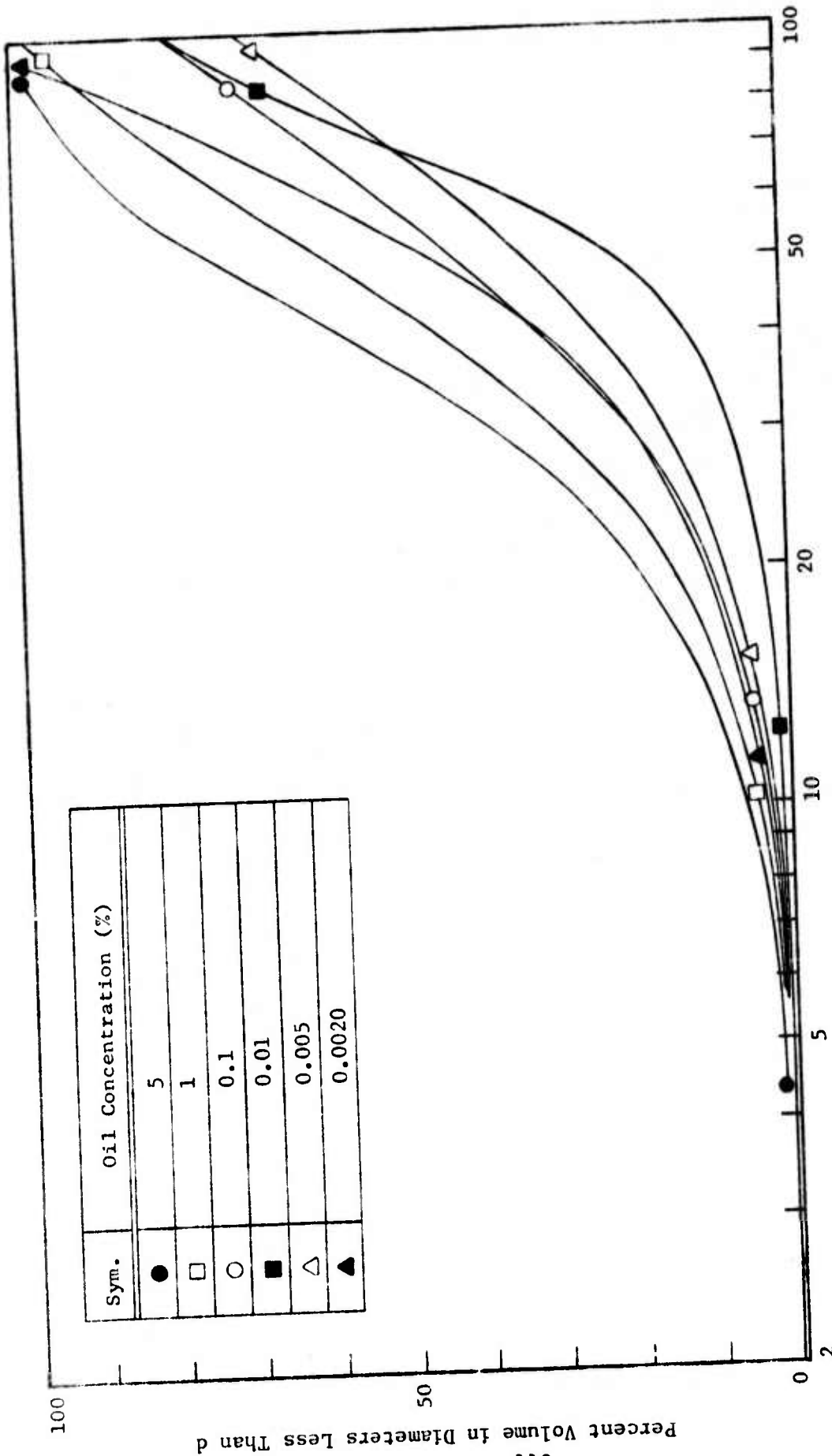
Cumulative Volumetric Drop Size Distributions Produced By a Sears Blender for 1% #2 Fuel Oil in a 2% Saline Solution.

Figure 21



Effect of Oil Concentration on Cumulative Volumetric Drop Size Distribution for #2 Fuel Oil Mixed in a Sears Blender for 5 Seconds.

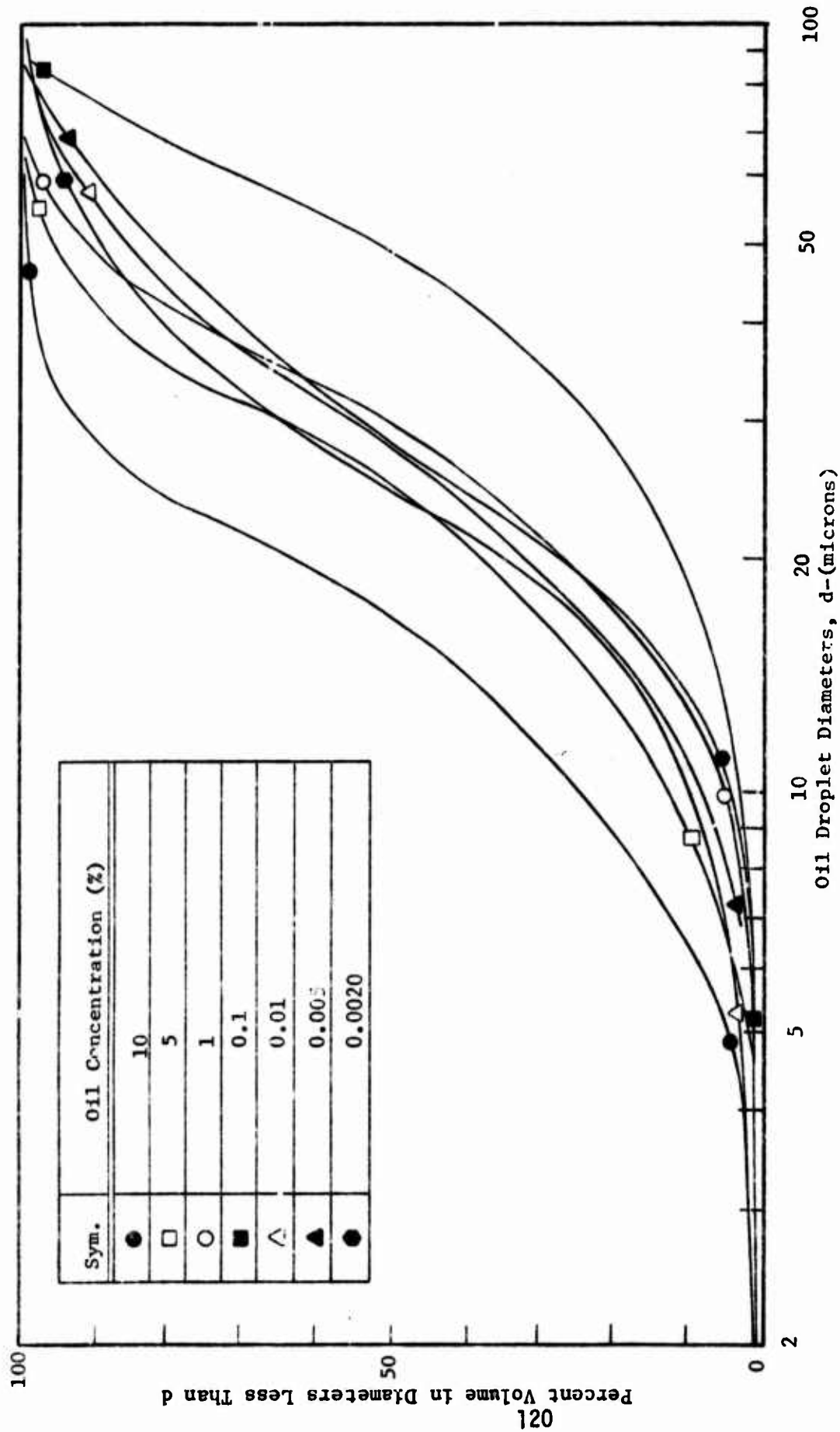
Figure 22



Oil Droplet Diameters, d-(microns)

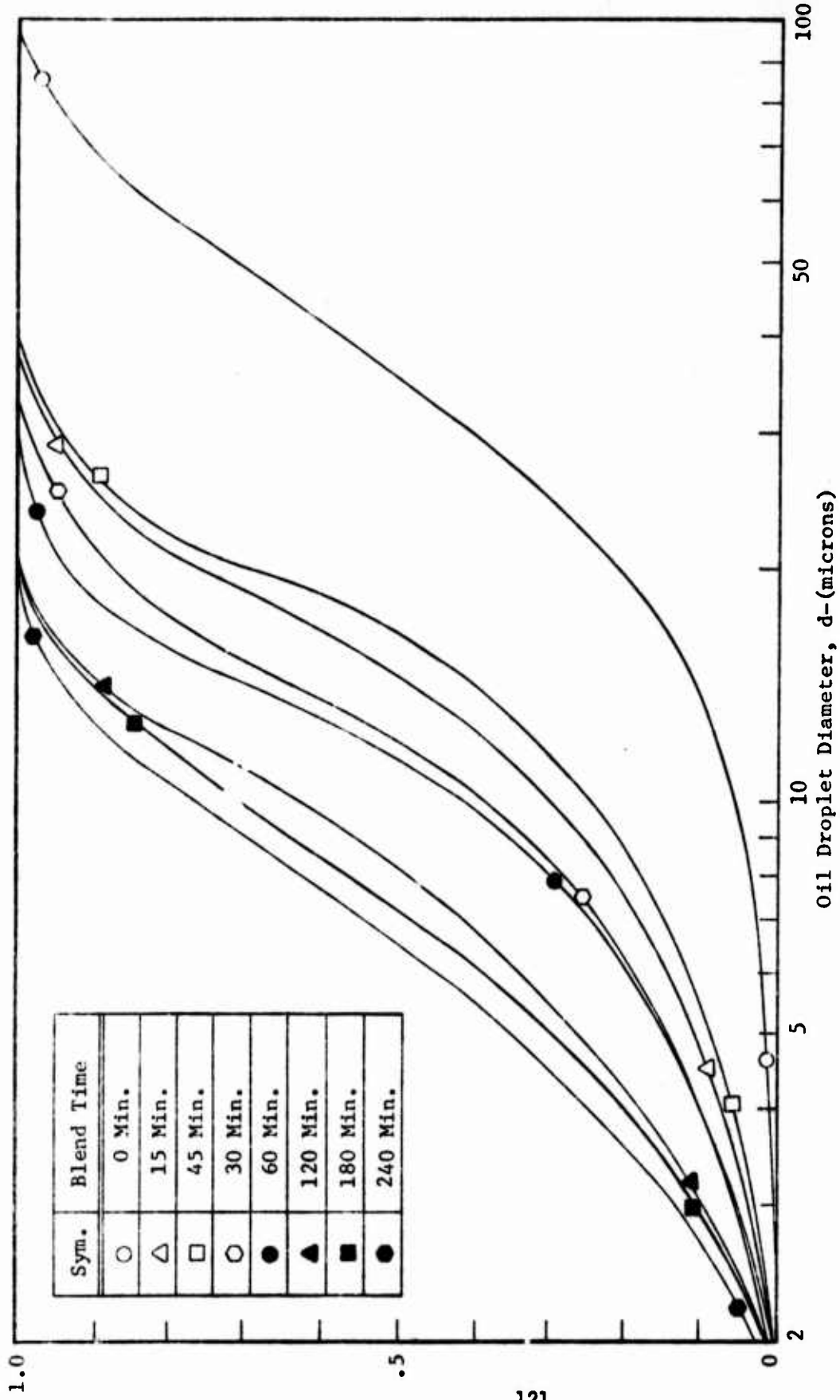
Effects of Oil Concentration on Cumulative Volumetric Drop Size Distribution for #4 Fuel Oil Mixed in a Sears Blender for 5 Seconds.

Figure 23



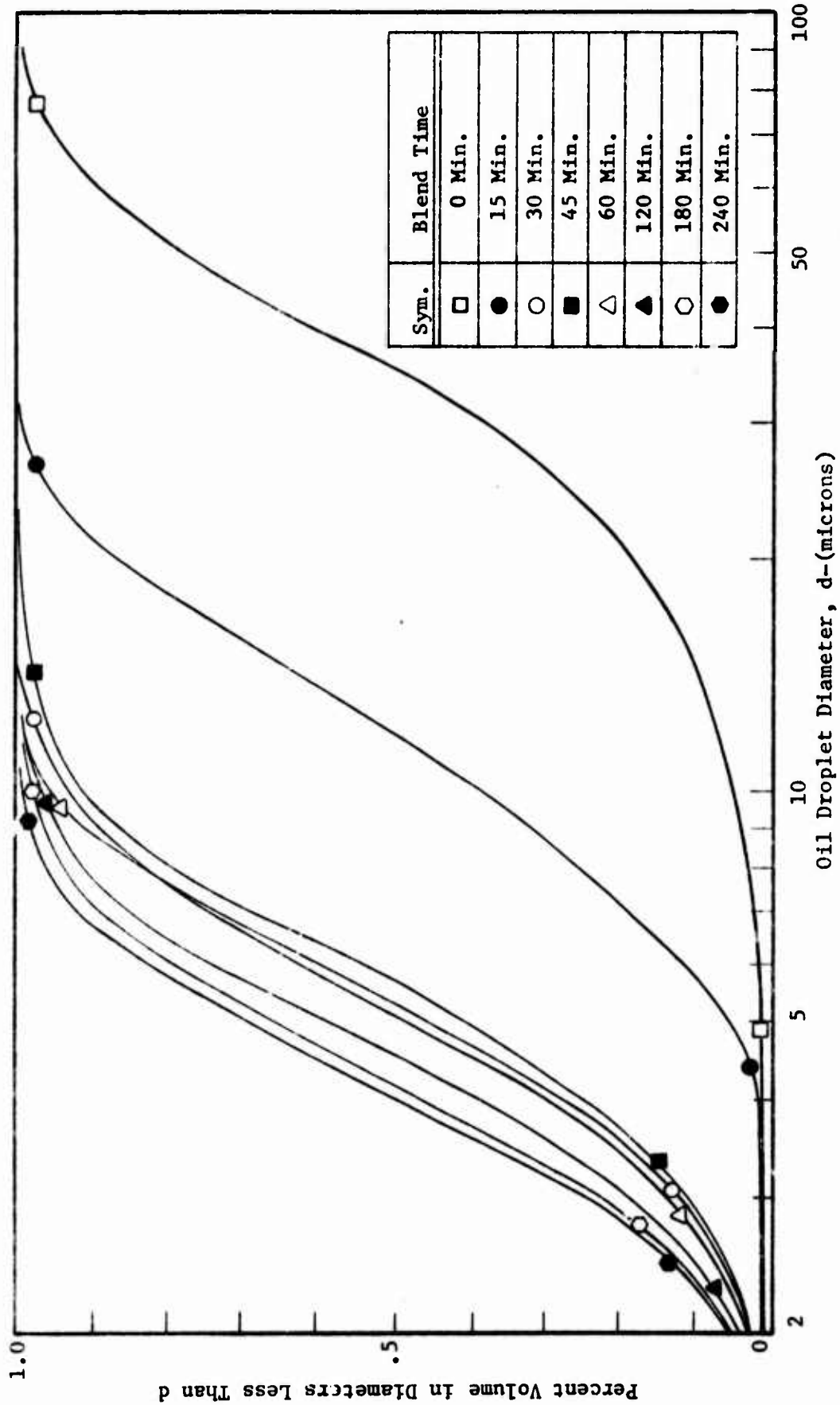
Effect of Oil Concentration on Cumulative Volumetric Drop Size Distribution for Nigerian Crude Oil Mixed in a Sears Blender for 5 Seconds.

Figure 24



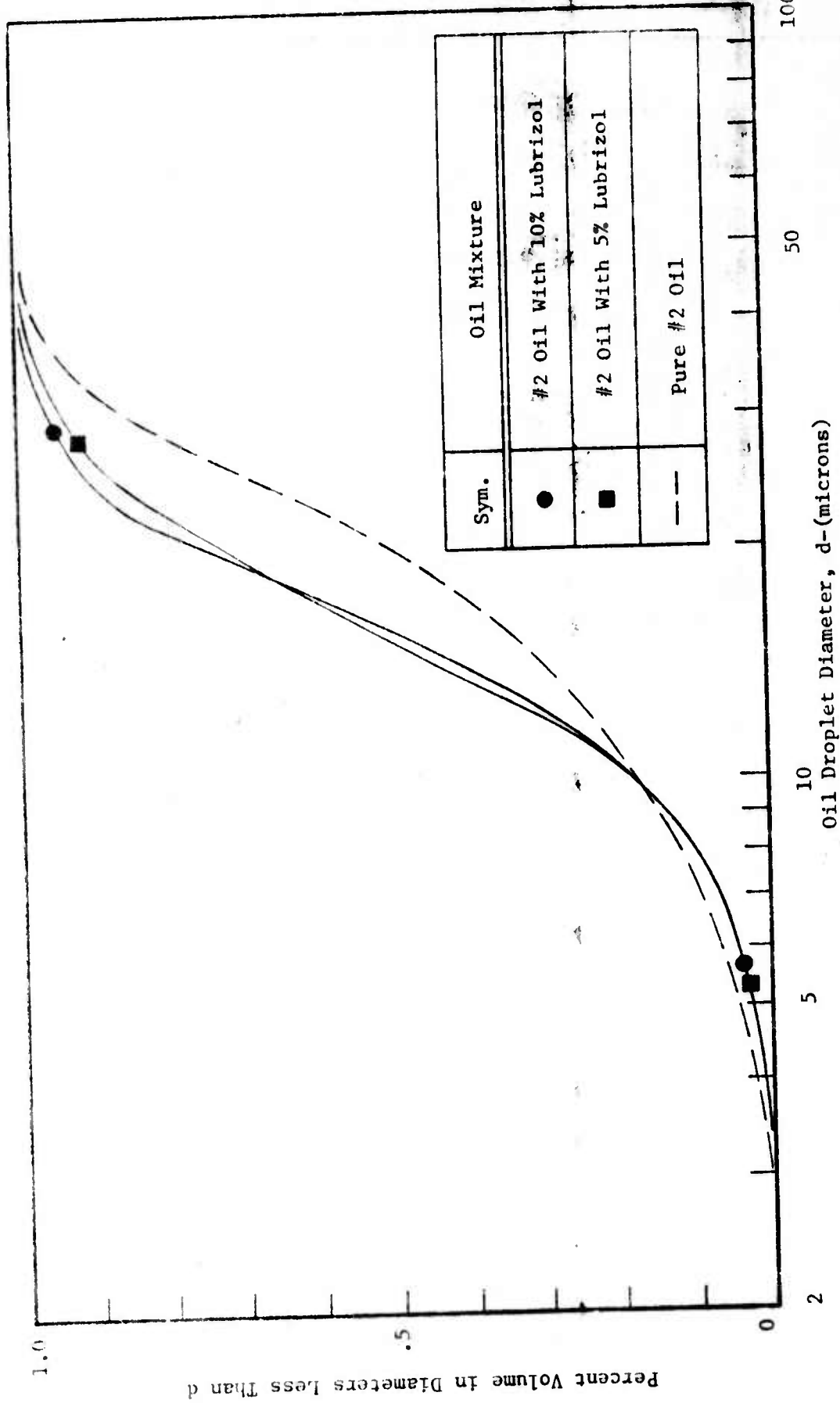
Cumulative Volumetric Drop Distribution as a Function of Blend Time for #4 Oil (1%) Mixed in a Sears Blender.

Figure 25



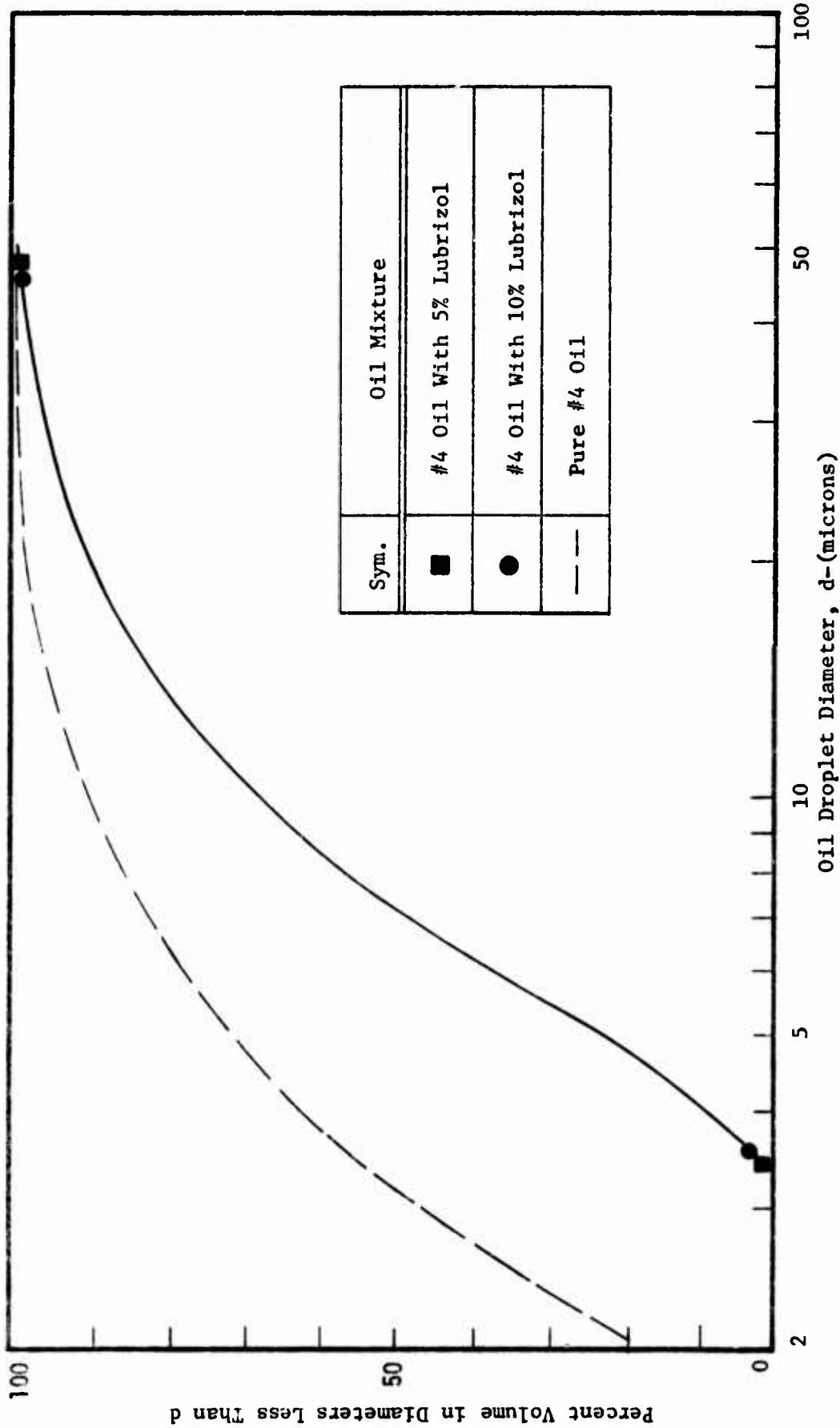
Cumulative Volumetric Drop Distributions as a Function of Blend Time for Nigerian Crude Oil (1%) Mixed in a Sears Blender.

Figure 26



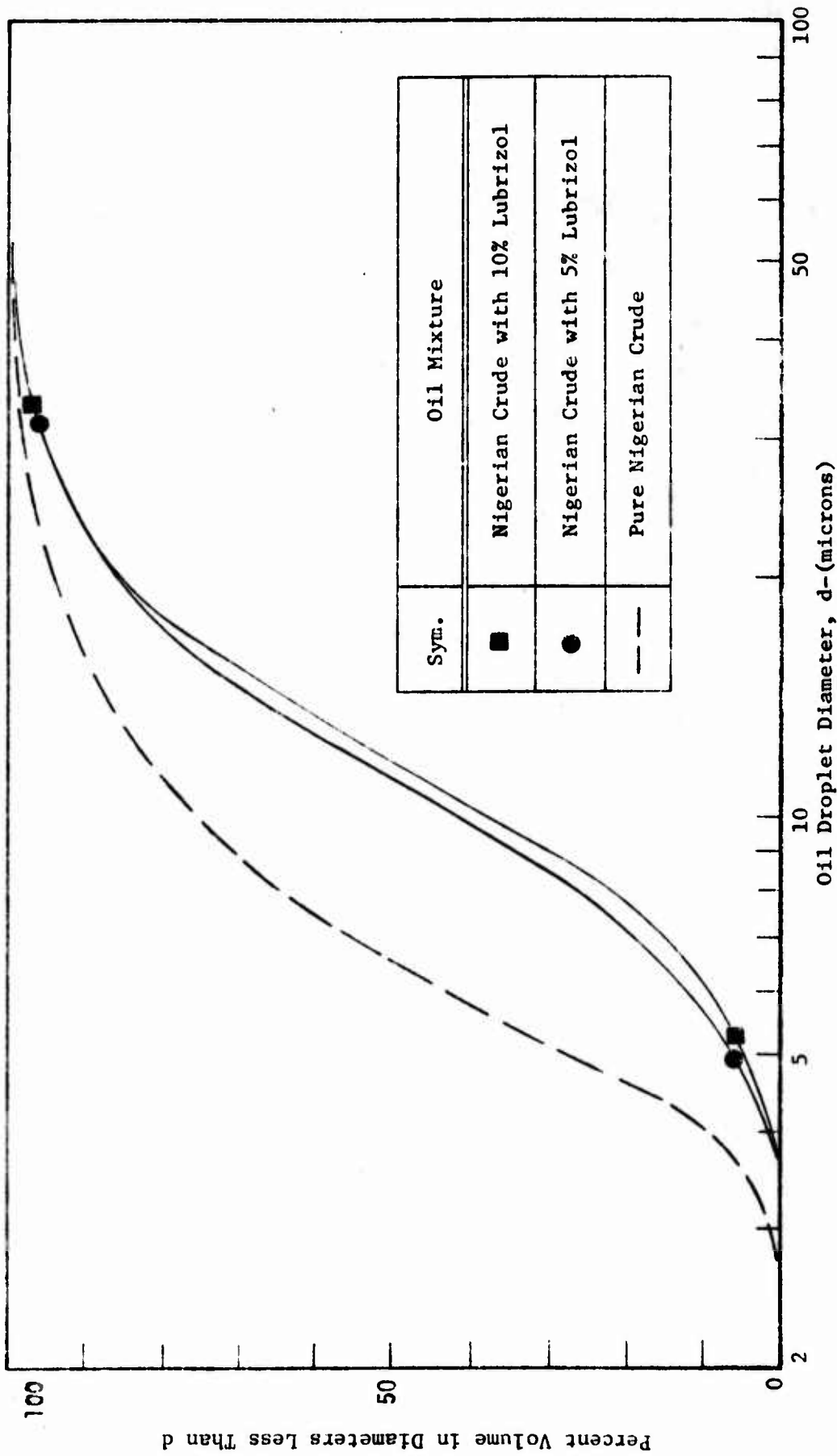
Effect of Detergent Additive (Lubrizol Corp. OS No. 29817A) on Cumulative Volumetric Distribution of a 1% Mixture of #2 Fuel Oil after a 5 Second Blend in a Sears Blender.

Figure 27



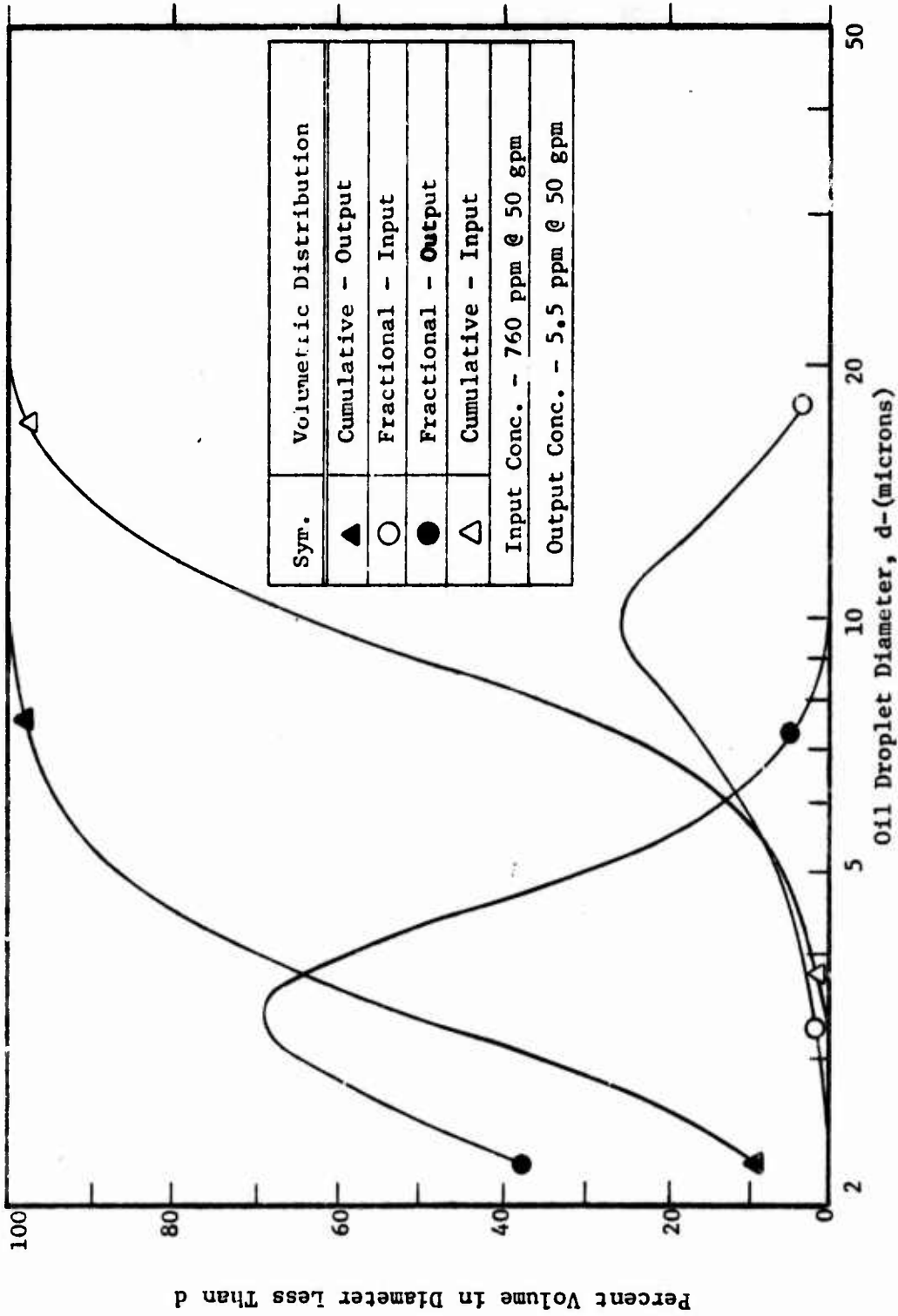
Effect of Detergent Additive (Lubrizol Corp. OS No. 29817A) on Cumulative Volumetric Distribution of a 1% Mixture of #4 Fuel Oil after a 5 Second Blend in a Sears Blender.

Figure 28



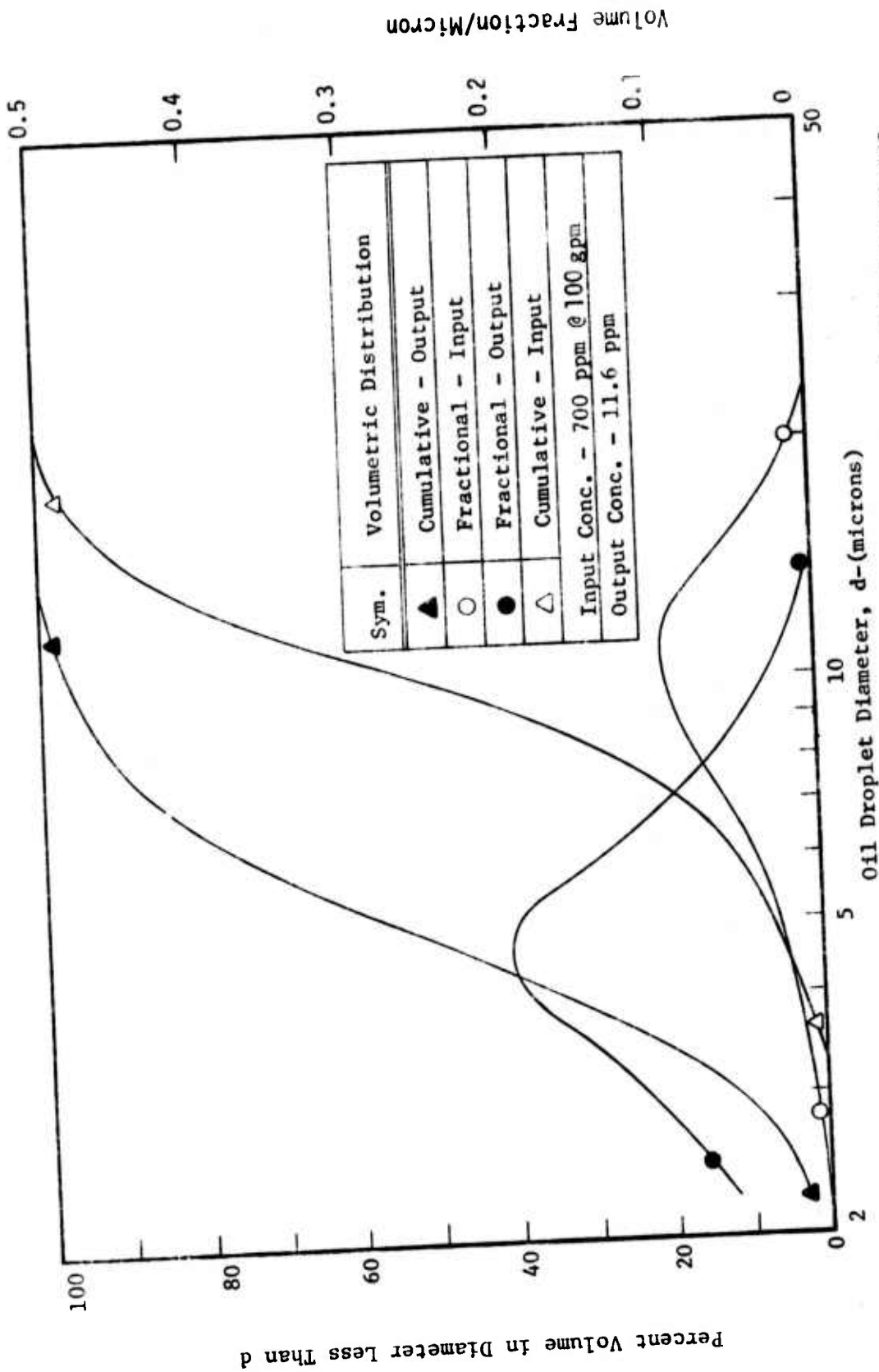
Effect of Detergent Additive (Lubrizol Corp. OS No. 29817A) on Cumulative Volumetric Distribution of a 1% Mixture of Nigerian Crude Oil (Tight) after a 5 Second Blend in a Sears Blender.

Figure 29



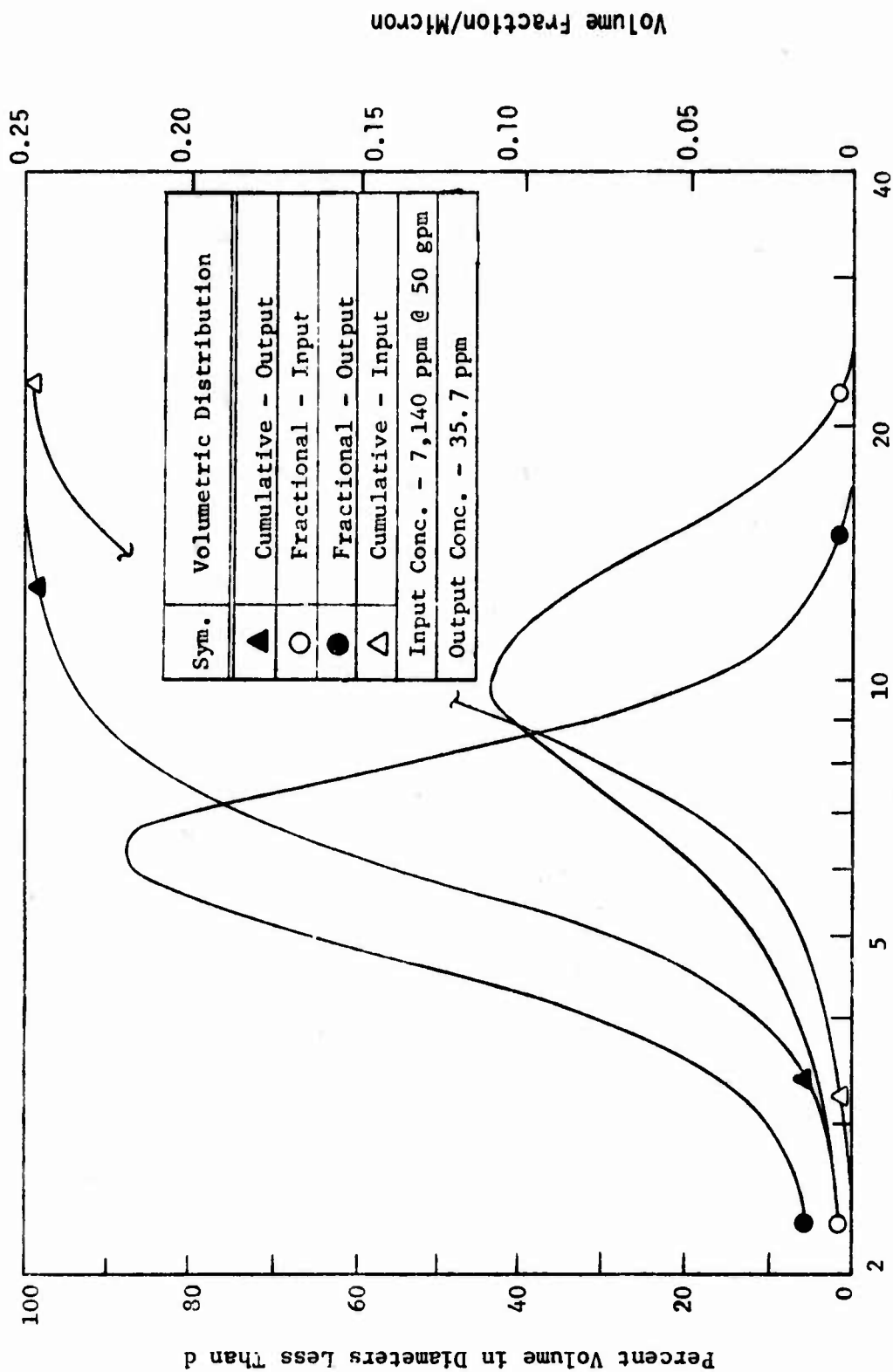
Drop Size Analyses of Centrifuge Separator Performance (3500 rpm) with #2 Fuel Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 30



Drop Size Analysis of Centrifuge Separator Performance (3500 rpm) With #2 Fuel Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

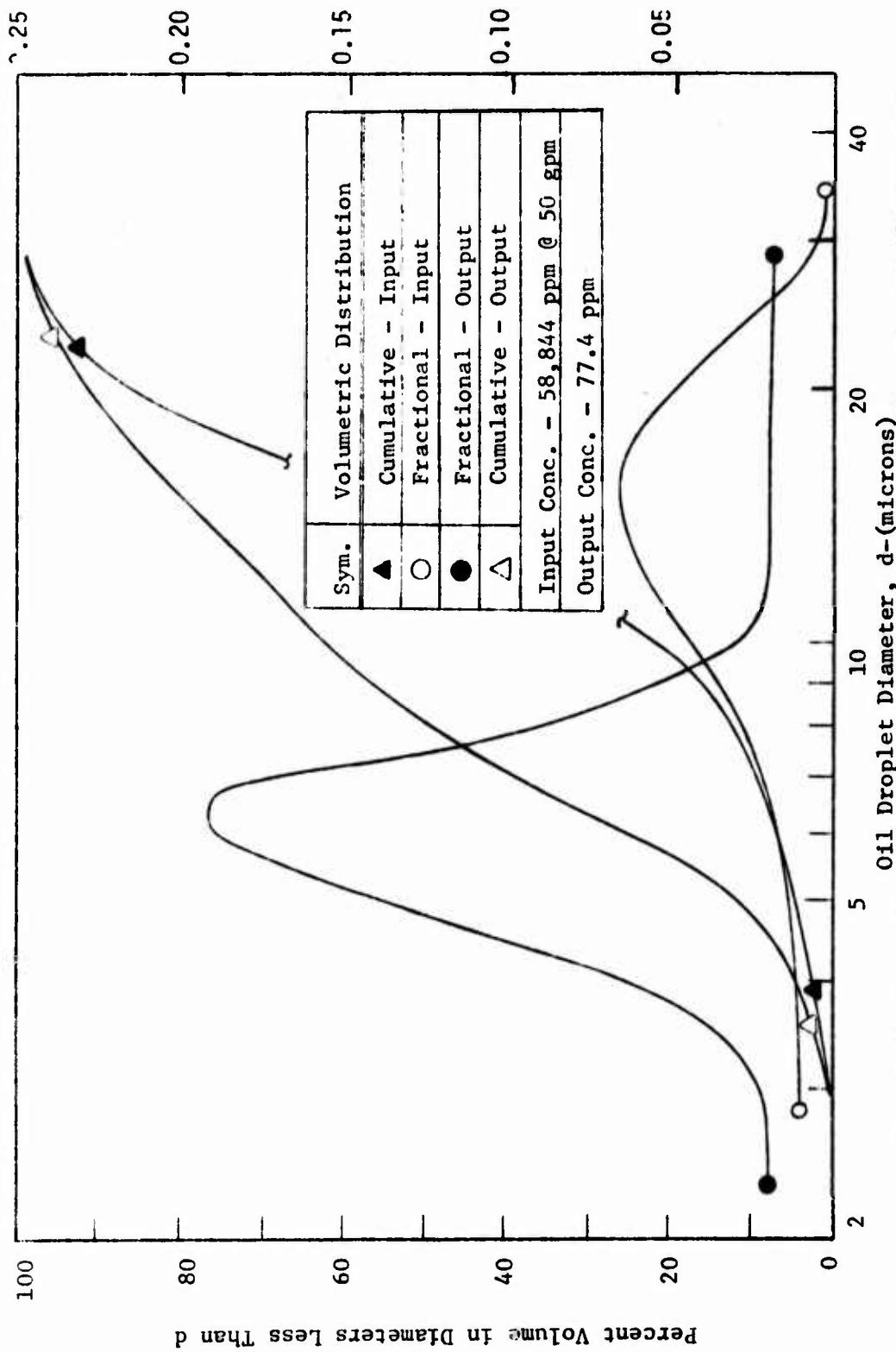
Figure 31



Oil Droplet Diameter, d-(microns)

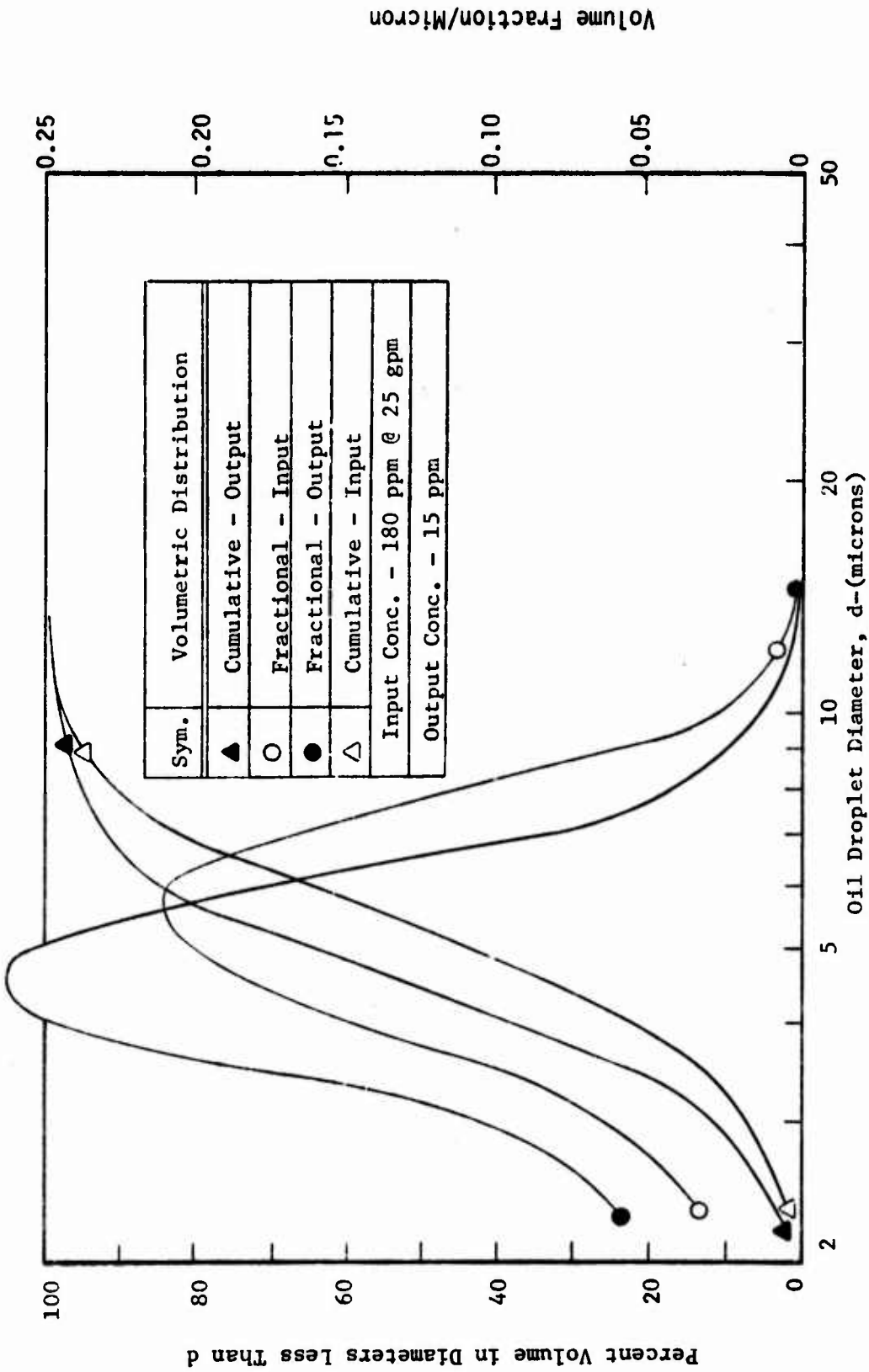
Drop Size Analysis of Centrifuge Separator Performance (3500 rpm) with #2 Fuel Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 32



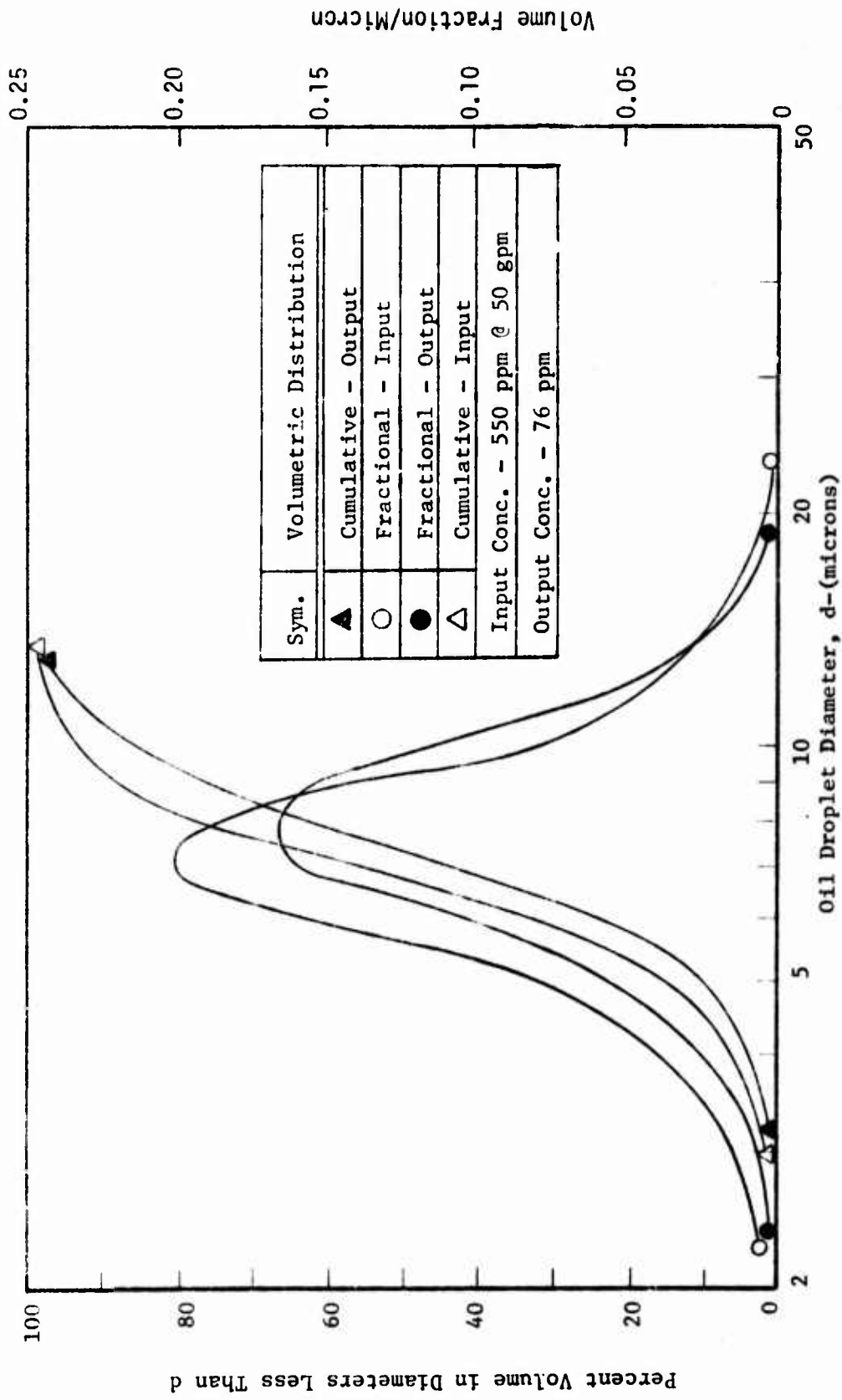
Drop Size Analysis of Centrifuge Separator Performance (3500 rpm) with #2 Fuel Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 33



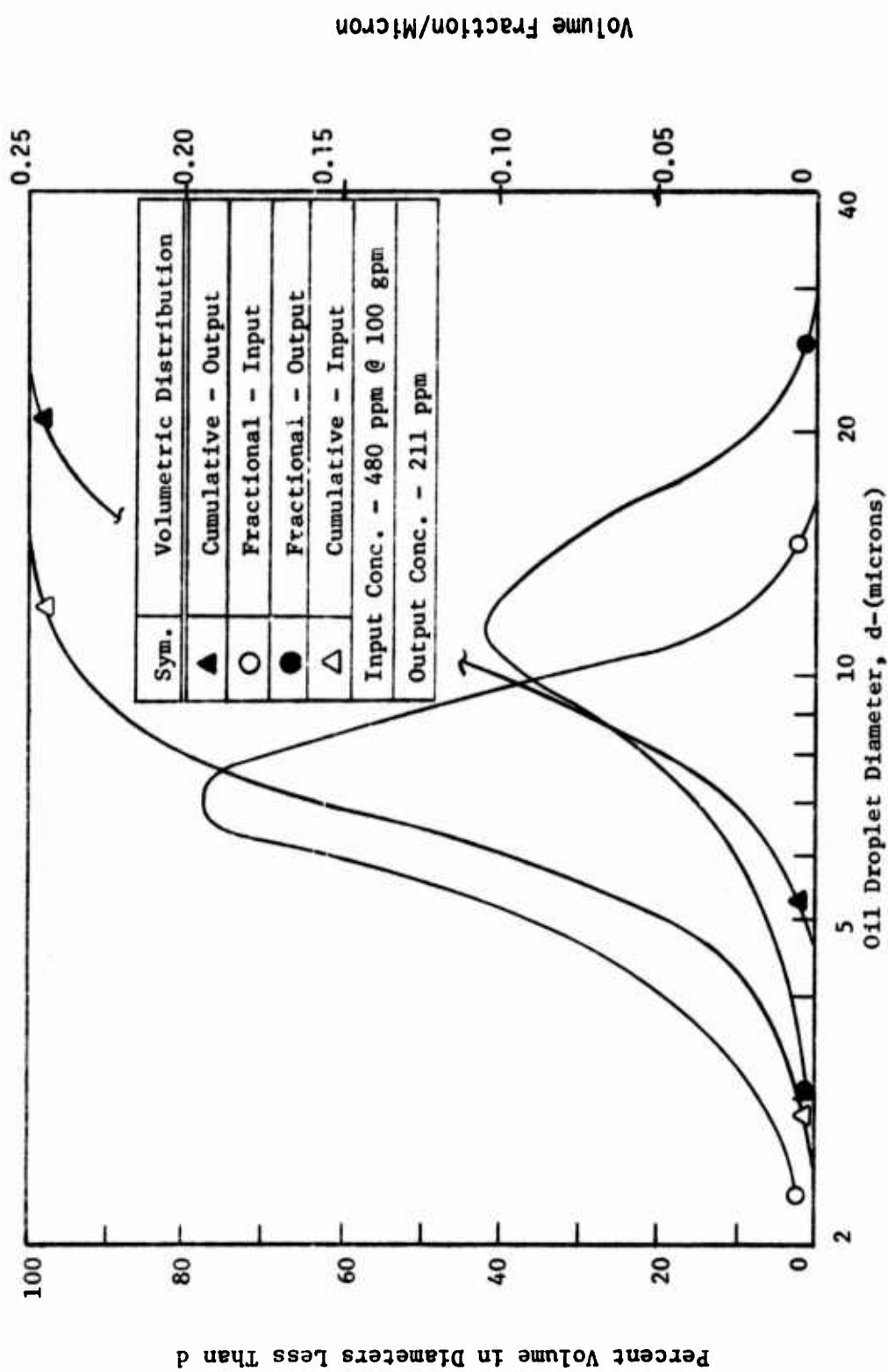
Droplet Size Analysis of Centrifuge Separator Performance (3500 rpm) with #2 Fuel Oil Containing 10% ( of Oil Concentration) Gamlen D Detergent. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 34



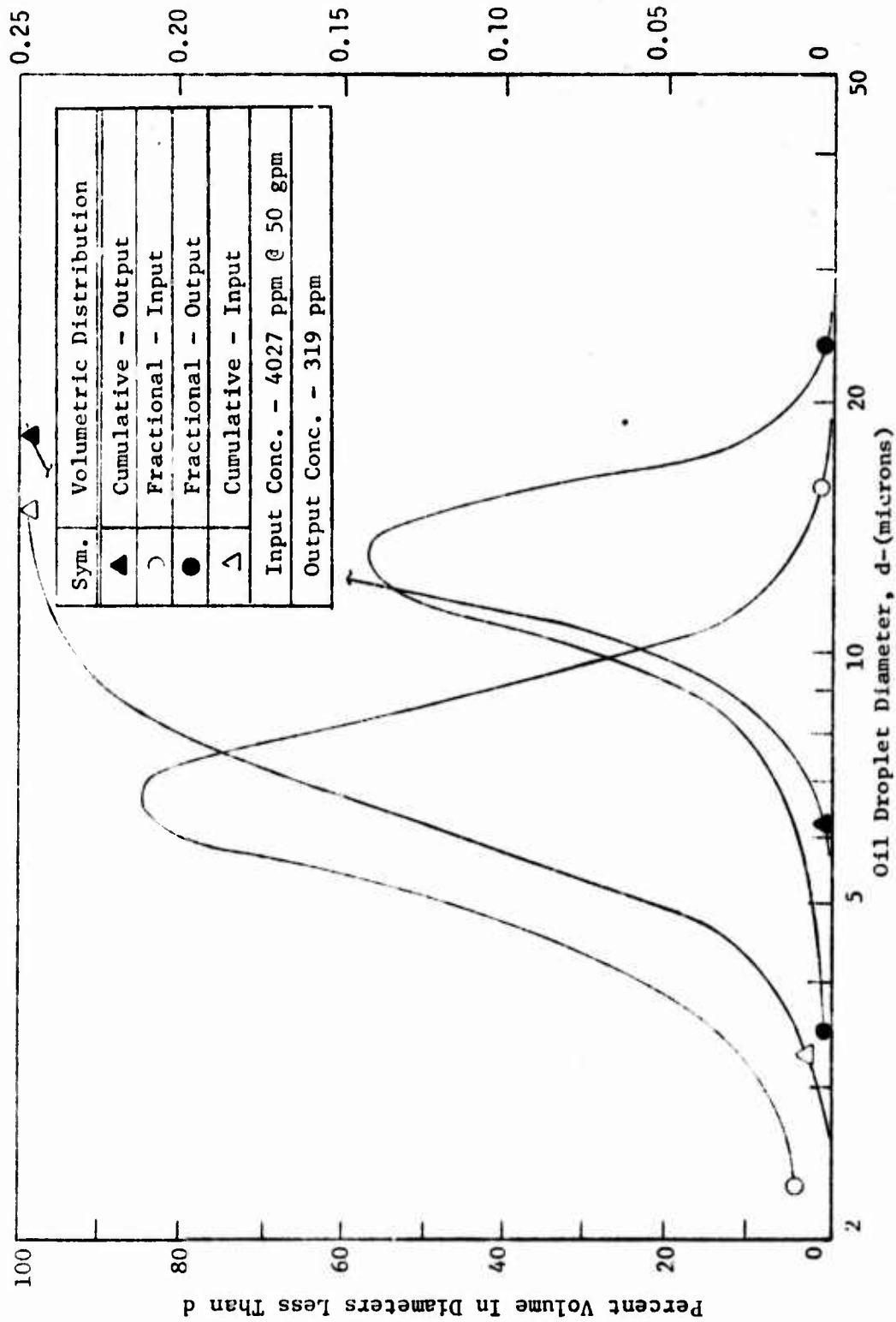
Drop Size Analysis of Centrifuge Separator Performance With #2 Fuel Oil Containing 10% (of Oil Concentration) Gamlen D Detergent. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 35



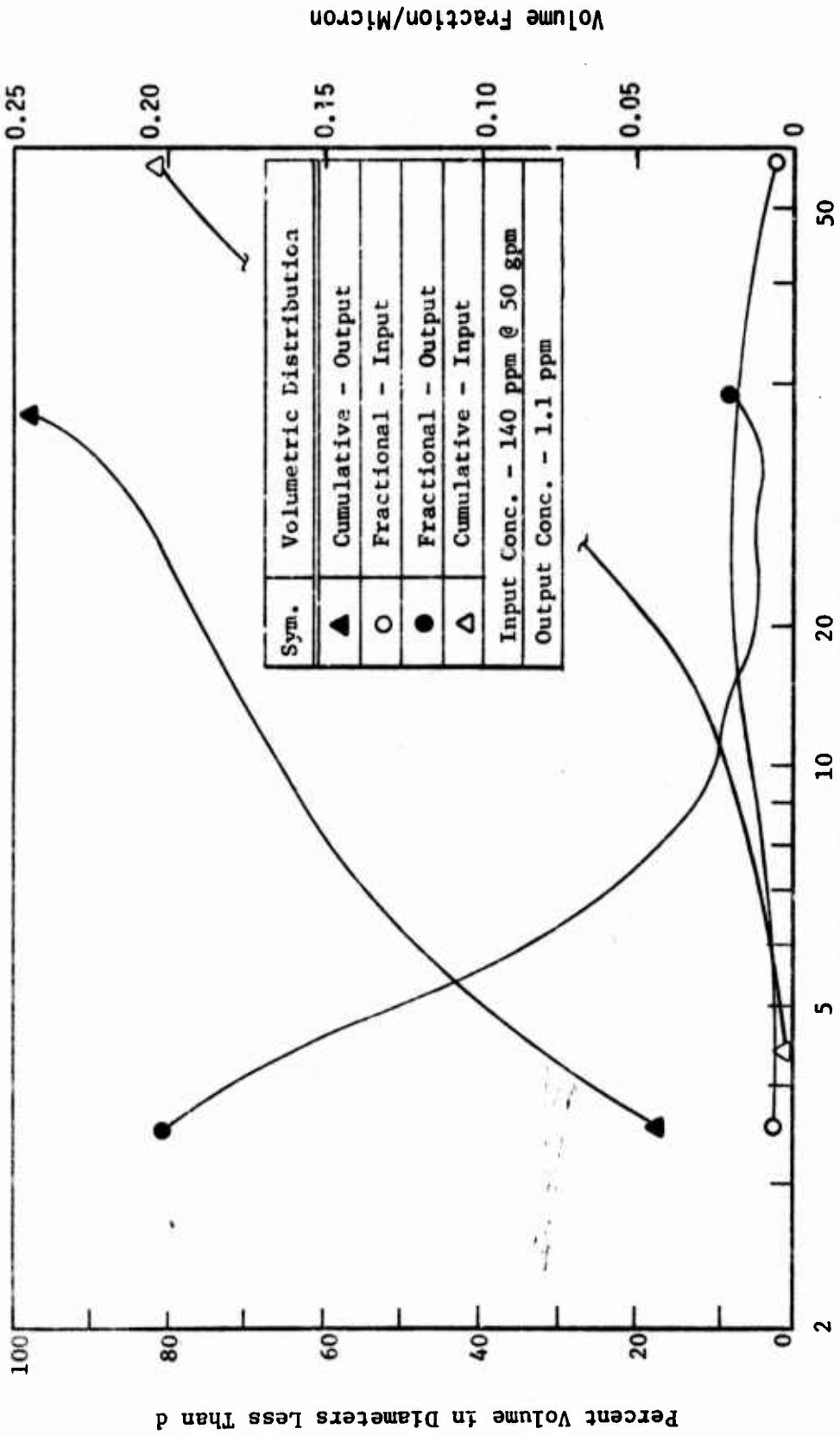
Drop Size Analysis of Centrifuge Separator Performance (3500 rpm) With #2 Fuel Oil Containing 10% (of Oil Concentration) Gamlen D Detergent. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 36



Drop Size Analysis of Centrifuge Separator Performance (3500 rpm) with #2 Fuel Oil Containing 10% (of Oil Concentration) Gamlen D Detergent. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

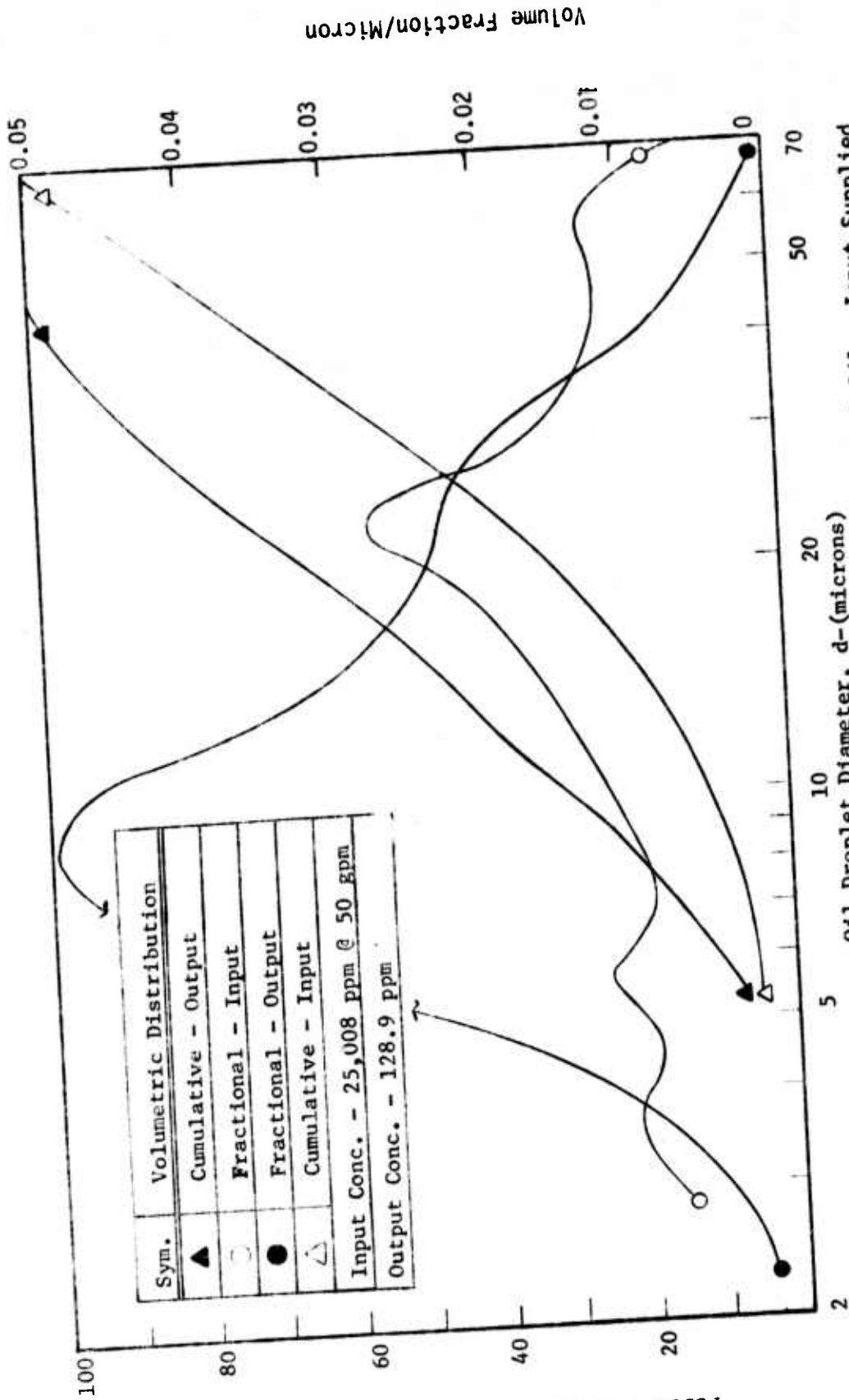
Figure 37



Drop Size Analysis of Centrifuge Separator Performance with #4 Fuel Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 38

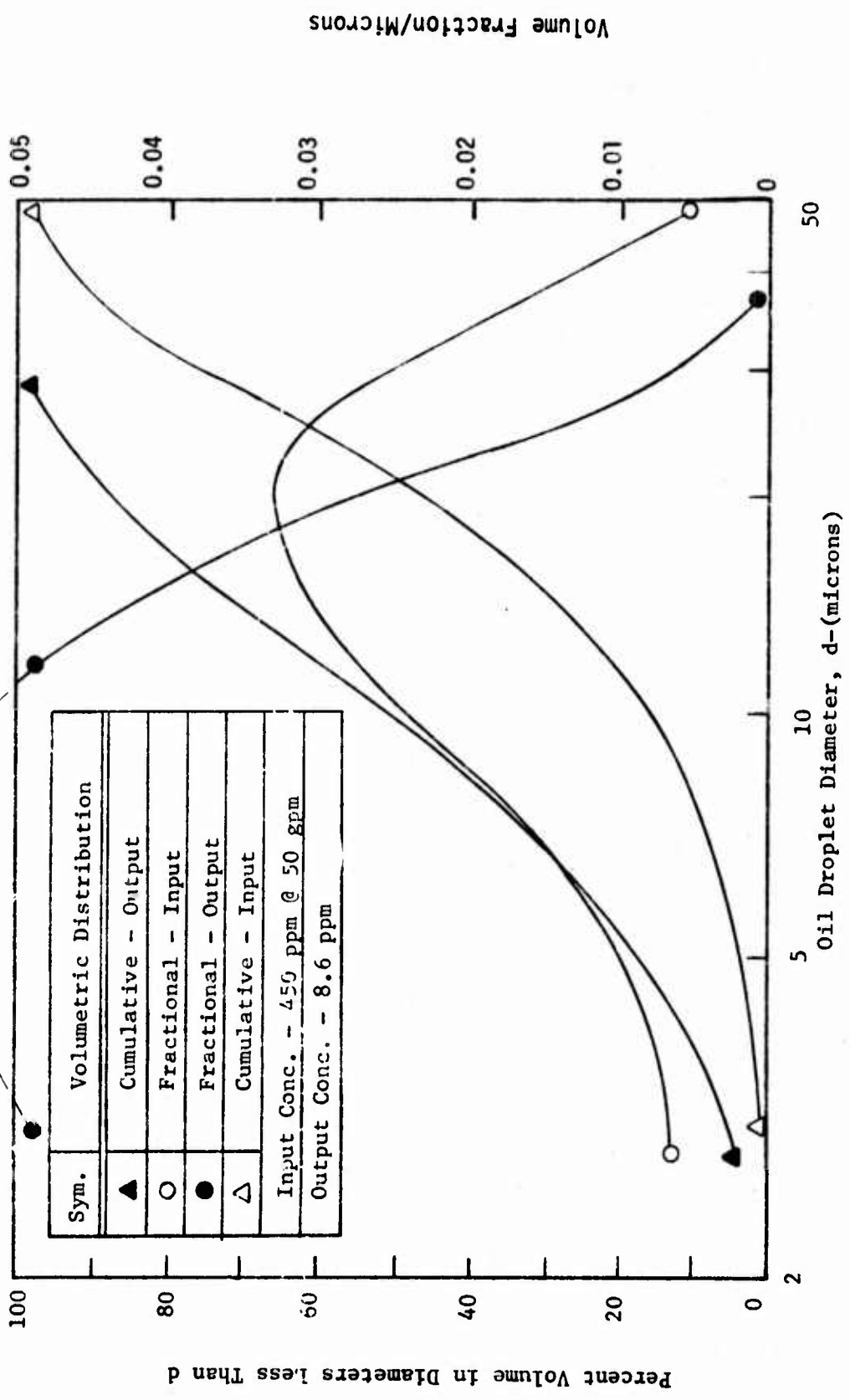
Percent Volume in Diameters Less Than d



Volume Fraction/Micron

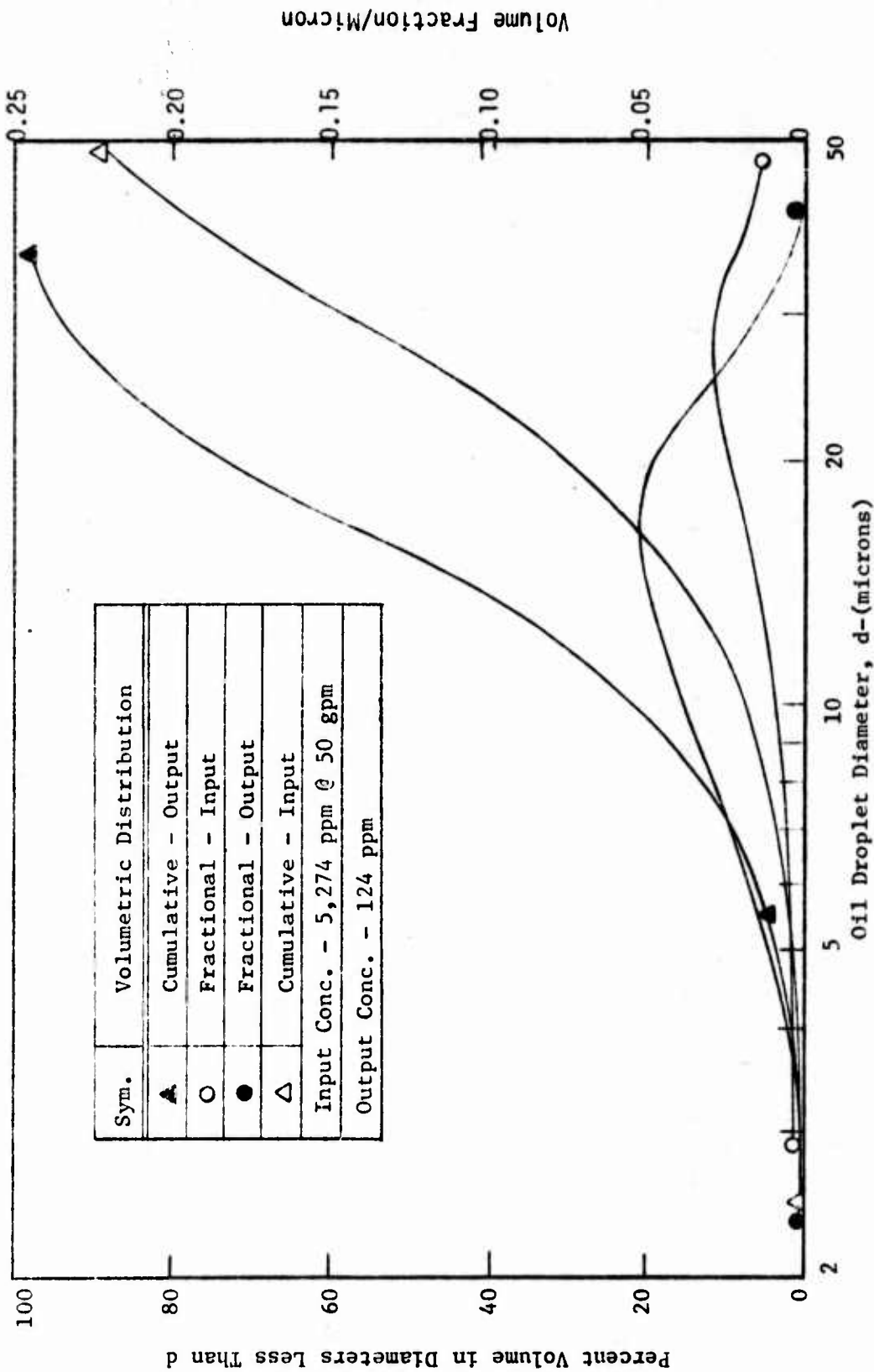
Drop Size Analysis of Centrifuge Separator Performance With #4 Fuel Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 39



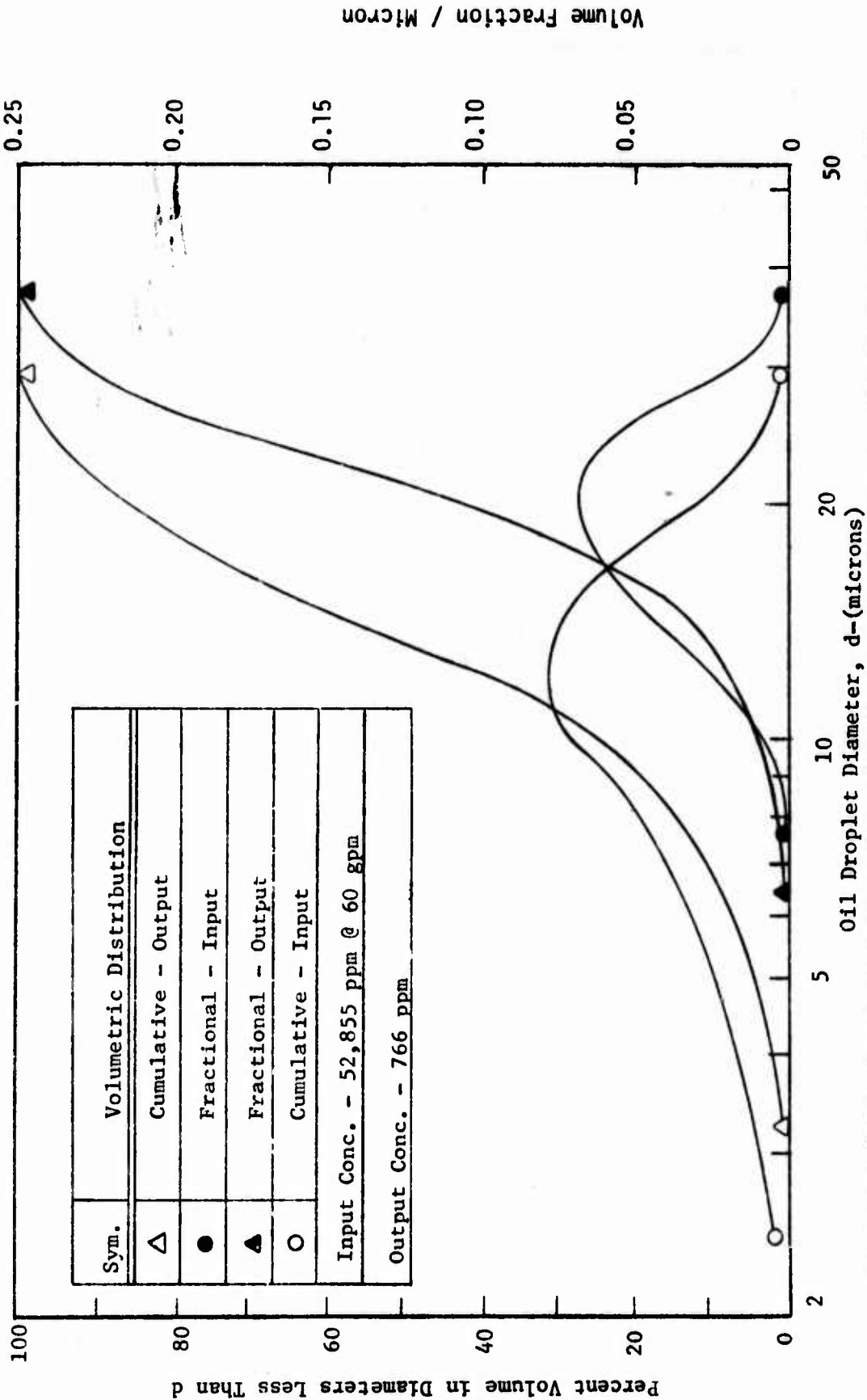
Drop Size Analysis of Centrifuge Performance With #4 Fuel Oil Containing 10% (of Oil Concentration) Gamlen D Detergent. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 40



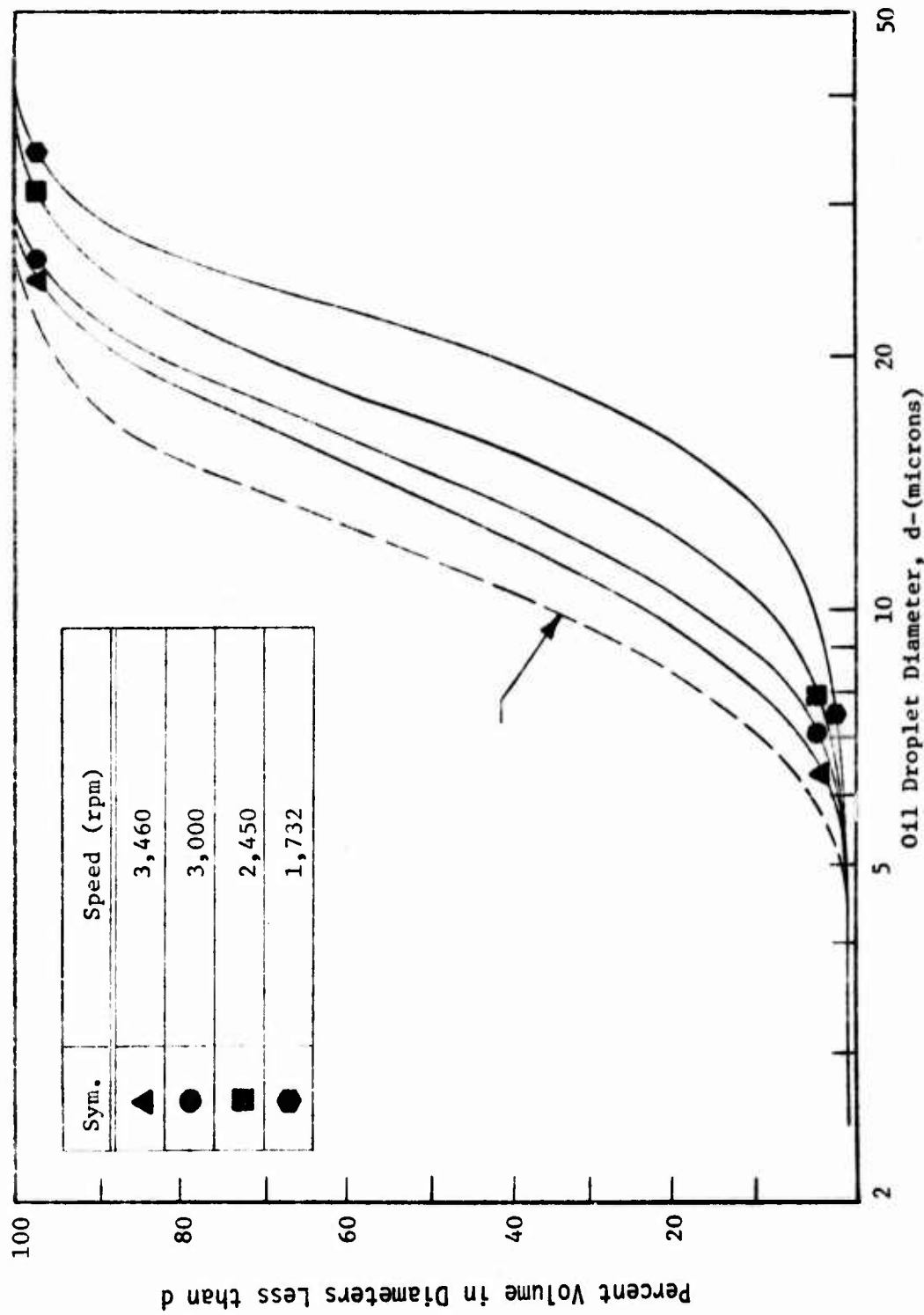
Drop Size Analysis of Centrifuge Performance With #4 Fuel Oil Containing Gamlen D.

Figure 4]



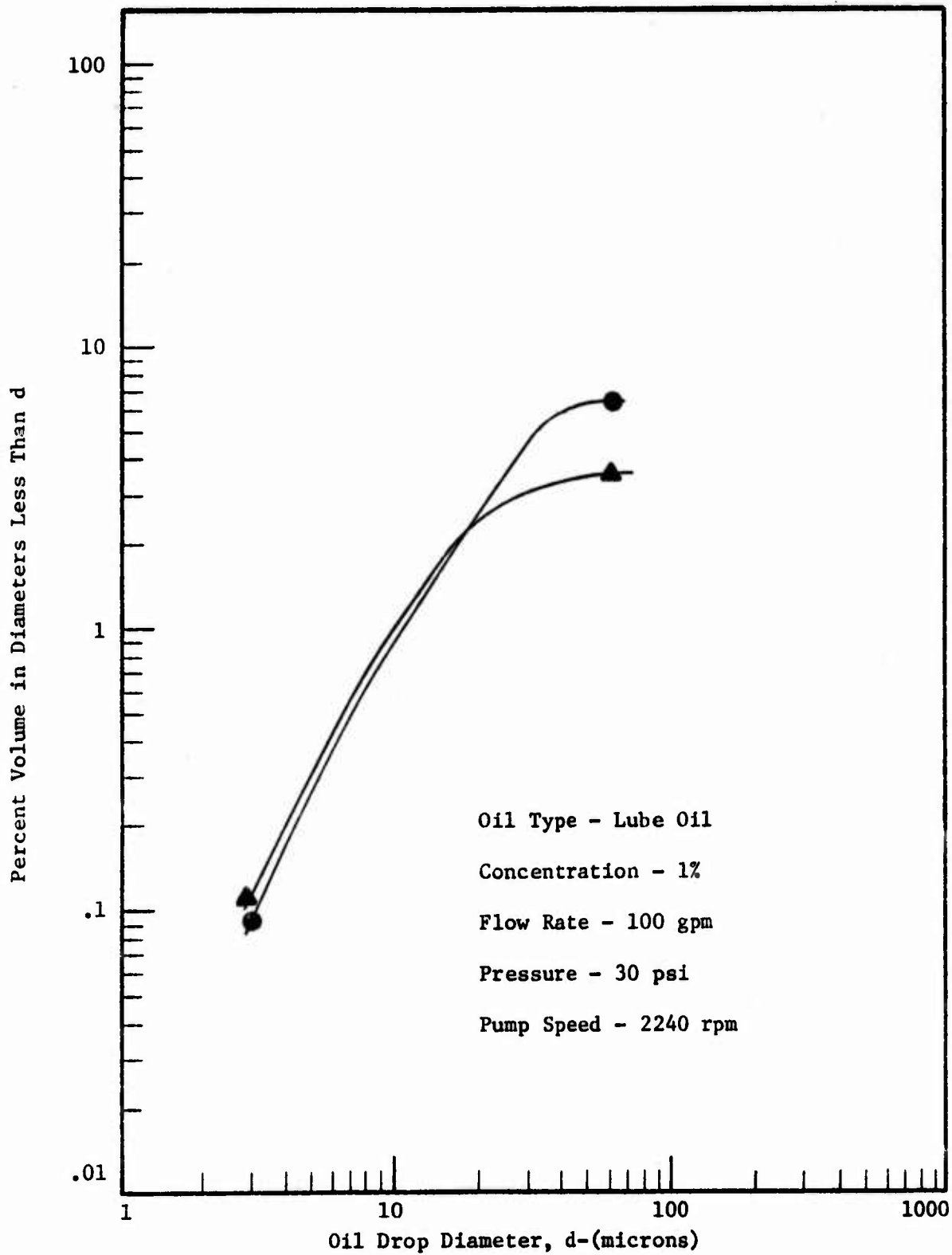
Drop Size Analysis of Centrifuge Separator Performance (3500 rpm) with Nigerian Crude Oil. Input Supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 42



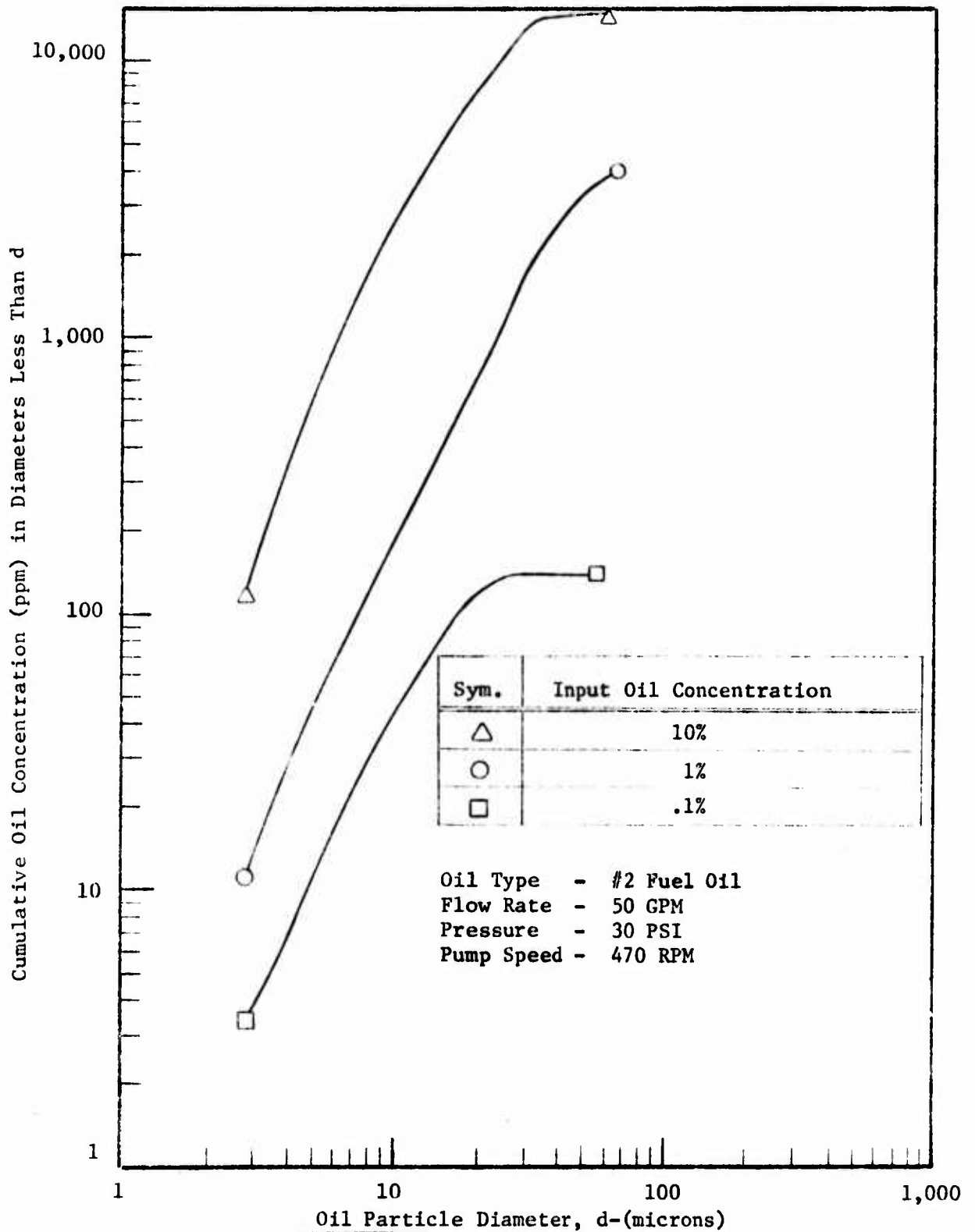
Effect of Centrifuge Separator Rotational Speed on the Cumulative Volumetric Distribution of the Effluent for #2 Oil. Input supplied by Centrifugal Pump. Emulsification by Direct Injection of Oil into Pump Inlet.

Figure 43



Reproducibility of Test Conditions, Ingersoll Rand Centrifugal Pump

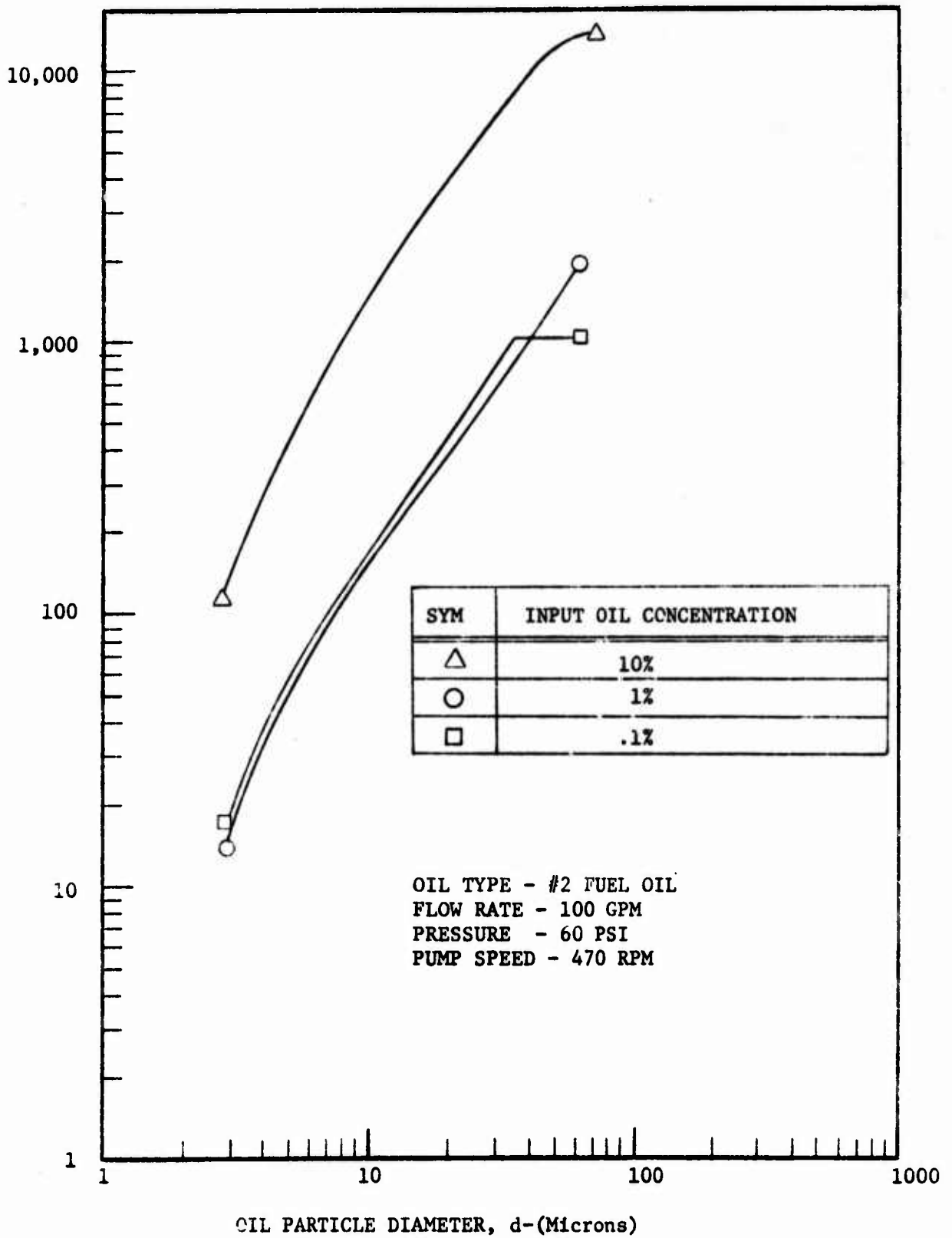
Figure 44



Effects of Oil Input Concentration on the Emulsification Performance of a Blackmer Sliding Vane Pump for #2 Fuel Oil.

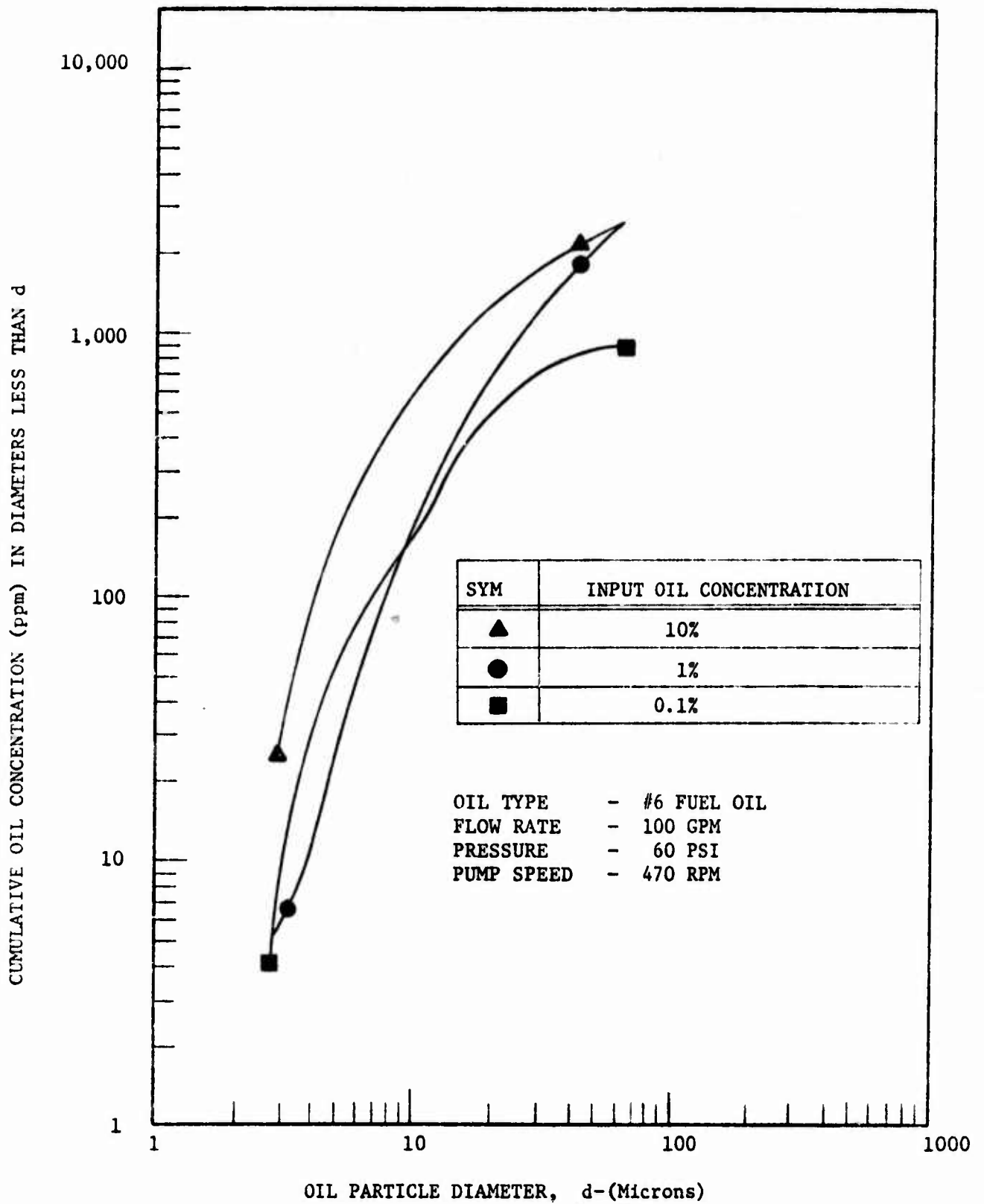
Figure 45

CUMULATIVE OIL CONCENTRATION (ppm) IN DIAMETERS  
LESS THAN  $d$



Effects of Oil Input Concentration on the Emulsification Performance of a Blackmer Sliding Vane Pump for #2 Fuel Oil.

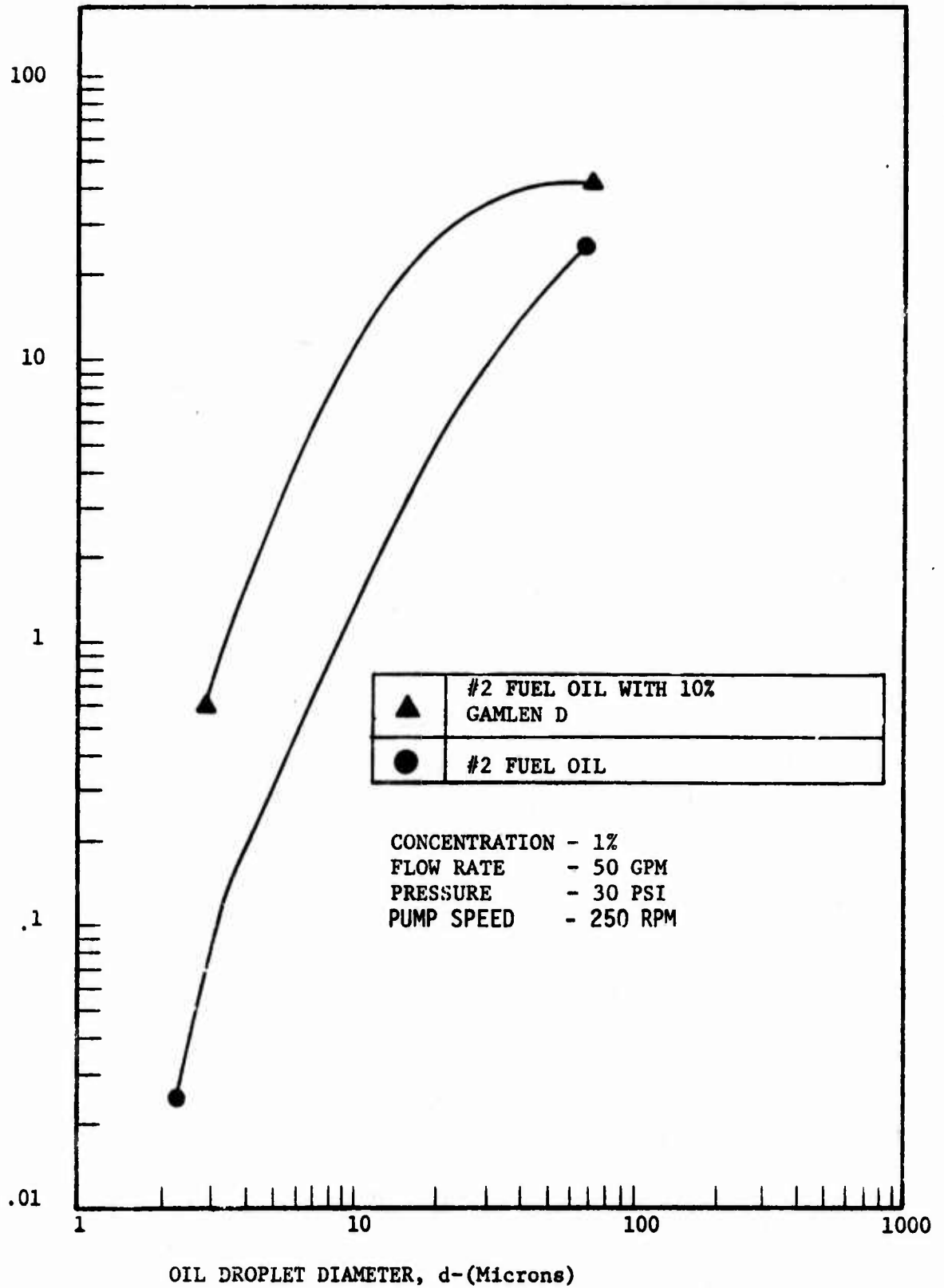
Figure 46



Effects of Oil Input Concentration on the Emulsification Performance of a Sliding Vane Pump for #6 Fuel Oil.

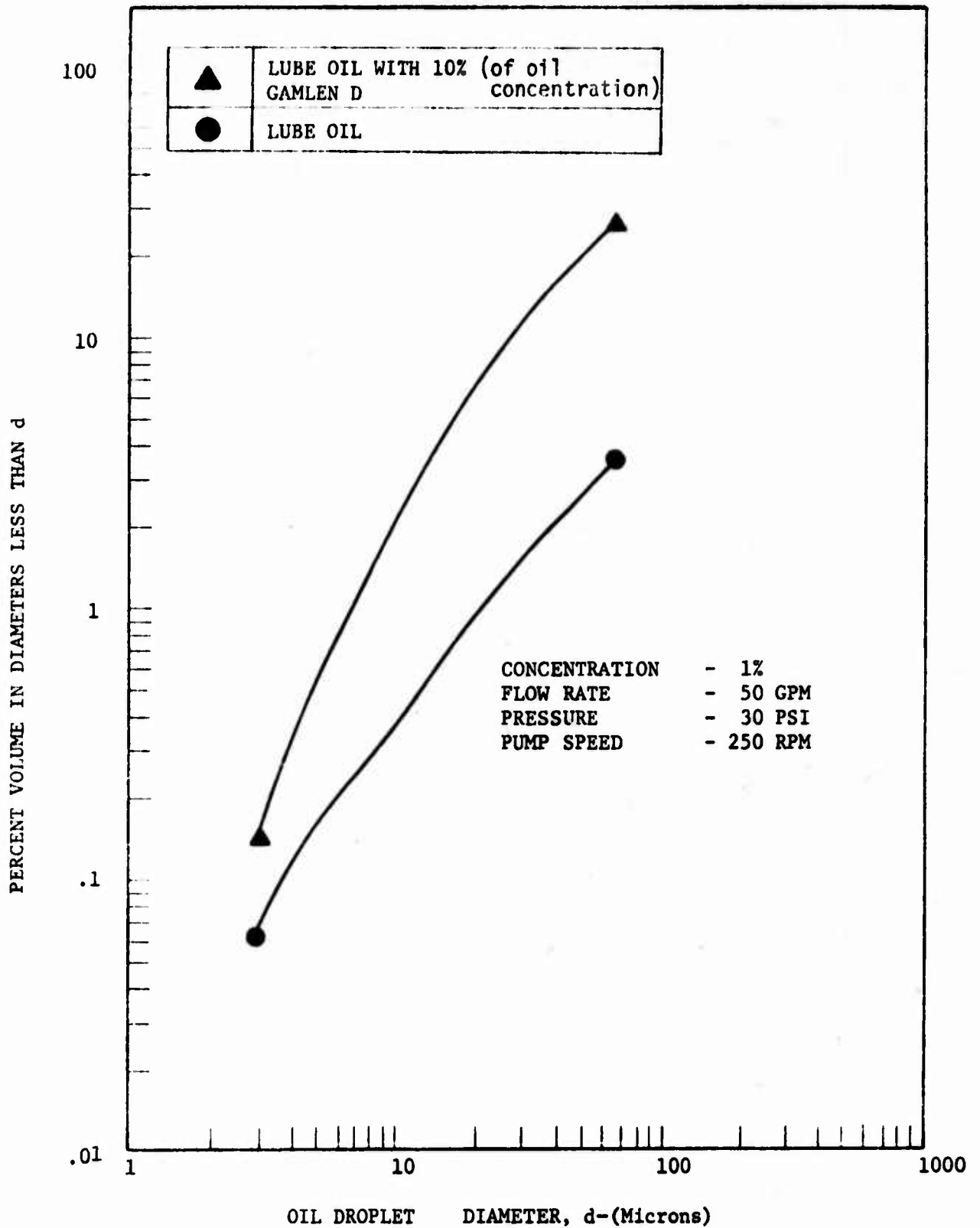
Figure 47  
143

PERCENT VOLUME IN DIAMETER LESS THAN d



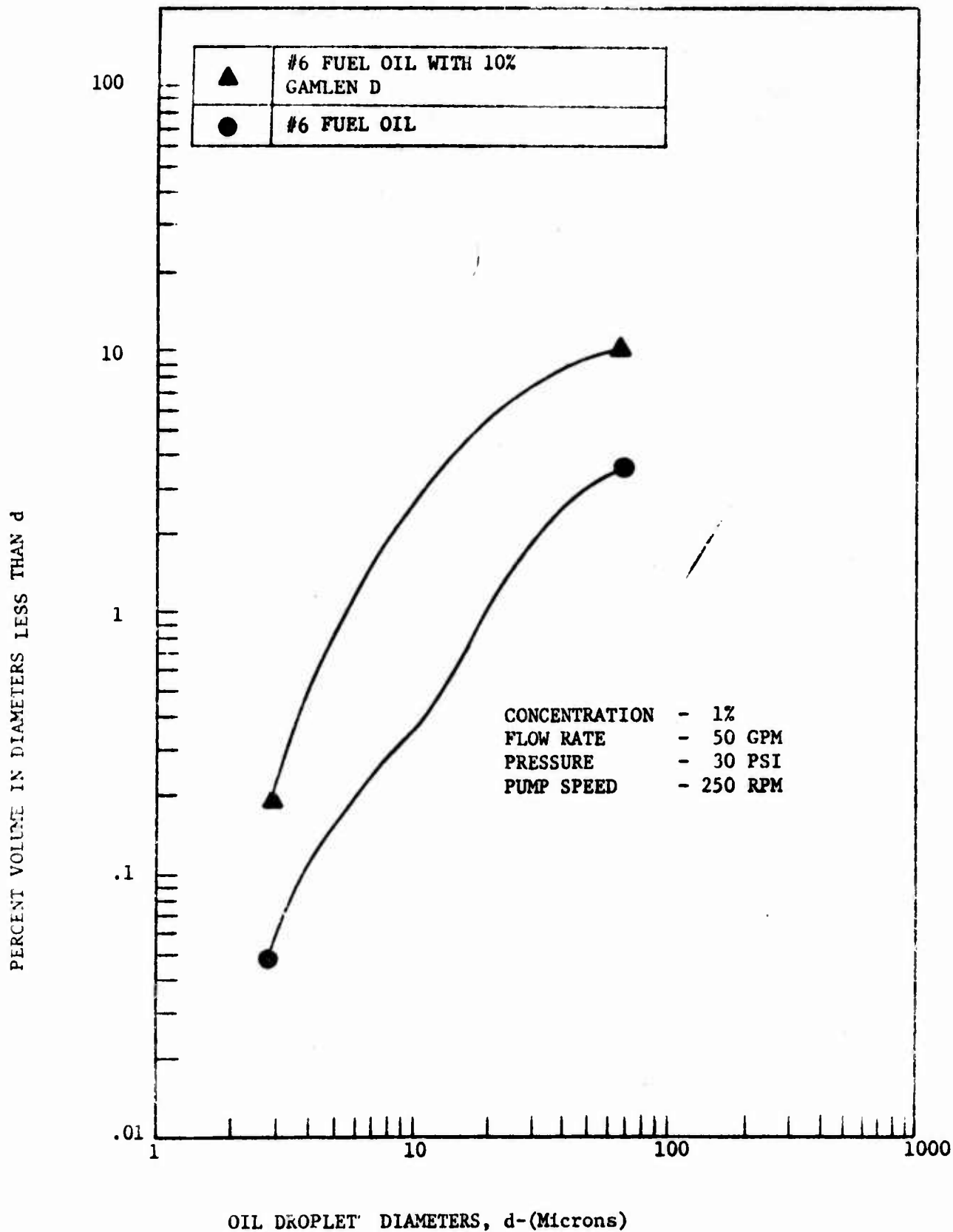
EFFECT OF DETERGENT ON THE EMULSIFICATION PERFORMANCE OF A SLIDING VANE PUMP WITH #2 FUEL OIL.

FIGURE 48



EFFECT OF DETERGENT ON THE EMULSIFICATION PERFORMANCE OF A SLIDING VANE PUMP FOR LUBE OIL.

FIGURE 49



Effect of Detergent on the Emulsification Performance of a Blackmer Sliding-Vane Pump with #6 Fuel Oil

Figure 50

PERCENT VOLUME IN DIAMETER LESS THAN d

100

10

1

.1

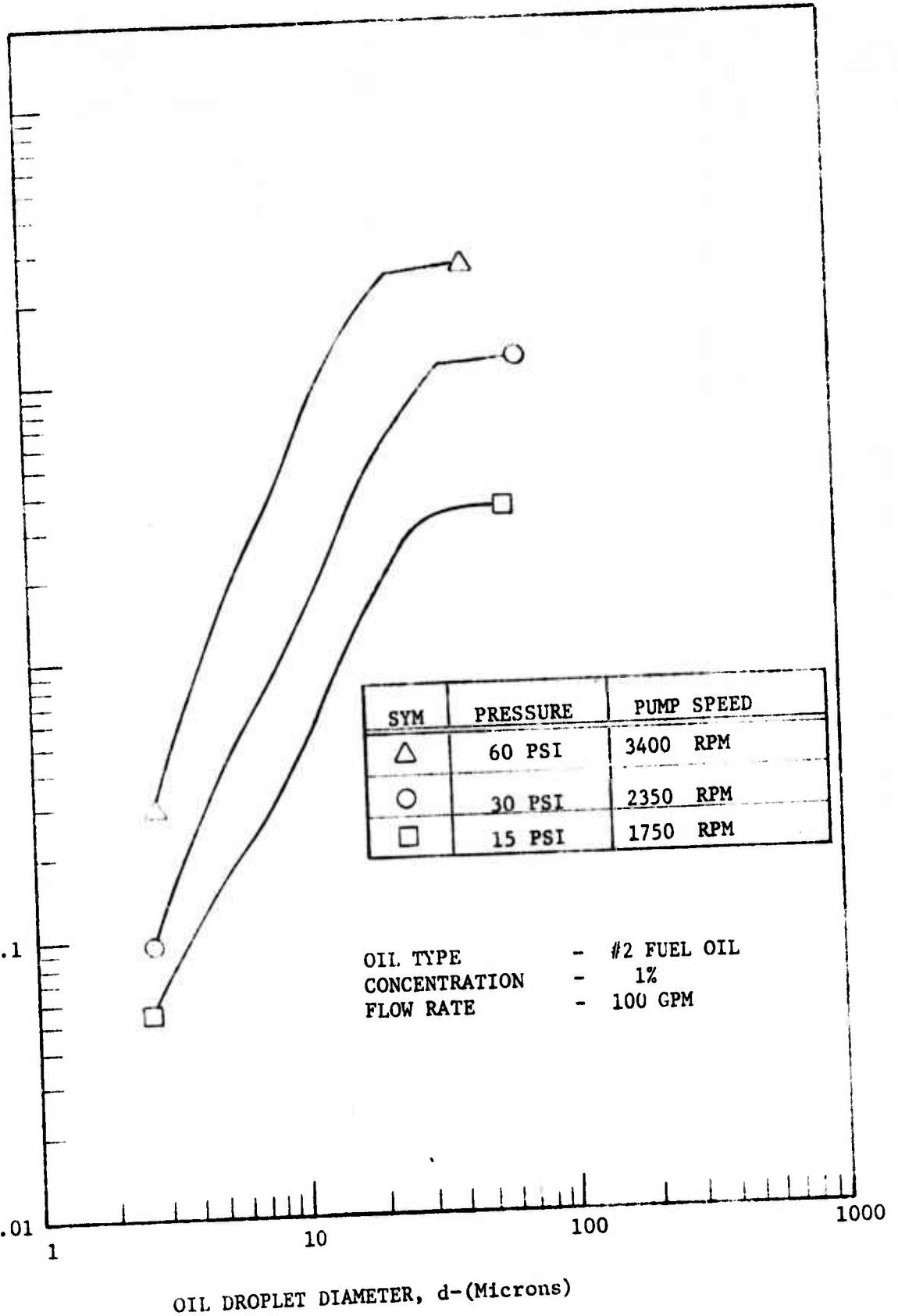
.01

1

10

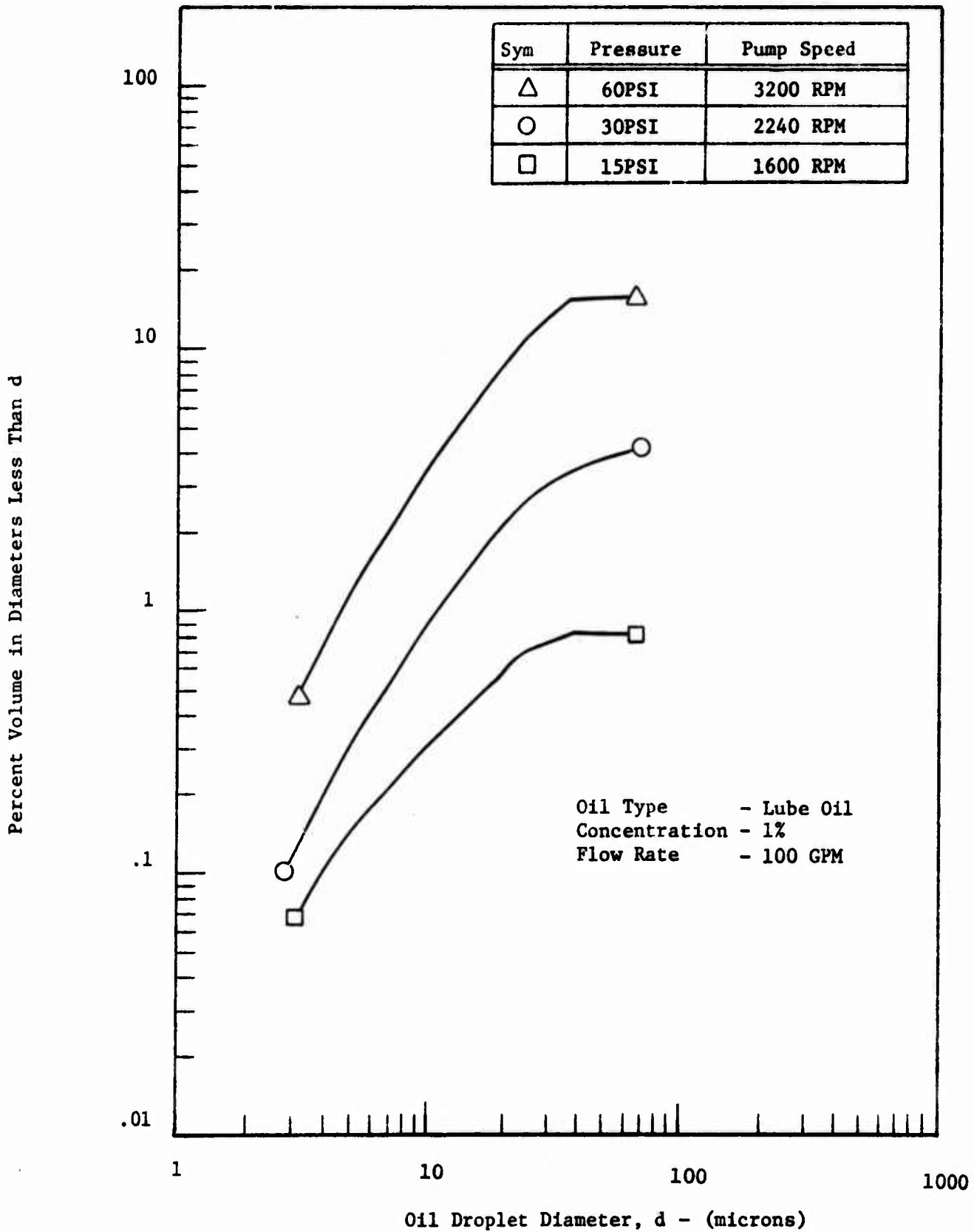
100

1000



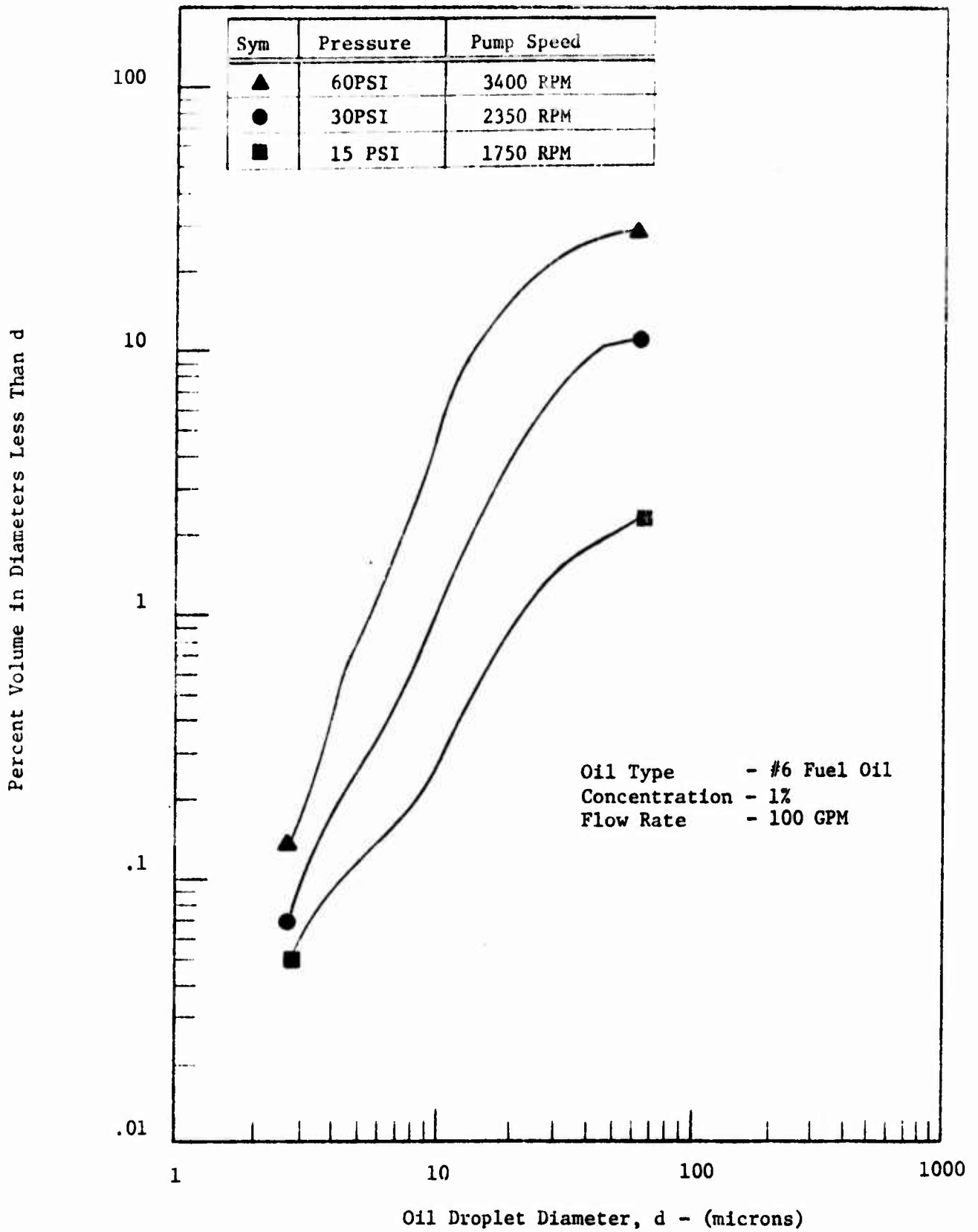
EFFECT OF PRESSURE ON THE EMULSIFICATION PERFORMANCE OF INGERSOLL - RAND CENTRIFUGAL PUMP WITH #2 FUEL OIL

FIGURE 51  
147



Effects of Pressure on the Emulsification Performance of an Ingersoll-Rand Centrifugal Pump with Lube Oil

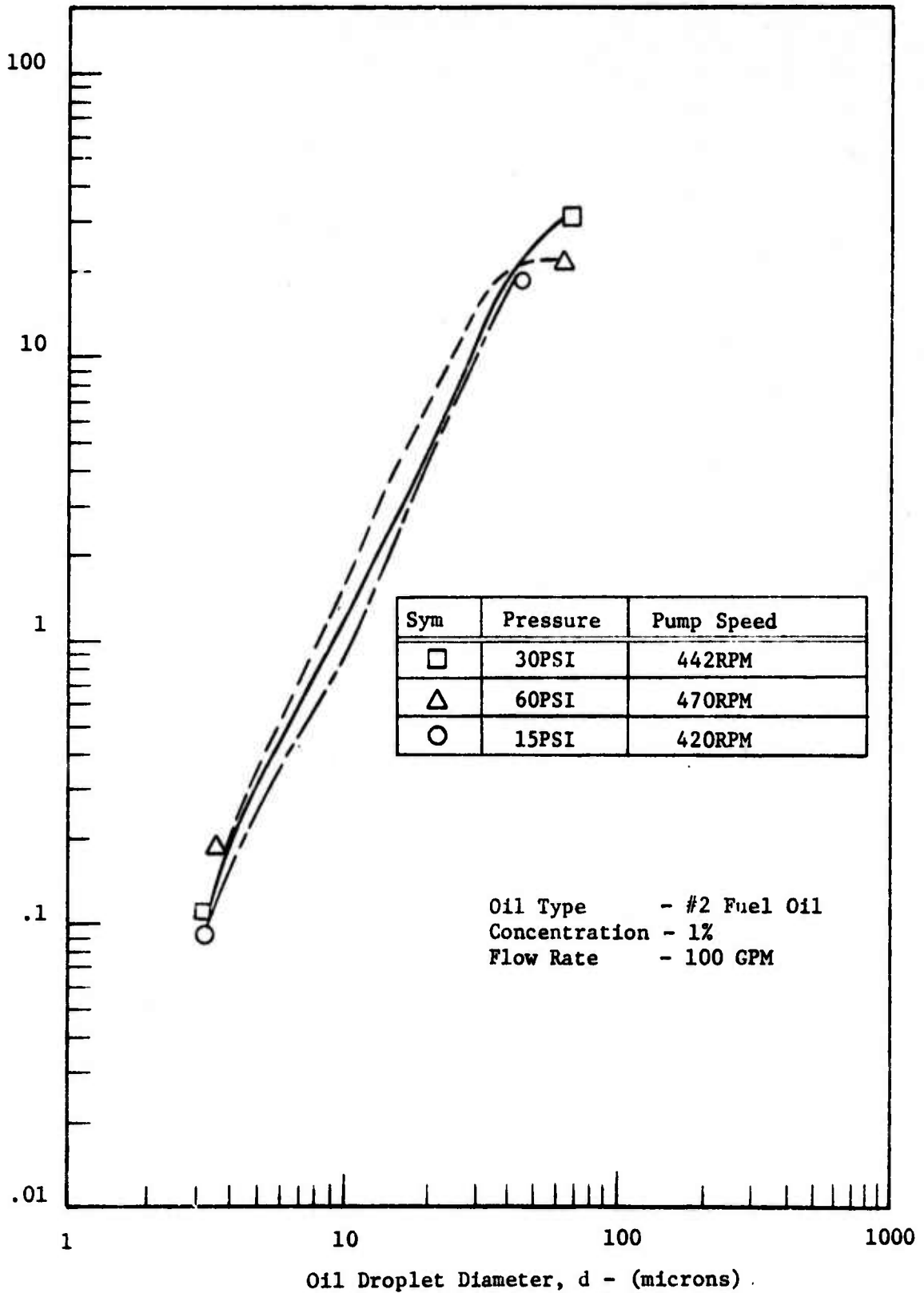
Figure 52  
148



Effects of Pressure on The Emulsification Performance of an Ingersoll-Rand Centrifugal Pump with #6 Fuel Oil

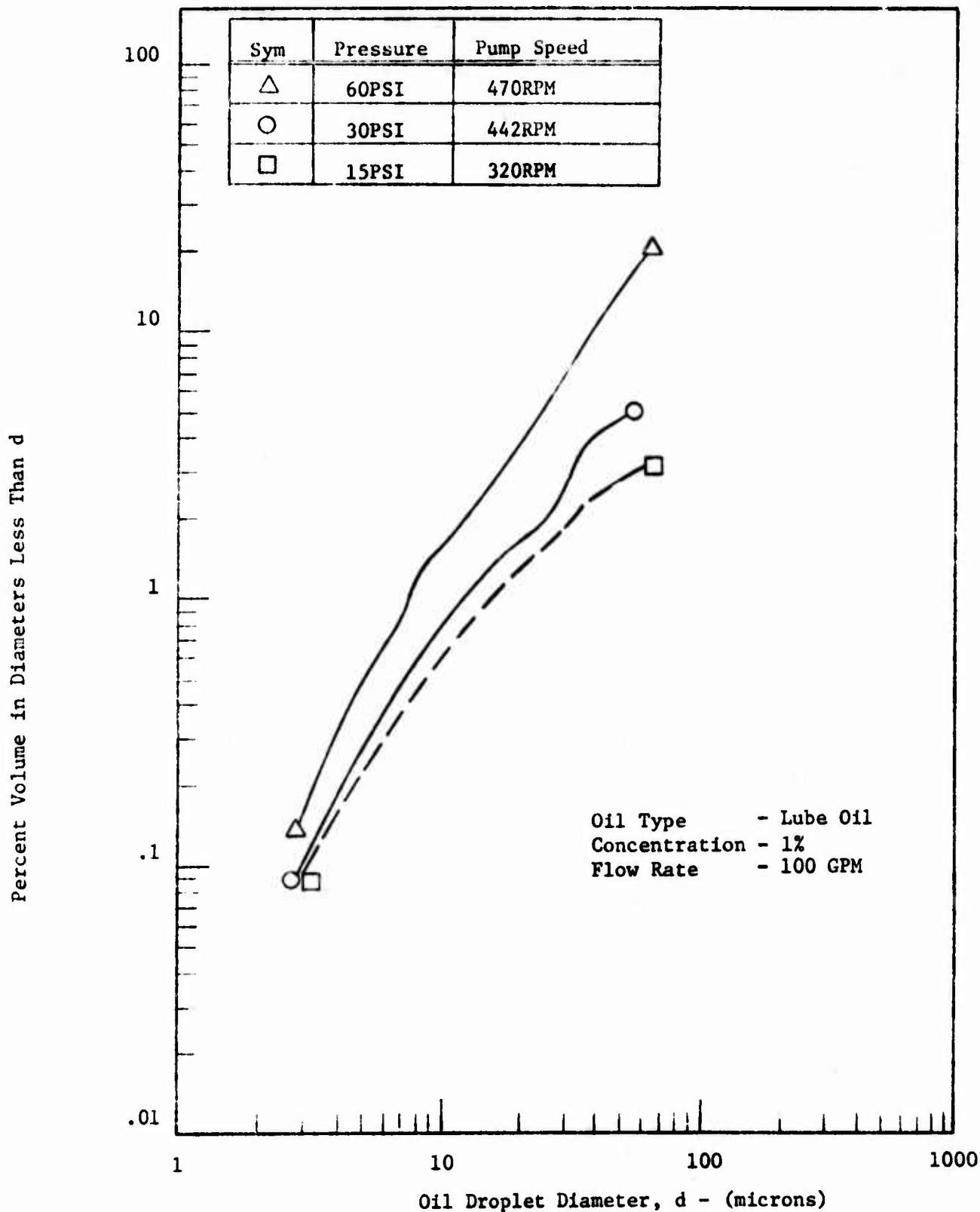
Figure 53  
149

Percent Volume in Diameters Less Than d



Effects of Pressure on The Emulsification Performance of a Blackmer Sliding Vane Pump with #2 Fuel Oil

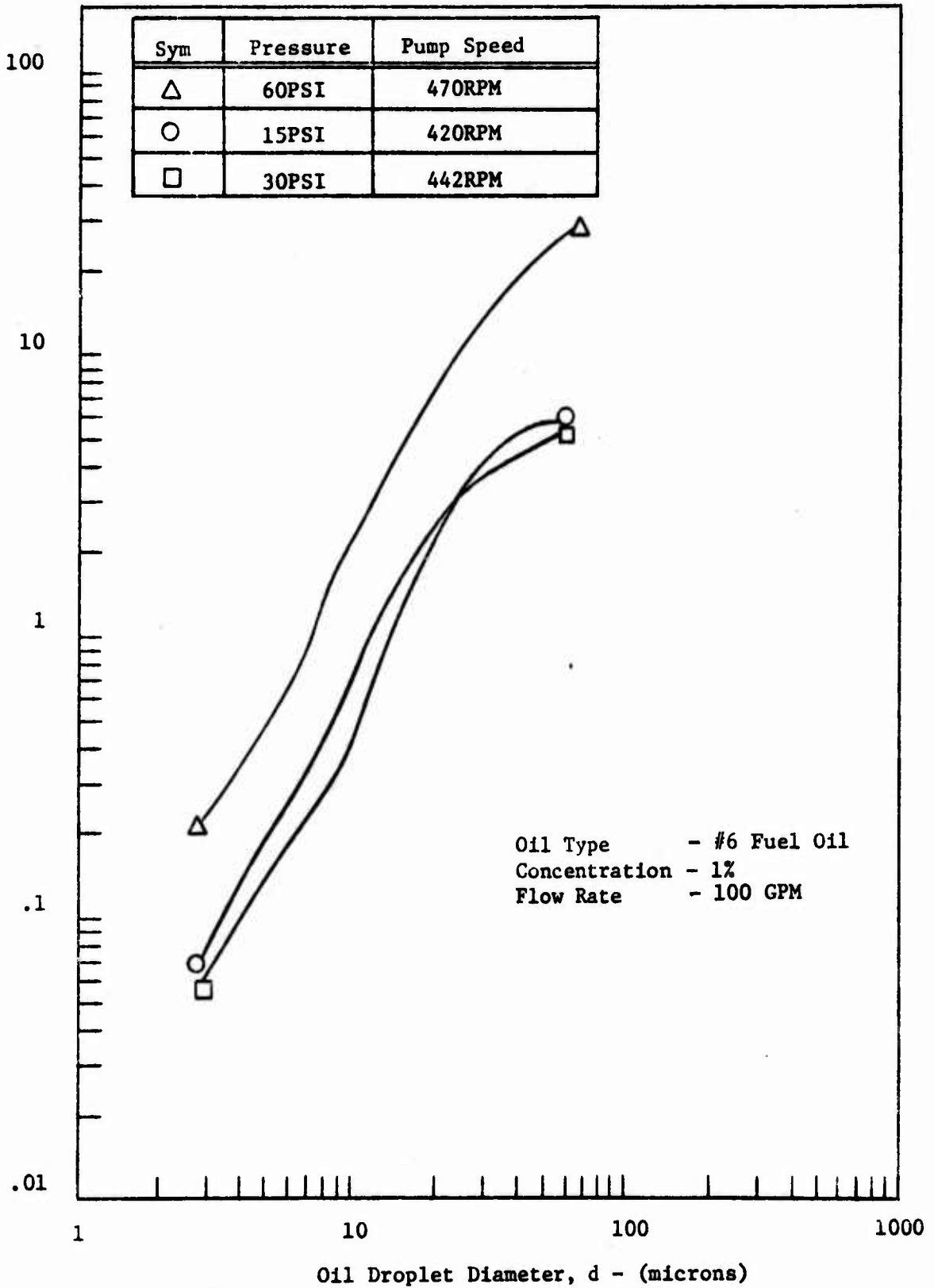
Figure 54



Effects of Pressure on The Emulsification Performance of a Blackmer Sliding Vane Pump

Figure 55

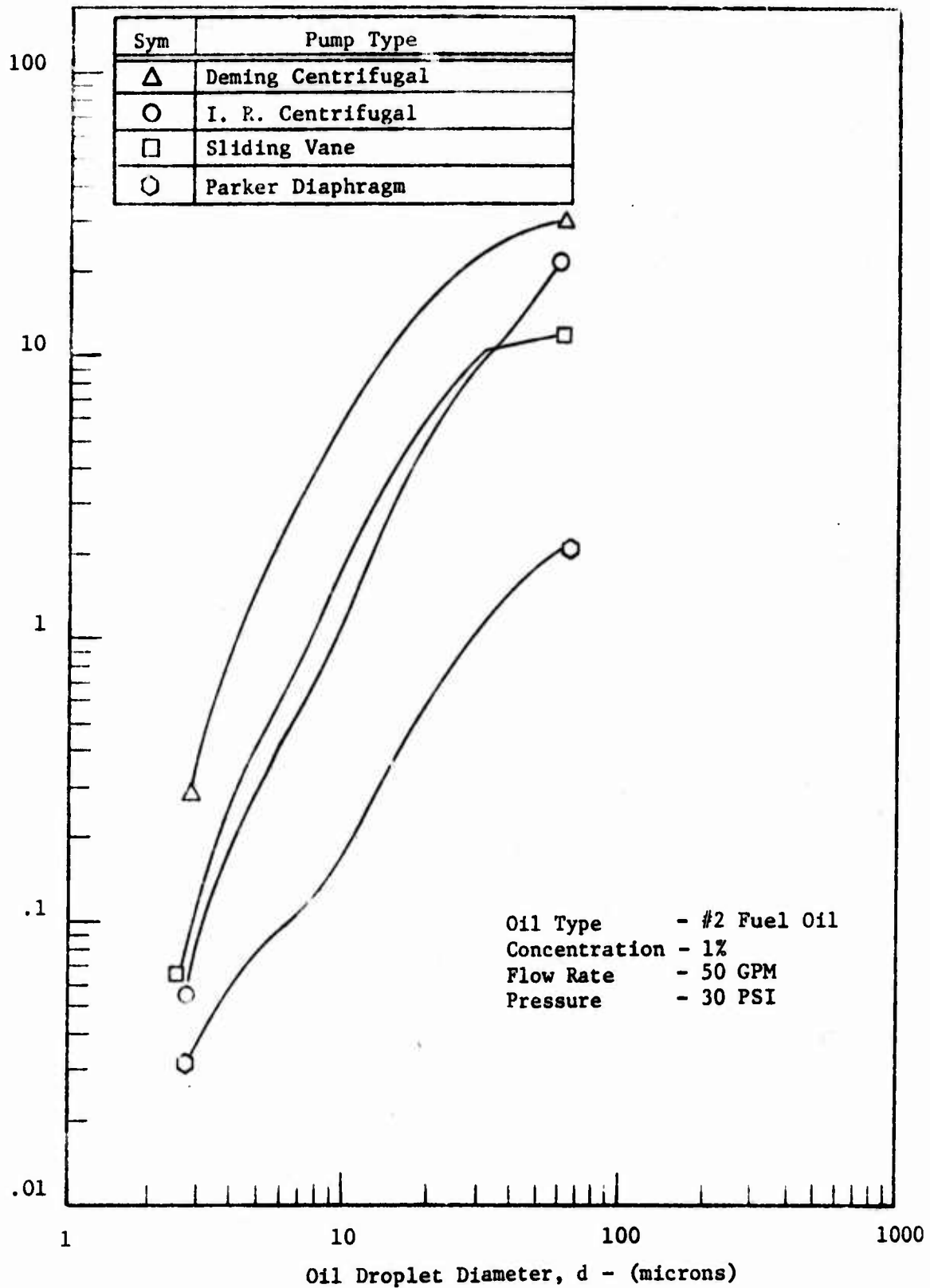
Percent Volume in Diameters Less Than d



Effects of Pressure on The Emulsification Performance of a Blackmer Sliding Vane Pump with #6 Fuel Oil

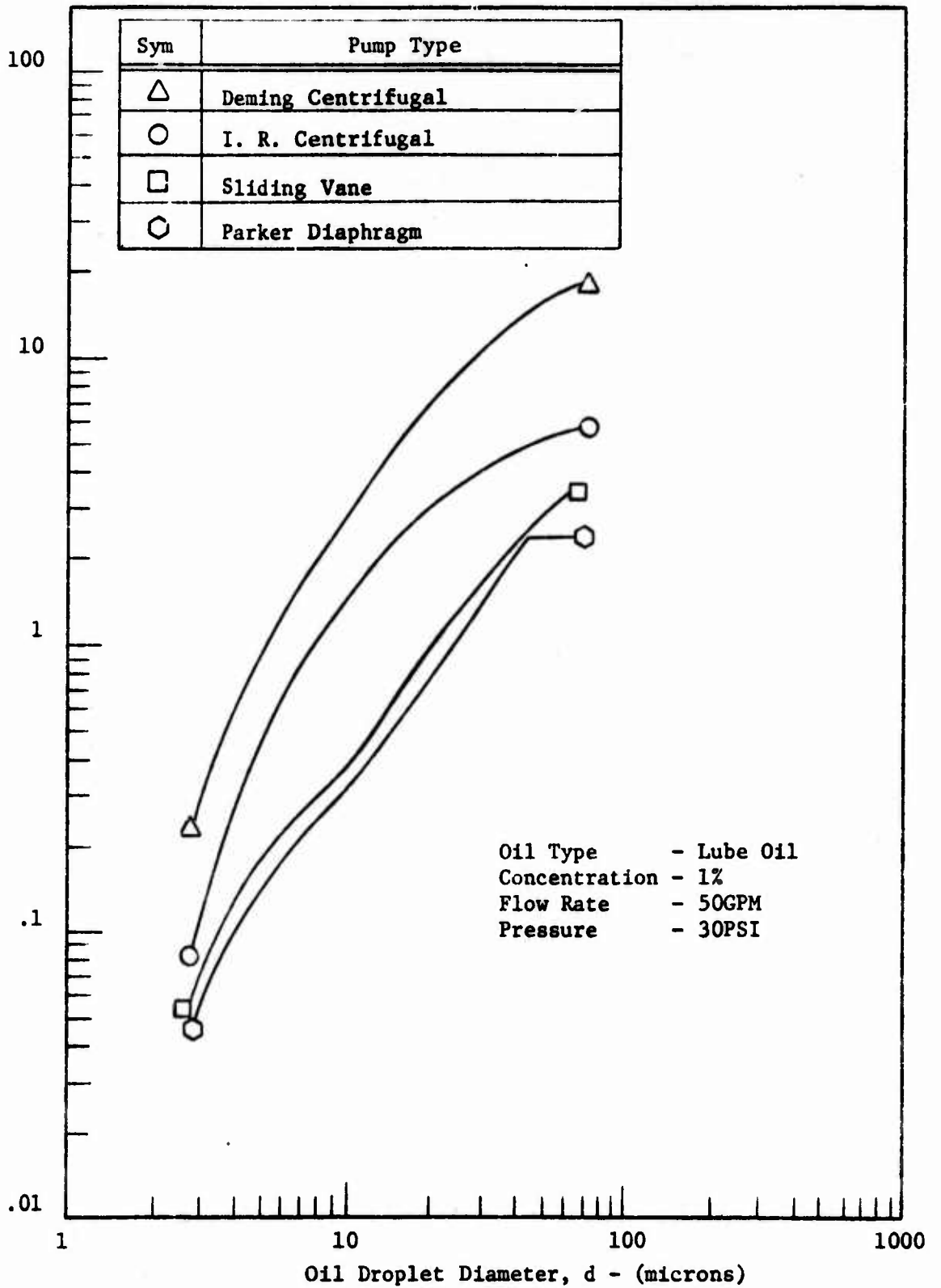
Figure 56

Percent Volume in Diameters Less Than d



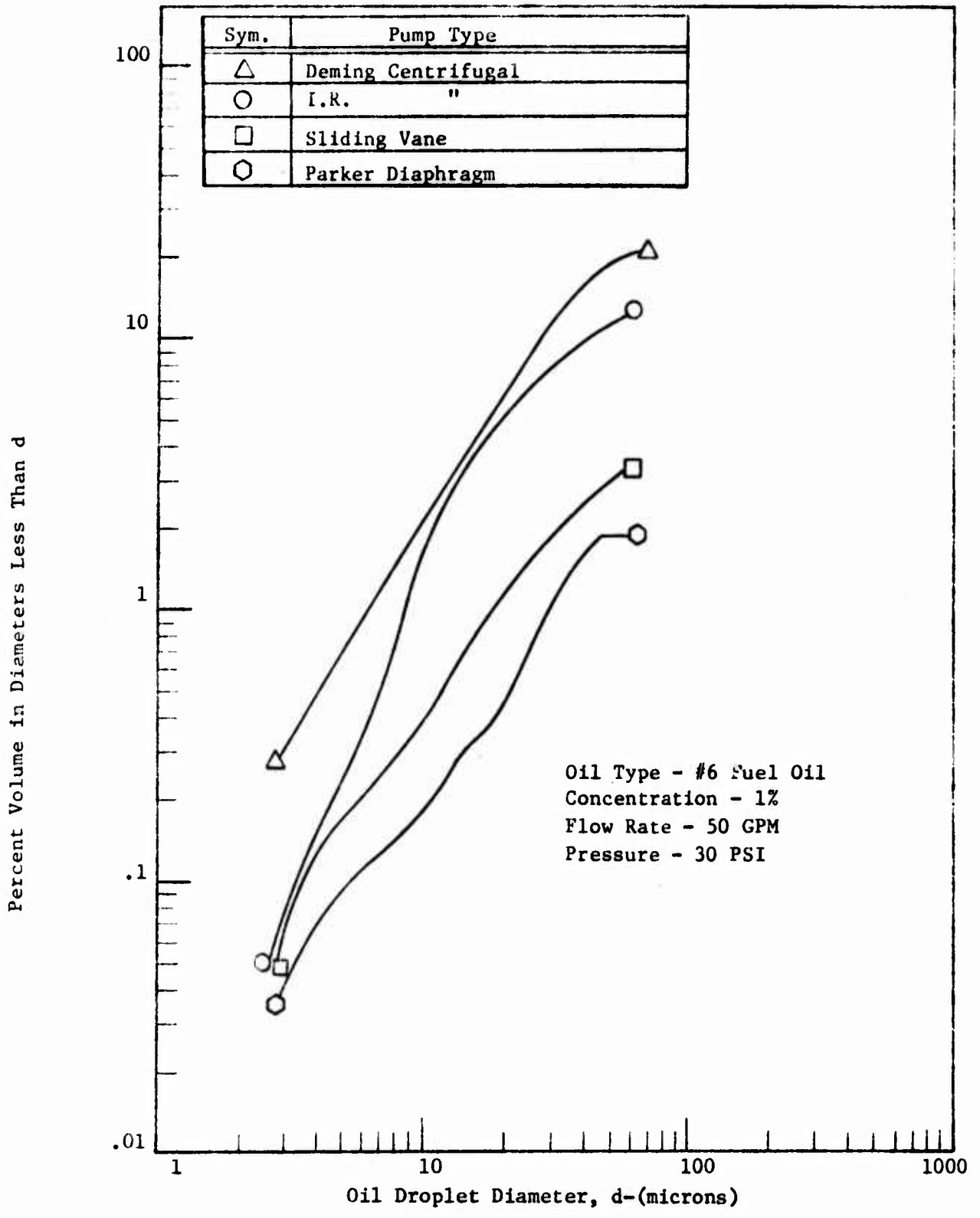
Comparison of Emulsification Performance for Various Pump Types with #2 Fuel Oil.

Percent Volume in Diameters Less Than d



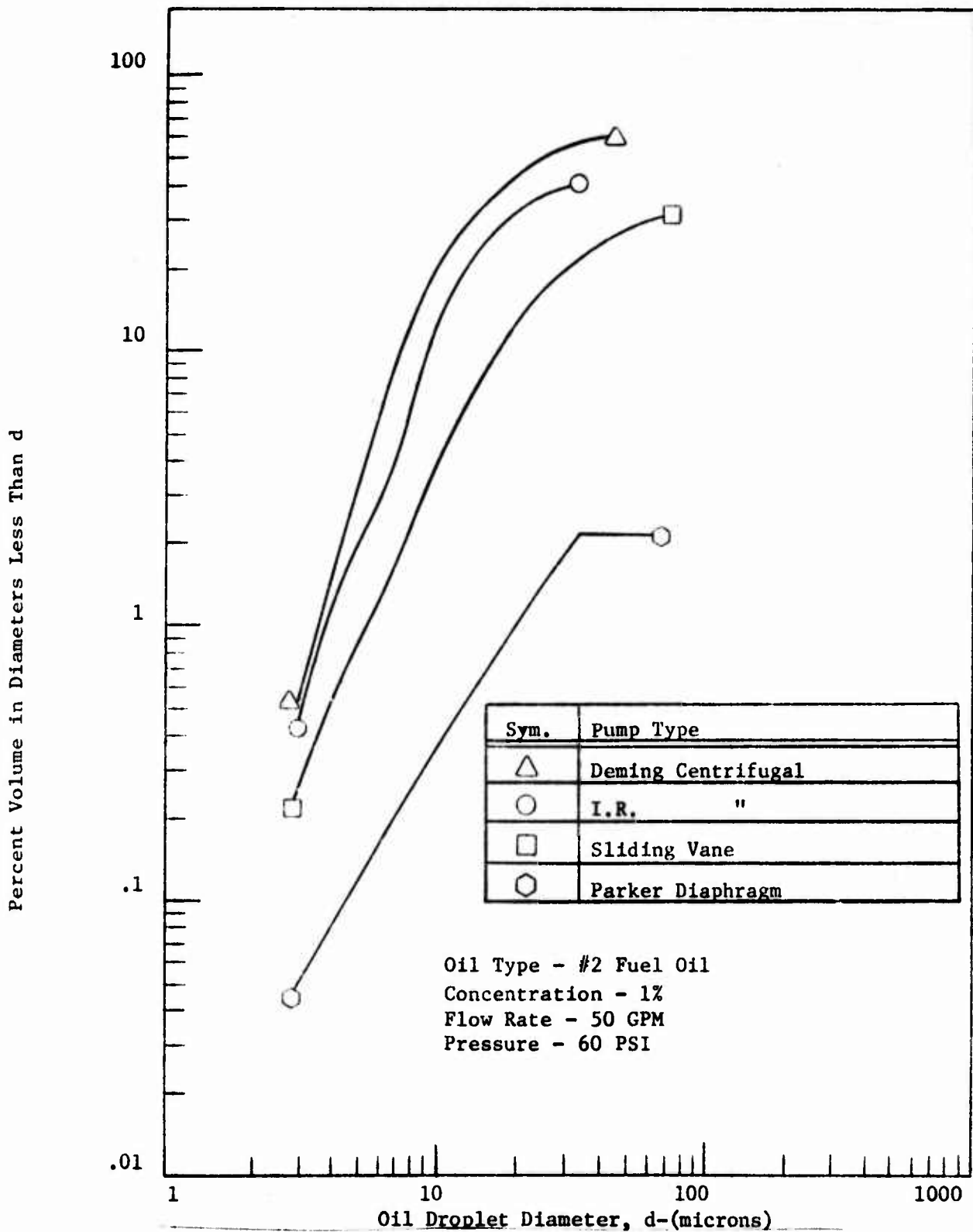
Comparison of Emulsification Performance for Various Pump Types with Lube Oil.

Figure 58



Comparison of Emulsification Performance for Various Pump Types with #6 Fuel Oil.

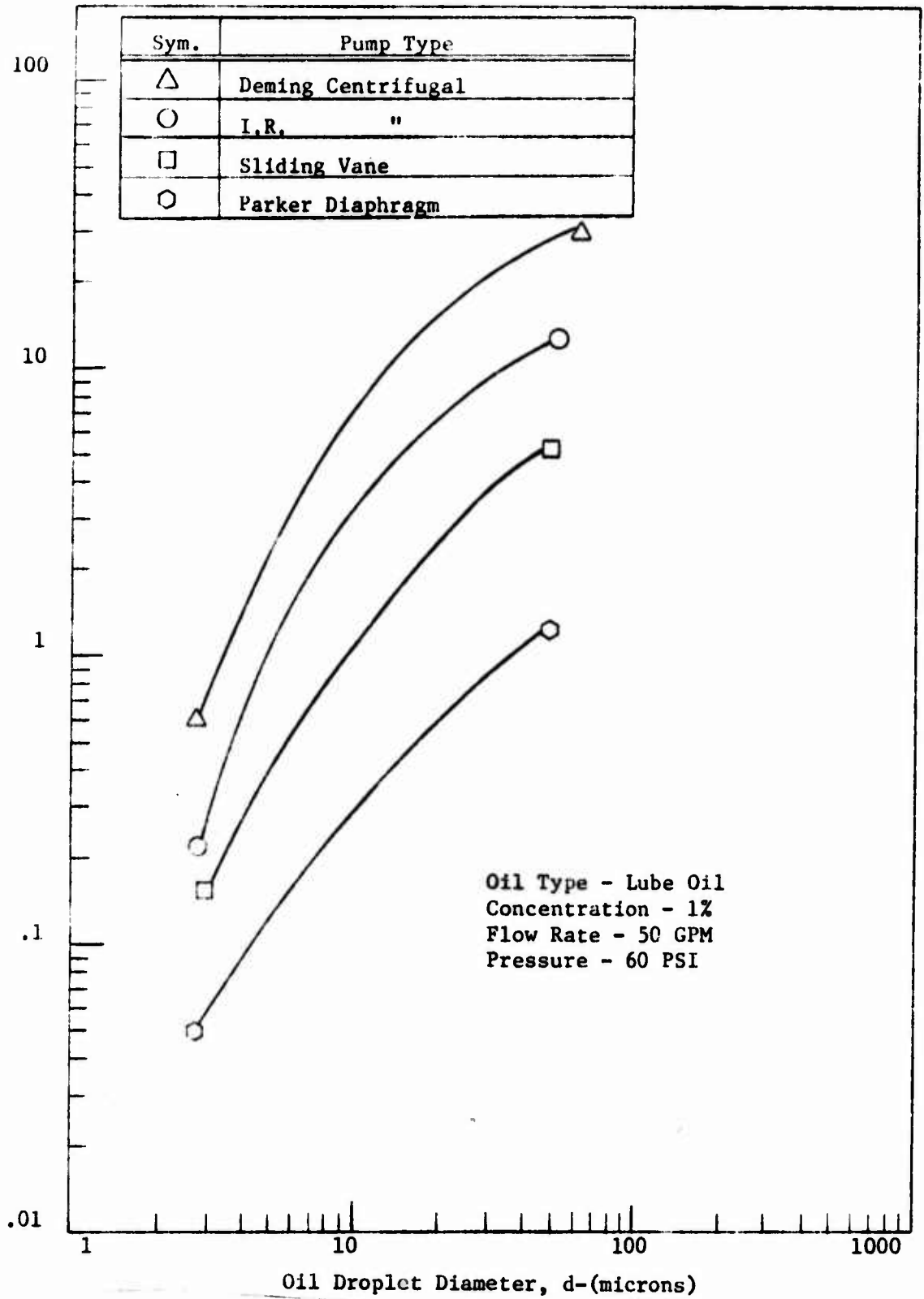
Figure 59



Comparison of Emulsification Performance for Various Pump Types with #2 Fuel Oil

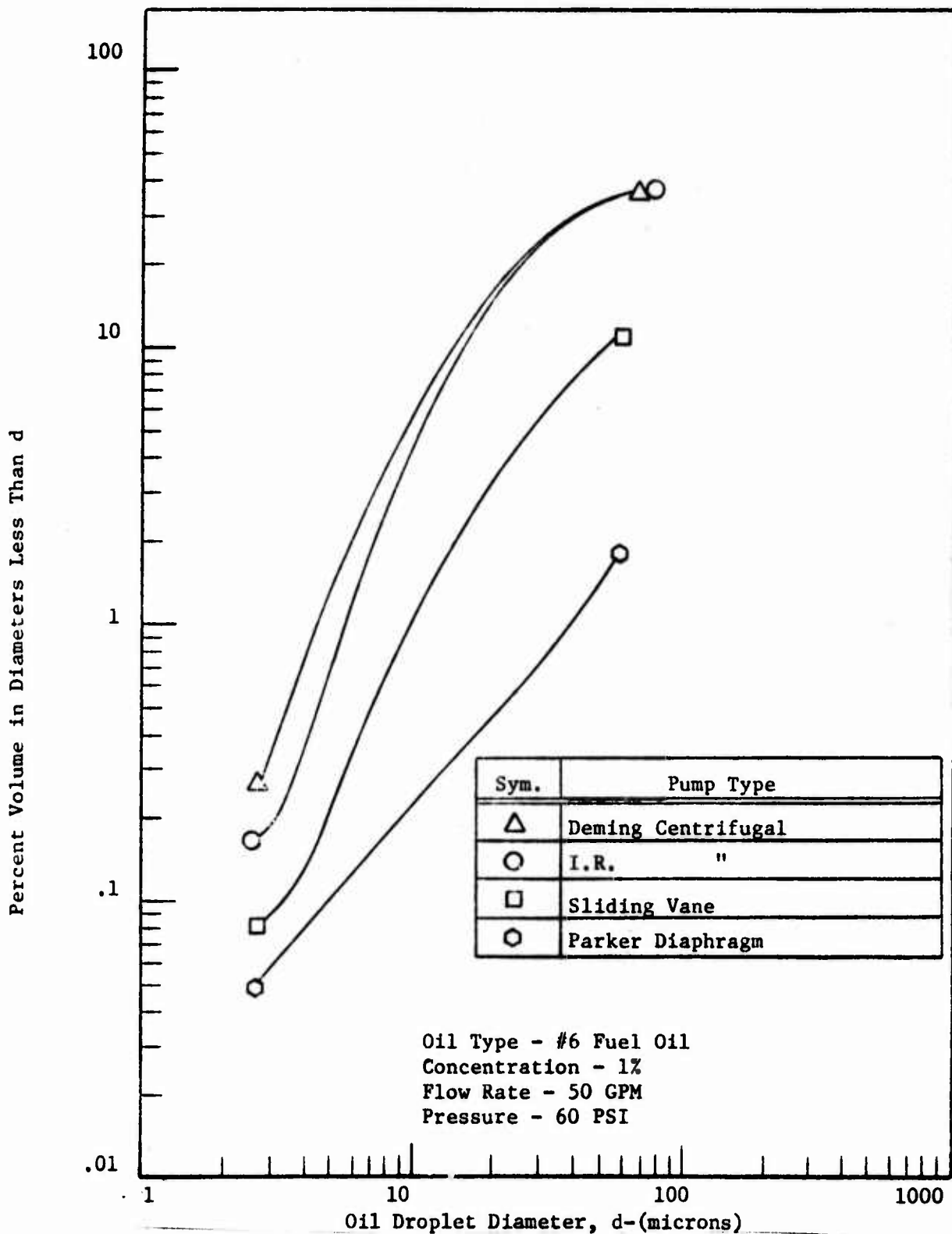
Figure 60

Percent Volume in Diameters Less Than d



Comparison of Emulsification Performance with Various Pump Types with Lube Oil

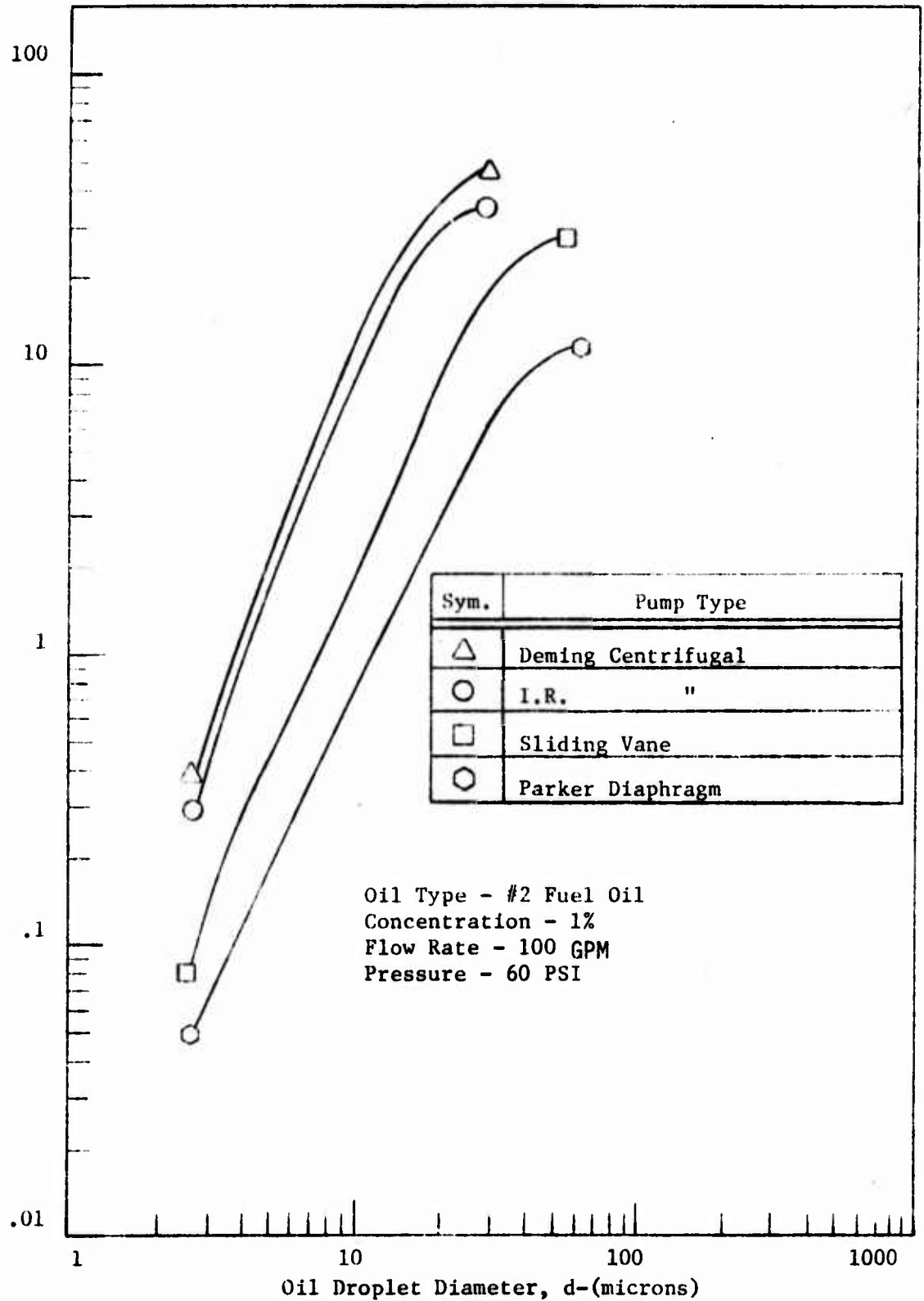
Figure 61



Comparison of Emulsification Performance for Various Pump Types with #6 Fuel Oil

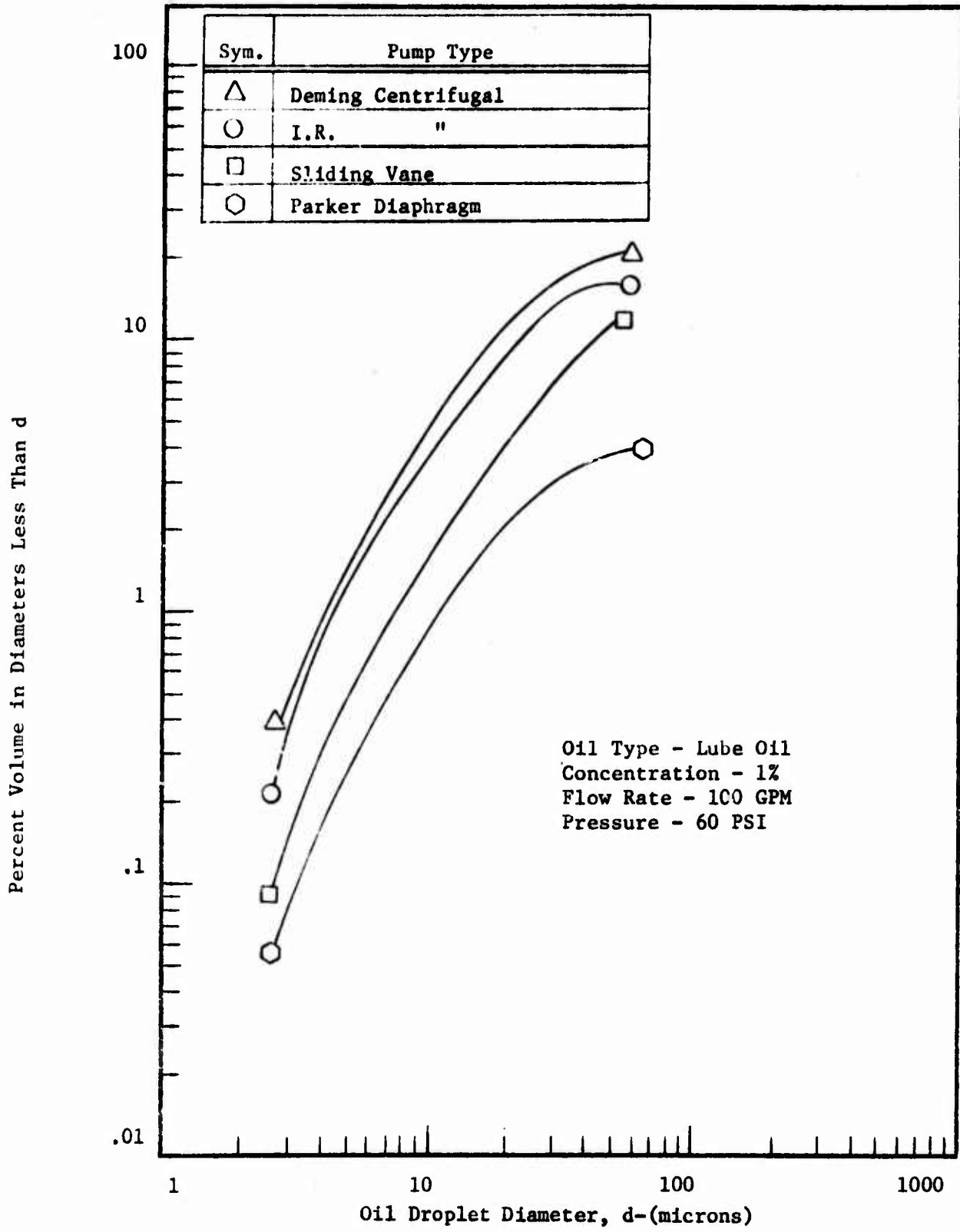
Figure 62

Percent Volume in Diameters Less Than d



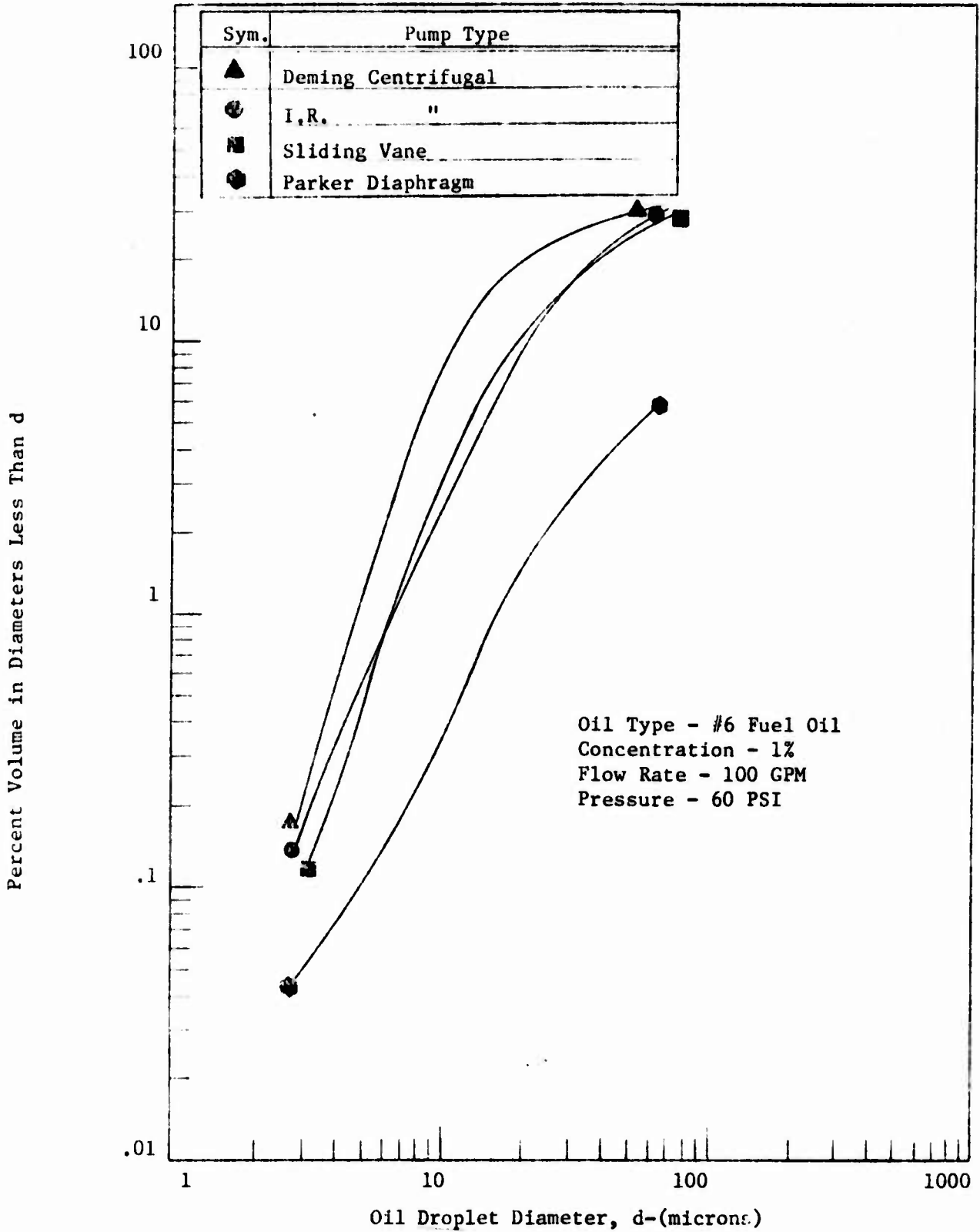
Comparison of Emulsification Performance With Various Pump Types with #2 Fuel Oil

Figure 63



Comparison of Emulsification Performance With Various Pump Types with Lube Oil.

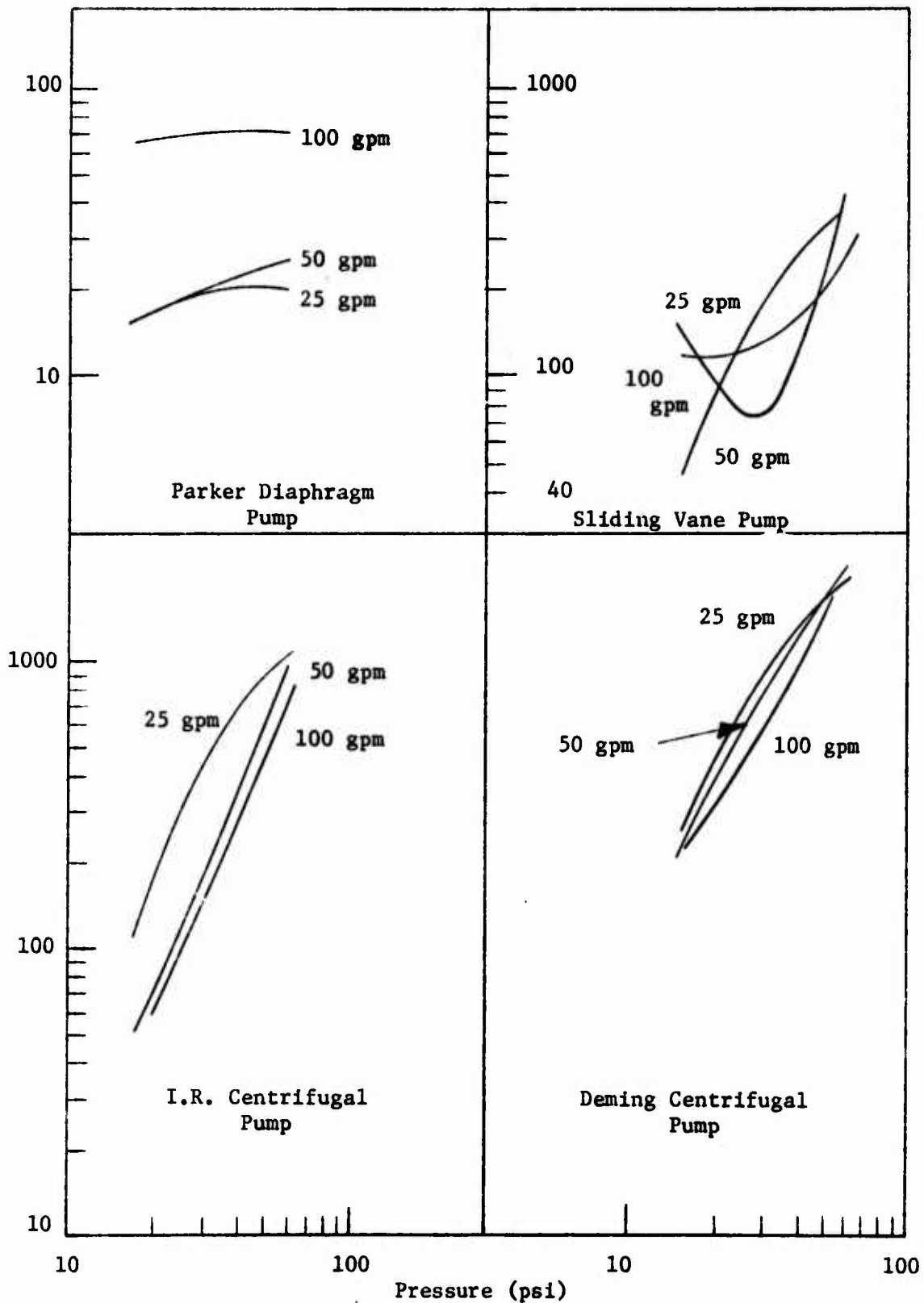
Figure 64



Comparison of Emulsification Performance with Various Pump Types with #6 Fuel Oil

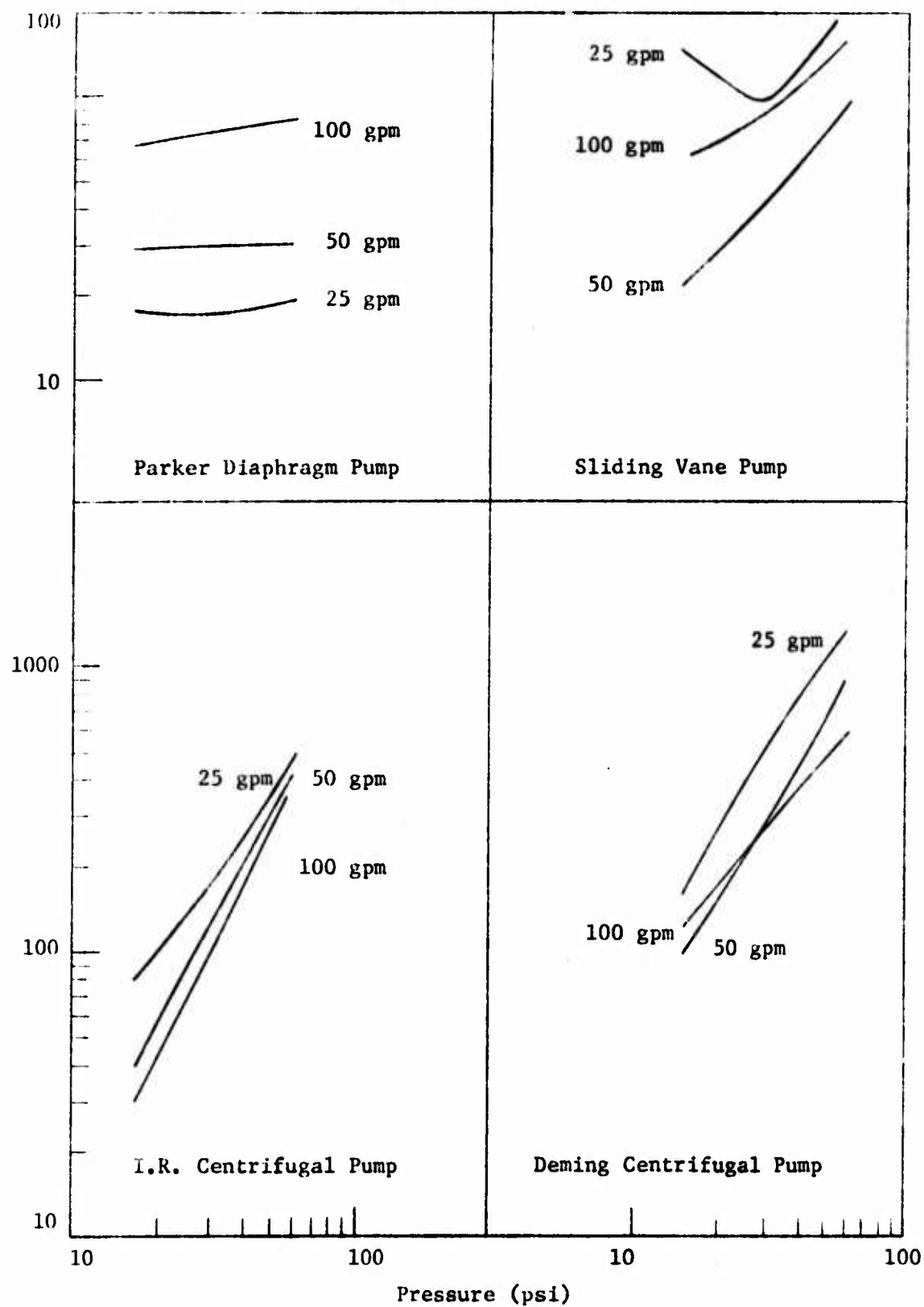
Figure 65

Cumulative Volume Concentration of Oil, ppm, in Drops up to Ten Microns Diameter



Comparison of Pump Emulsification Performance with 1 Percent No. 2 Fuel Oil. Cross-Plotted from the Foregoing Data.

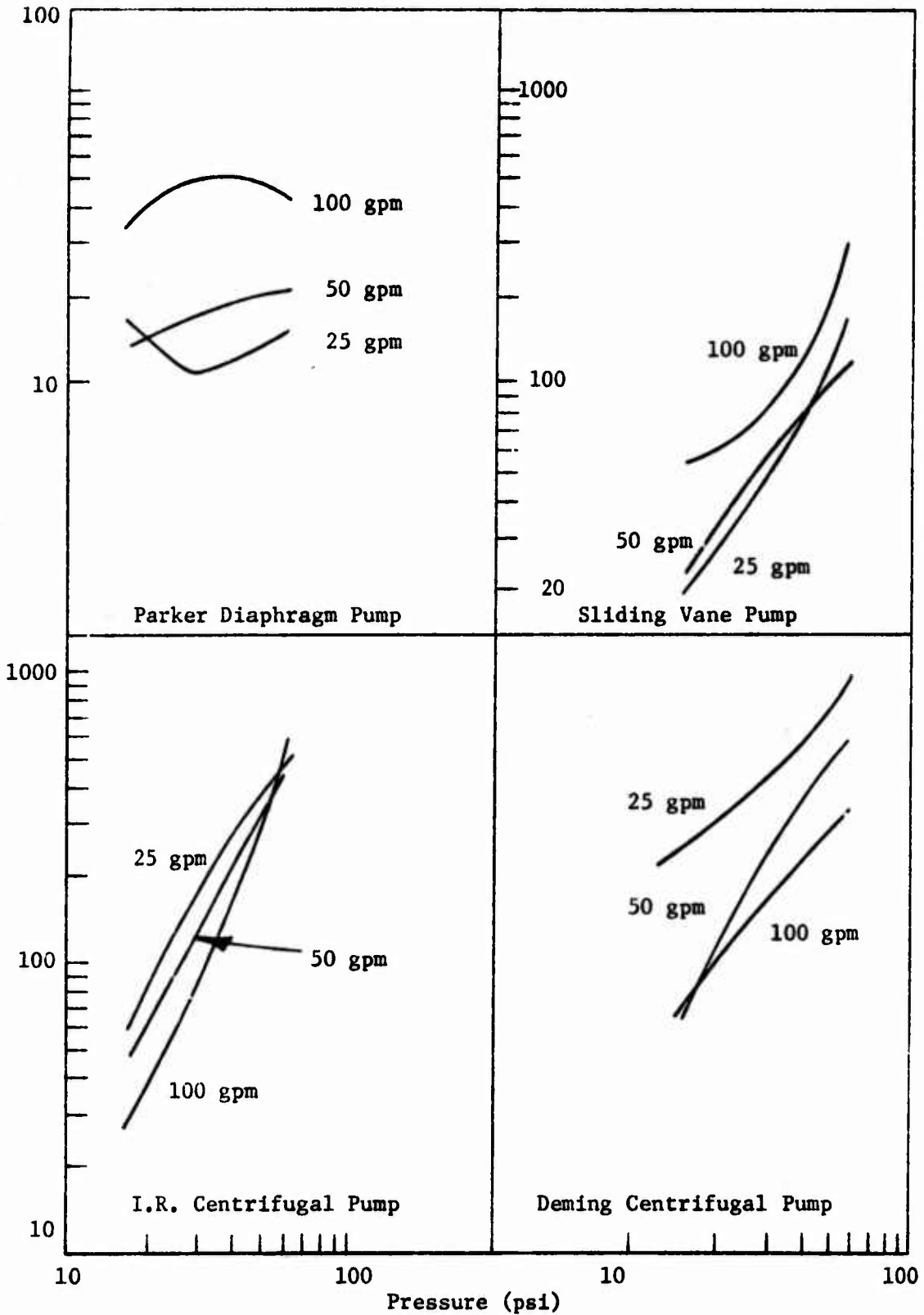
Figure 66  
162



Comparison of Pump Emulsification Performance with 1 Percent Lube Oil. Cross-Plotted from the Foregoing Data.

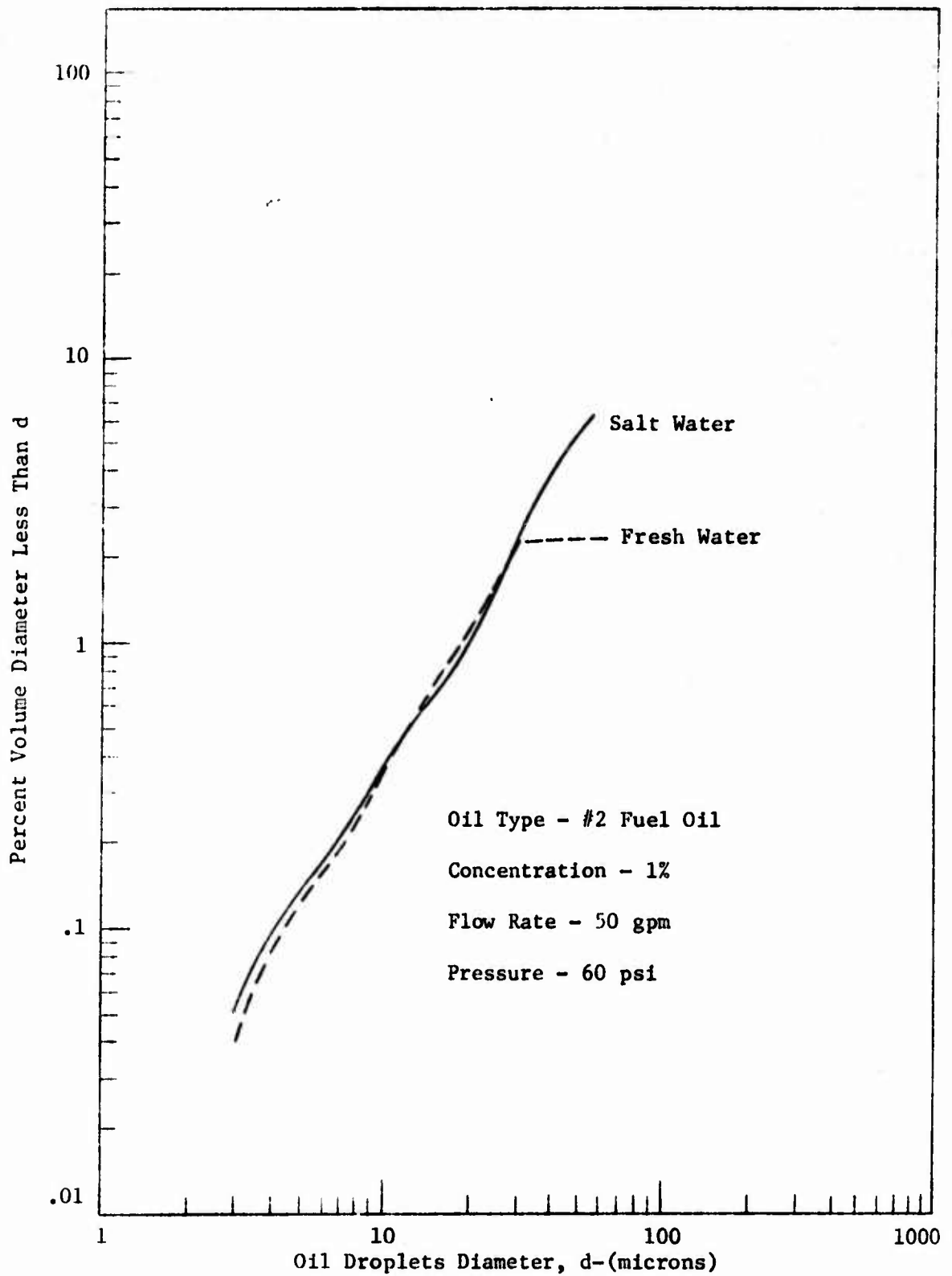
Figure 67  
163

Cumulative Volume Concentration of Oil, ppm, in Drops up to Ten Microns Diameter

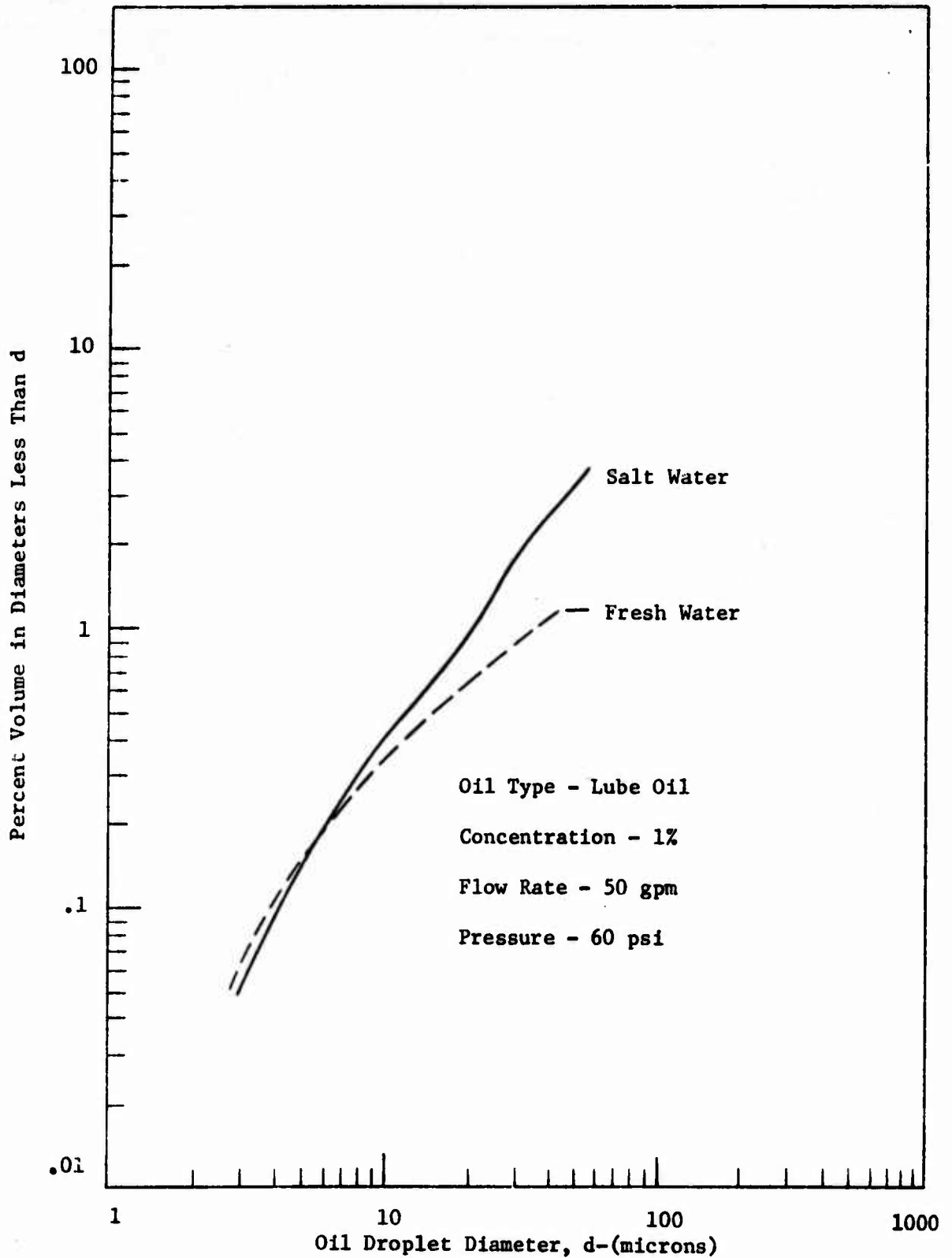


Comparison of Pump Emulsification Performance with No. 6 Fuel Oil Cross-Plotted from the foregoing data.

Figure 68  
164

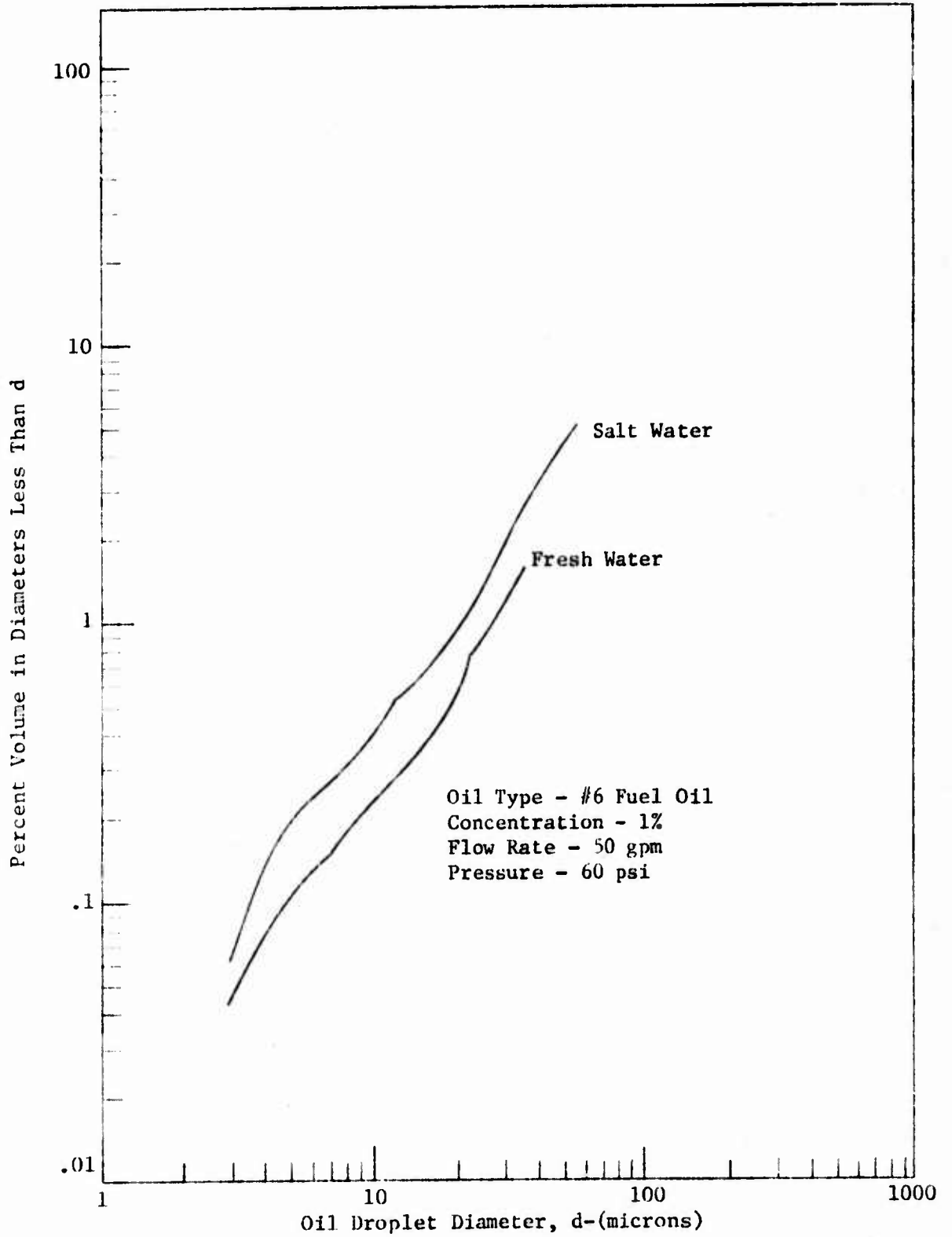


Effects of Salt Water on the Emulsification Performance of a Parker Diaphragm Pump with #2 Fuel Oil.



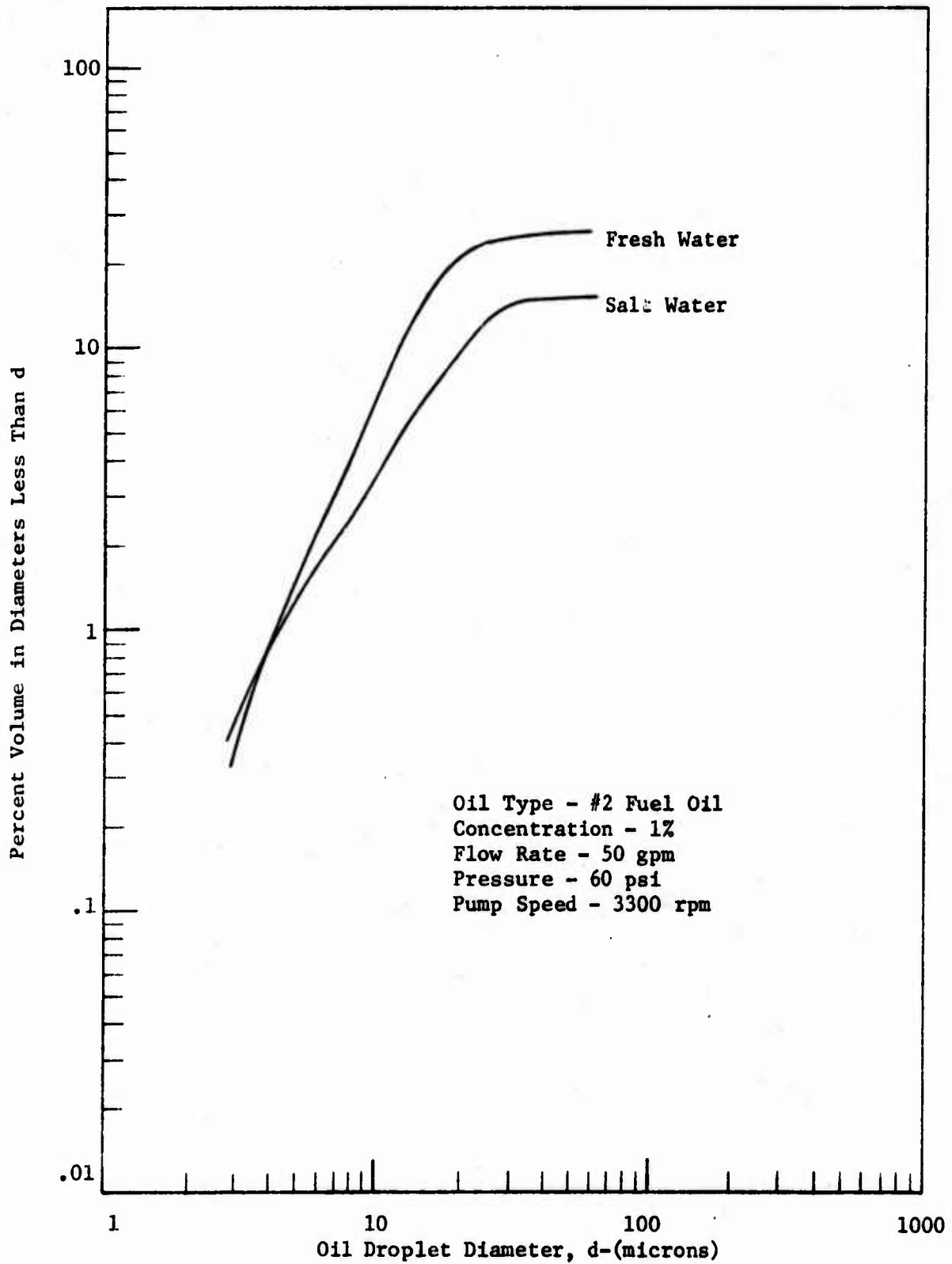
Effects of Salt Water on the Emulsification Performance of a Parker Diaphragm Pump with Lube Oil.

Figure 70



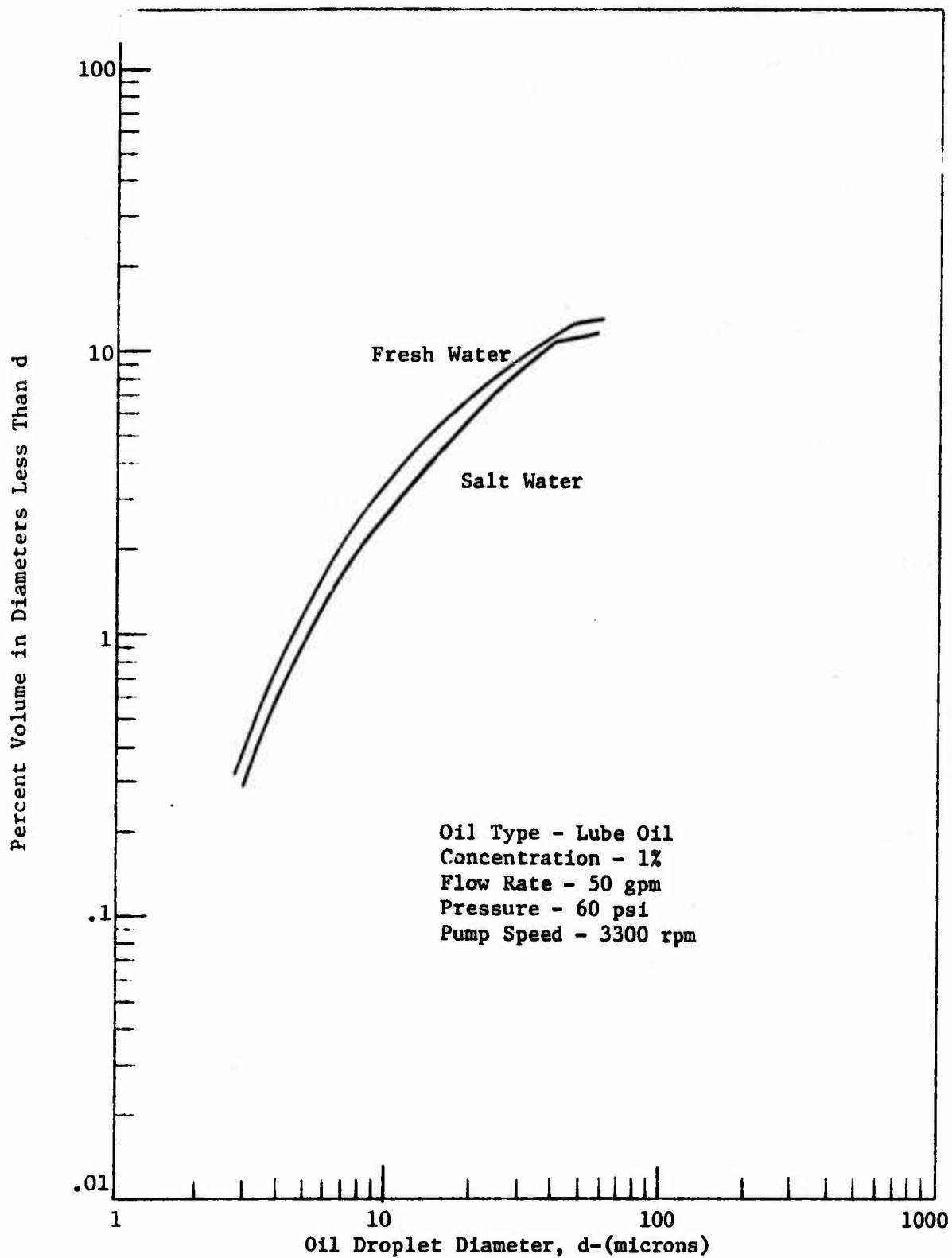
Effects of Salt Water on the Emulsification Performance of a Parker Diaphragm Pump with #6 Fuel Oil.

Figure 71



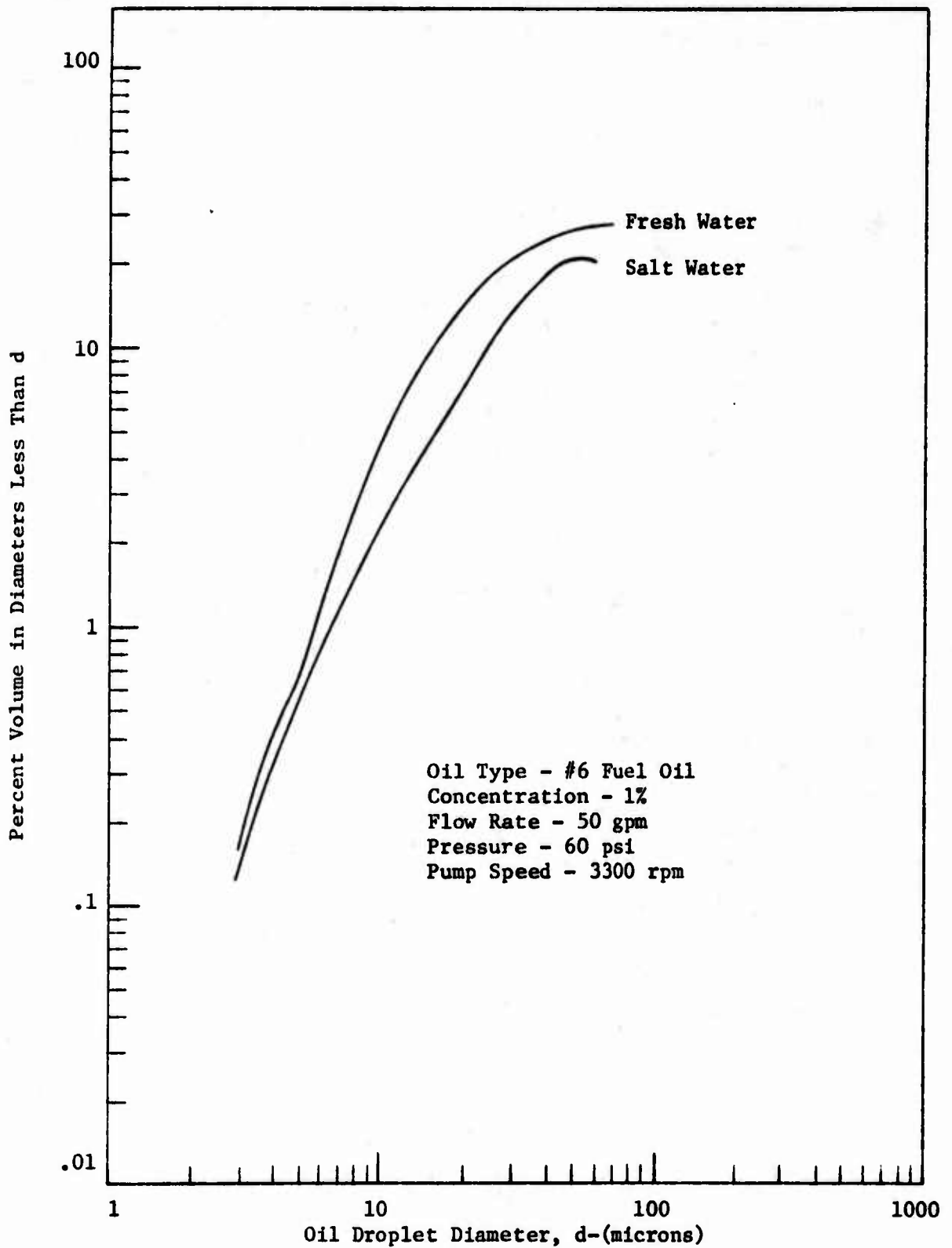
Effects of Salt Water on the Emulsification Performance of an Ingersoll-Rand Centrifugal Pump with #2 Fuel Oil.

Figure 72  
 168



Effects of Salt Water on the Emulsification Performance of an Ingersoll-Rand Centrifugal Pump with Lube Oil.

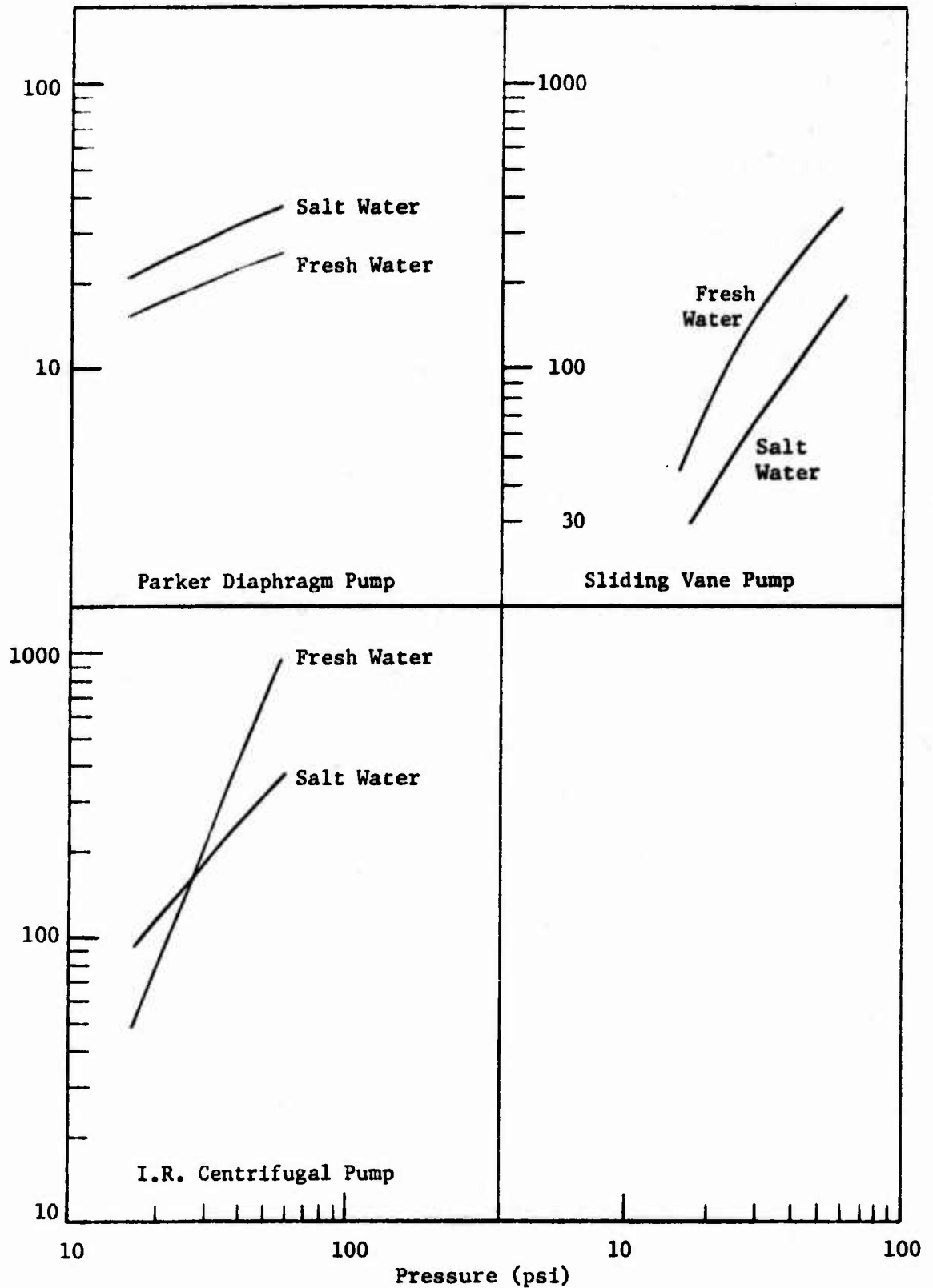
Figure 73



Effects of Salt Water on the Emulsification Performance of an Ingersoll-Rand Centrifugal Pump with #6 Fuel Oil.

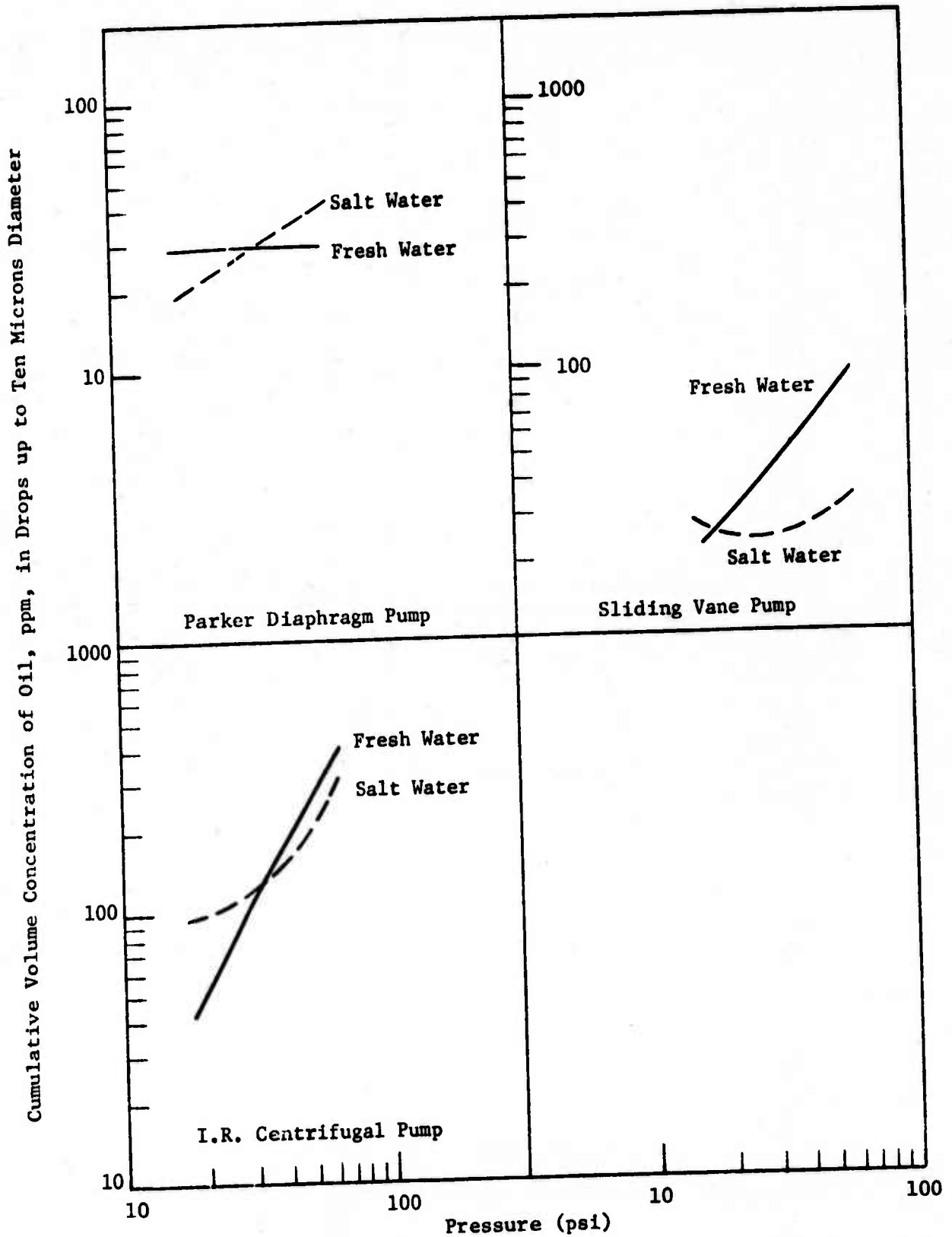
Figure 74  
 170

Cumulative Volume Concentration of Oil, ppm, in Drops up to Ten Microns Diameter



Effect of Salt Water on the Emulsification Performance of Pumps with 1 Percent No. 2 Fuel Oil at 50 gpm, Cross-Plotted from the foregoing data.

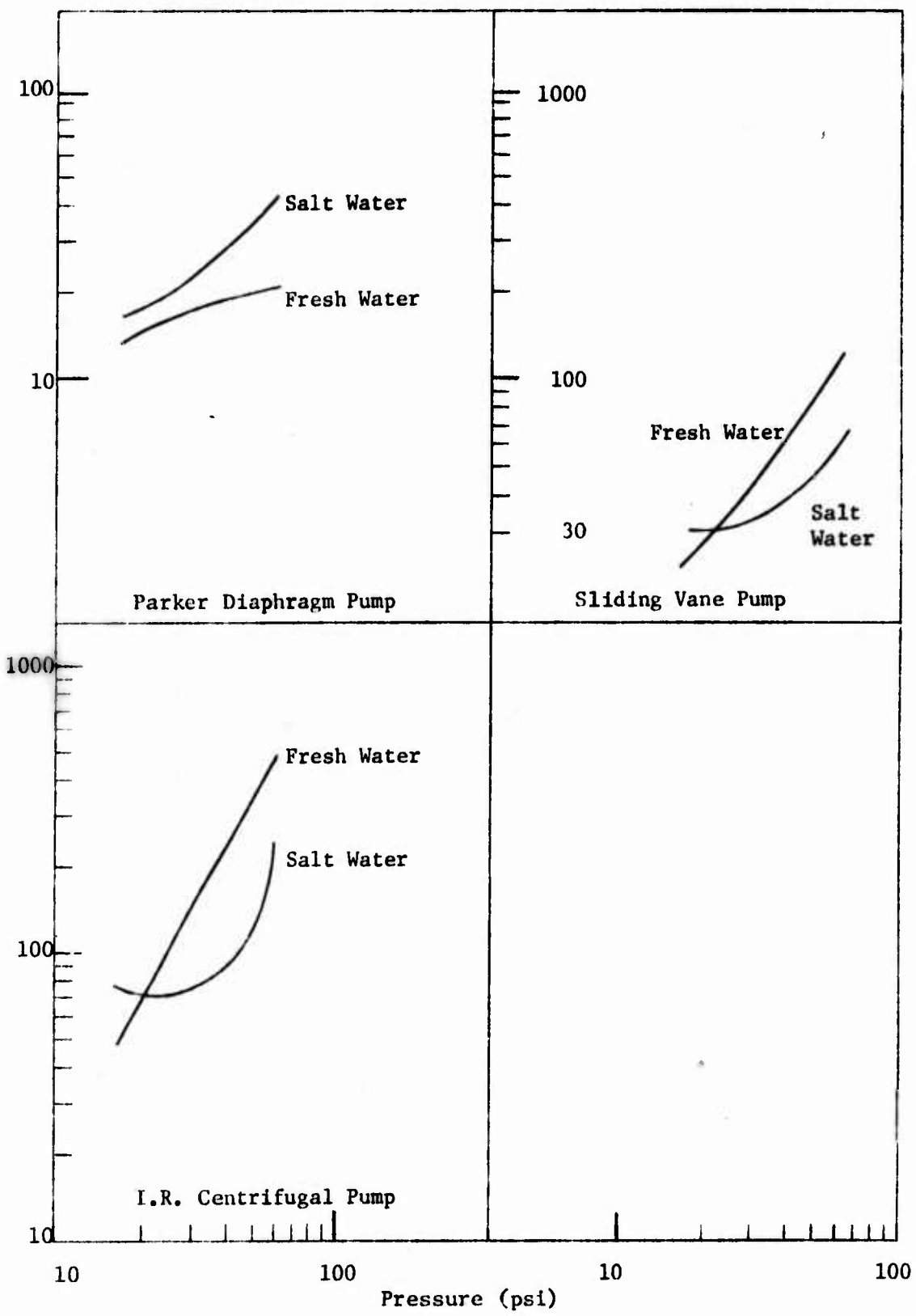
Figure 75



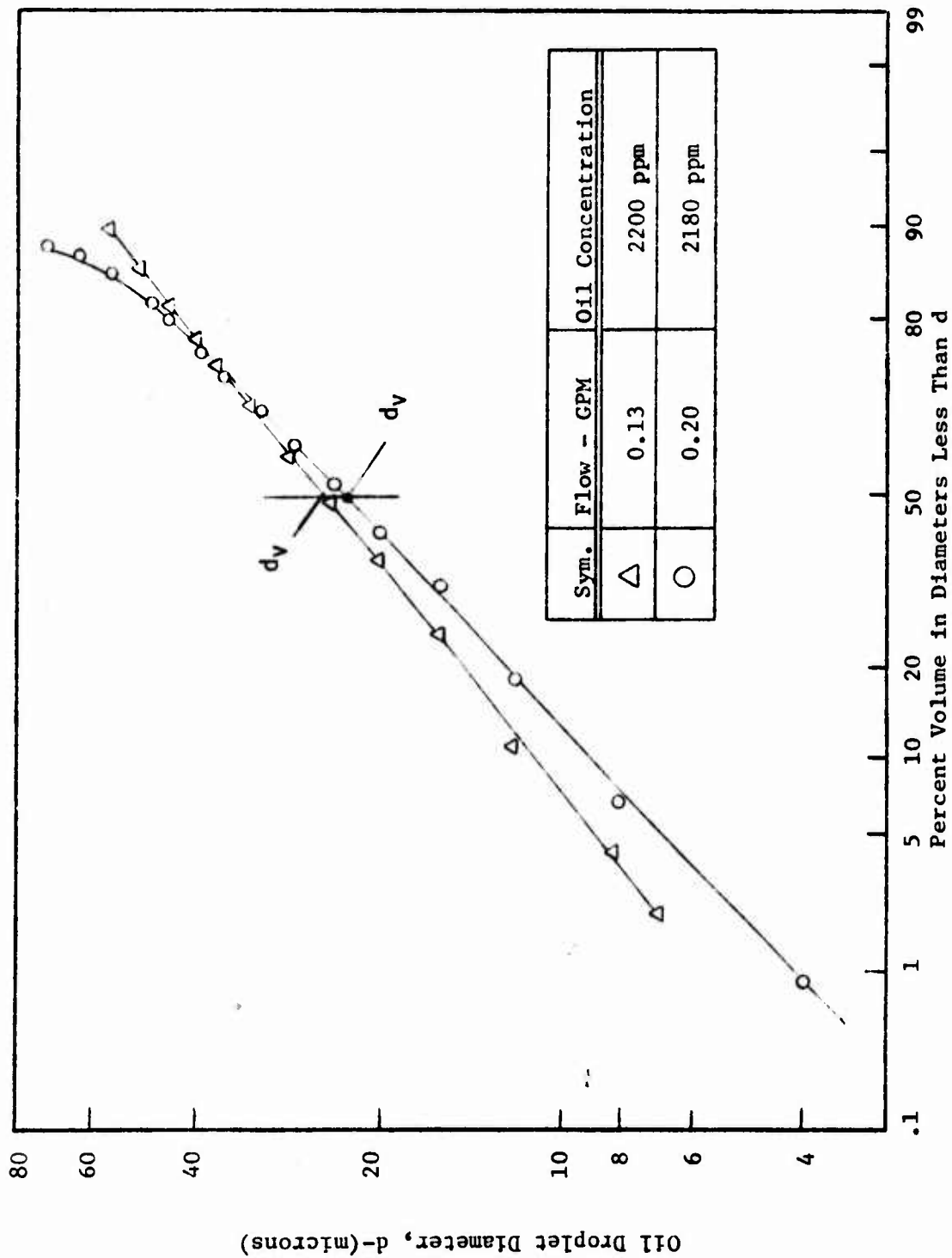
Effect of Salt Water on the Emulsification Performance of Pumps with 1 Percent Lube Oil at 50 gpm. Cross-Plotted from the foregoing data.

Figure 76

Cumulative Volume Concentration of Oil, ppm, in Drops up to Ten Microns Diameter

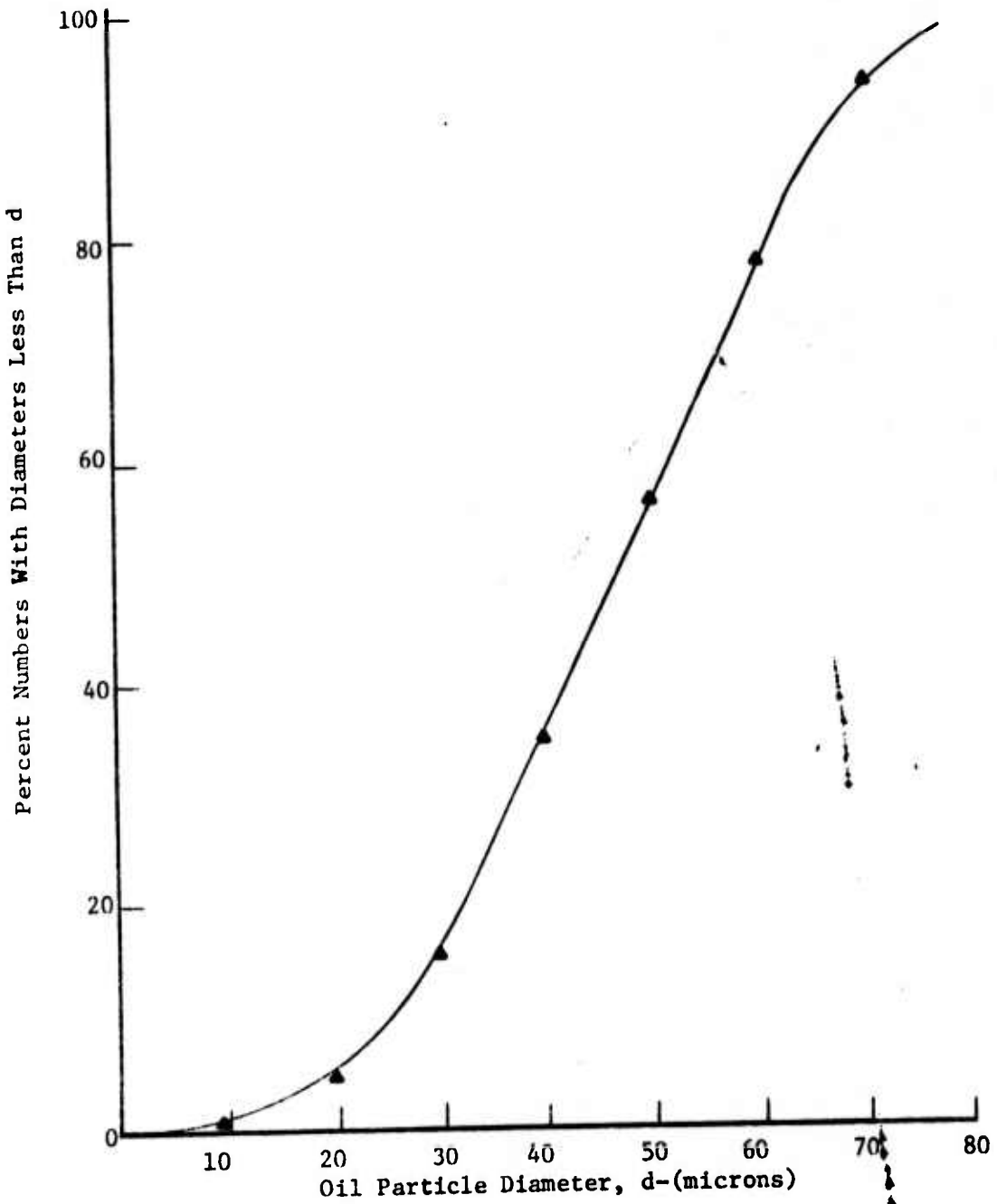


Effect of Salt Water on the Emulsification Performance of Pumps with 1 Percent No. 6 Fuel Oil at 50 gpm. Cross-Plotted from the foregoing data.



Representative Influent Oil Droplet Size Distribution for Kuwait Crude Generated by a Dispersing Orifice, Operating at a Pressure Constant Drop (10 psi)

Figure 78



Estimate of the Droplet Size Distribution Associated With the Discharge of Dirty Kuwait Crude Oil Through Representative Tanker Plumbing Systems.

Figure 79

RAW DATA APPENDIX

LIST OF TEST OILS

<u>MATRIX CODE:</u>	<u>OIL TYPE:</u>	<u>SPECIFICATIONS:</u>
A	Kuwait Crude	API Reference Oil #1
B	2190-TEP	MIL-L-17331
C	Marine Diesel	MIL-F-16884
D	Navy Distillate	MIL-F-24397
E	Navy Special Fuel Oil	MIL-F-859
F	Lubricating Oil 9250	MIL-L-9000
G	Hydraulic Oil	MIL-L-17672
H	South Louisiana Crude	API Reference Oil#2

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	Mixing Parameters				Particle Count and Distribution				
		Agitation*	RPM	Time Minutes	Time After Mixing	2-5	5-10	10-20	20-40	40-60
Oil Added by Pipet										
Marine Diesel 1000	9/6	1	3000	6	5	6146	684	90	7	-
Marine Diesel 1000	9/6	"	3000	"	"	4239	890	114	-	-
Marine Diesel 1000	9/6	"	"	"	"	5123	1283	89	-	-
Comments Inadequate mixing, oil layered on surface										
Marine Diesel 1000	9/10	1	3000	2	5	690	47	11	-	-
Comments dispersion with smaller volumes; inadequate mixing										
Marine Diesel 5000	9/10	2	3000	2.5	5	145	16	2	-	-
Marine Diesel 5000	9/10	1	1000	2.5	5	297	9	4	1	-
Marine Diesel 5000	9/12	2	2500	1	5	193	38	7	-	-
Marine Diesel 5000	9/12	1	1000	0.5	5	76	11	-	-	-
Comments Inadequate mixing, oil layered on surface										

- \* Agitation
1. S-25 Mixer
  2. S-30 Mixer
  3. Ultrasonic Bath Plate Current 60 ma
- A. Step A  
B. Step B

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration ppm	Mixing Parameters					Particle Count and Distribution				
	Date	Agitation*	RPM	Time Minutes	Time After Mixing	2-4 $\mu$	4-6 $\mu$	5-8 $\mu$	8-10 $\mu$	10-60 $\mu$
Oil Added by Pipet Marine Diesel 5000	9/12	1	3000	8	5	2236	625	180	83	45
Oil Injected thru #27 Needle Marine Diesel 5000	9/16	1	6000	1	5	2336	2772	2548	2313	5761
Comments: Trial #1 Marine Diesel 5000	9/16	"	"	"	"	2518	2956	2811	2601	5079
Comments: Trial #2 Marine Diesel 5000	9/16	"	"	"	"	649	"	"	"	"
Comments: Trial #3 Non-reproducible dispersions (counts monitored up to 20 min. after mixing) Marine Diesel 5000	9/18	3	-	0.5	5	3944	3583	2907	2215	2609
Comments: Trial #1 Count rate too high Marine Diesel 5000	9/18	3	-	0.5	5	5177	4414	3402	2388	1739
Comments: Trial #2 Count rate too high Marine Diesel 5000	9/18	3	-	0.5	5	5635	4531	3201	2077	1677
Comments: Trial #3 Count rate too high, large variation in last channel.										

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Mixing Parameters

Particle Count and Distribution

Counts/ml less Background

Oil Type and Concentration ppm	Date	Agitation *	RPM	Time Minutes	Time After Mixing	Particle Count and Distribution						
						2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$		
Oil Injected thru #25 Needle												
Marine Diesel 5000 Comments: Count rate too high	9/19	3	-	0.5	5	5133	5889	6304	394	11		
Marine Diesel 5000 Comments: Dispersion with smaller volumes	9/19	3	-	1	5	4583	5216	5577	174	0		
Marine Diesel 5000 Comments: Two step dispersion process investigated - ultrasonic agitation (Step A) followed by Dispersion (Step B)	9/19	3	-	0.75	5	4214	4805	4776	239	1		
Marine Diesel 5000 Comments: 5 sec. of ultrasonic agitation with 500 ppm Aerosol C-61 added;	9/19	3	-	0.75	5	4106	5619	8800	1157	57		
Marine Diesel 1000 Comments:	9/20	3	-	0.5	5	4625	5856	6303	119	0		
Marine Diesel 1000 Comments: With 50 ppm Aerosol C-61; Count rate too high	9/20	3	-	0.5	5	3466	4716	7557	387	28		
Oil water plus detergent Added to test tube which then was subjected to sonification												
Marine Diesel 5000 Comments: Completely opaque white emulsion; did not permit transmittal of light for particle counting measurement	9/24	3	-	0.75	Cell blocked, sensor inoperable							
Marine Diesel 5000 Comments: Allowed 9 minutes settling; count rate too high	9/25	3	-	0.42	10	4367	5313	6008	95	0		
Marine Diesel 1000 Comments: Allowed 9 minutes settling; count rate too high	9/25	3	-	0.42	15	5425	5687	3900	22	0		
Marine Diesel 100 Comments:	9/26	3	-	0.17	5	3768	1591	199	0	0		
Marine Diesel 100 Comments: With 50 ppm Aerosol C-61	9/26	3	-	0.17	5	1055	1493	944	52	1		

\* Agitation: 3-Ultrasonic Bath Plate Current 60 ma

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Mixing Parameters				Particle Count and Distribution					
	Date	Agitation*	RPM	Time Minutes	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test tube which then was subjected to Sonification										
Marine Diesel 100	9/26	3	-	0.17	5	6575	6116	3280	45	4
Comments: With 10 ppm Aerosol	9/27	3	-	0.17	5	4084	5147	5434	112	2
Marine Diesel 100										
Comments: With 5 ppm Aerosol										

\* Agitation 3-Ultrasonic Bath; Plate Current 60 ma

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Mixing Parameters					Particle Count and Distribution				
	Date	Agitation*	RPM	Time Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test Tube which then was Subjected to Sonification										
Marine Diesel 100 and Aerosol C-61 10 Comments: To verify run of 9/26; poor reproducibility	9/27	A3 B Mechanical	-	10	5	3567	4197	3724	96	4
Marine Diesel 100 and Retarder Lan 50 Comments:	9/27	A3 B Mechanical	-	10	10	3678	4883	6651	208	0
None Comments: High background count indicated residue in sensor	9/30	-	-	-	-	1767	630	52	0	0
None Comments: Extensive cleaning process of hexane, air water required	10/1	-	-	-	-	562	111	1	0	0
Marine Diesel 100 and Aerosol OT-75 20 Comments:	10/1	A3 B Mechanical	-	10	5	5042	3609	1114	31	1
Navy Special Fuel Oil 100 Comments: Sensor required rigorous hexane, air, water cleaning	10/1	A3	-	10		5296	2545	734	34	2

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	Mixing Parameters				Particle Count and Distribution				
		Agitation*	RPM	Time Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to test tube which then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to intake side of Mixer (Step B)										
Marine Diesel 100	10/1	A3 B1	- 2,000	10 20	5	5450	3633	854	9	4
Comments:										
Marine Diesel 500	10/1	A3 B1	- 2,000	10 10	5	6460	5356	1725	8	-
Comments: Count rate too high										
Marine Diesel 500	10/2	A3 B1	- 2,000	10 10	5	6103	3098	434	4	2
Comments: Count rate near Saturation										
Marine Diesel 500	10/2	A3 B1	- 2,000	10 10	5	7520	4315	738	17	1
Comments: Count rate too high										
Marine Diesel 100	10/2	A3 B1	- 2,000	10 10	5	120	46	11	-	-
Comments: Count rate too low										
Marine Diesel 500	10/3	A3 B1	- 2,000	30 10	5	3736	3956	2218	68	-
Comments: Half of emulsion generated by the first agitation step (A) was drawn back into Syringe and Re-injected.										
Marine Diesel 500	10/3	A3 B1	- 2,000	30 10	5	4991	5520	1884	13	-
Comments:										
Marine Diesel 500	10/3	A3 B1	- 2,000	20 20	5	1460	1529	586	235	57
Comments: Mixing vessel for ultrasonic agitation was beaker, not test tube.										

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	Mixing Parameters				Particle Count and Distribution				
		* Agitation	RPM	Seconds time	Mixing Time After	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test Tube which then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)	10/3	A3 B1	- 2000	20 20	5	2745	3215	1574	549	84
Comments:										
Mixture generated with ultrasonic agitation was poured into 30 cc glass syringe (test tube rinsed with two 10 ml portions of distilled water), then injected into the volume of water with non-aerating dispersator operating gas; cylinder now used to force sample into sensor, in place of pump										
Marine Diesel	10/7	A3 B1	- 2000	10 20	5	5234	2780	667	153	34
Comments: Heavy oil film on surface										
Marine Diesel	10/8	A3 B1	- 2000	10 20	5	6551	3688	914	218	19
Comments: Heavy oil film on surface										
Marine Diesel	10/8	A3 B1	- 2000	10 25	5	6619	4820	1325	203	17
Comments:										
Marine Diesel	10/8	A3 B1	- 2000	10 25	20	1868	674	186	63	8
Comments: Extended Monitoring										
Navy Special Fuel Oil	10/8	A3 B1	- 2000	10 25	5	1593	511	122	42	16
Comments: Extended Monitoring occurred with time										

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	Mixing Parameters			Particle Count and Distribution					
		Agitation*	RPM	Time Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)	10/8	A3	-	10		1610	547	97	56	12
		B1	2000	25						
Comments: Extended Monitoring with time										
Navy Special Fuel Oil 500	10/8	A3	-	10		1495	481	100	35	11
		B1	2000	25						
Comments: Extended monitoring occurred with time										
Navy Special Fuel Oil 500	10/8	A3	-	10		1449	463	88	31	9
		B1	2000	25						
Comments: Extended monitoring occurred with time										
Navy Special Fuel Oil 500 and Aerosol OT-75	10/10	A3	-	10		7093	3776	905	187	29
		B1	2000	25						
Comments: Extended monitoring occurred with time										
Navy Special Fuel Oil 500 and Aerosol OT-75	10/10	A3	-	10		7112	3635	882	209	25
		B1	2000	25						
Comments: Extended monitoring occurred with time										
Navy Special Fuel Oil 500 and Aerosol OT-75	10/10	A3	-	10		7105	3612	880	188	20
		B1	2000	25						

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Mixing Parameters				Particle Count and Distribution Counts/ml less Background					
	Date	Agitation*	RPM	Time Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)										
Navy Special Fuel Oj1 500 and Aerosol OT-75 50 Comments: Extended monitoring on same with time.	10/10	A3 B1	--- 2000	10 25	45	7200	3615	816	161	17
Navy Special Fuel Oil 500 and Aerosol OT-5 50 Comments: Extended monitoring on same time.	10/10 10/10	A3 B1	--- 2000	10 75	50 25	7135	3633	807	165	21

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	Mixing Parameters				Particle Count and Distribution				
		Agitation*	RPM	Time seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)										
2190 TEP 500	10/11	A3 B1	--- 2000	10 25	2	14448	5238	1026	312	104
Comments: Extended monitoring to determine if significant changes in PSD were occurring with time.										
2090 TEP 500	10/11	A3 B1	--- 2000	10 25	10	14921	4991	855	258	61
Comments: Extended monitoring to determine if significant changes in PSD were occurring with time.										
2190 TEP 500	10/11	A3 B1	--- 2000	10 25	30	14379	4944	836	235	52
Comments: Extended monitoring to determine if significant changes in PSD were occurring with time.										
2190 TEP 500	10/11	A3 B1	--- 2000	10 25	45	14360	4869	650	150	17
Comments: Extended monitoring to determine if significant changes in PSD were occurring with time.										
2190 TEP and Retarder Lan 50	10/14	A3 B1	--- 2000	10 25	10	24685	16429	6310	2588	680
Comments: Counts recorded up to 45 minutes.										
2190 TEP and Retarder Lan 100	10/14	A3 B1	--- 2000	10 25	10	23098	12403	3847	1154	230
Comments: Counts recorded up to 45 minutes.										

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Mixing Parameters				Particle Count and Distribution					
	Date	Agitation*	RPM	Time Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)										
2190 TEP and Retarder Lan 500 25 Comments: Counts recorded	10/15	A1	---	10	10	24807	18623	7913	2711	716
	10/15	B1	2000	25						
	up to 45 Minutes									
2190 TEP and Aerosol C-61 500 50 Comments: Counts recorded	10/15	A1	---	10	10	23813	18005	9703	4096	932
		B1	2000	25						
	up to 45 minutes									
2190 TEP and Aerosol C-61 500 100 Comments: Counts recorded	10/16	A1	---	10	10	19353	15506	8860	3888	996
		B1	2000	25						
	up to 45 minutes									
2190 TEP and Aerosol C-61 500 25 Comments: Counts recorded	10/16	A3	---	10	10	29375	19905	9193	3710	995
		B1	2000	25						
	up to 45 minutes, count rate too high,									
2190 TEP and Aerosol C-61 500 50 Comments: Counts recorded	10/17	A3	---	10	10	20324	17125	11110	5766	1994
		B1	2000	25						
	up to 40 minutes.									
Distilled Water Comments: Background count	10/21	---	---	---	---	1016	193	62	35	8
		---	---	---	---					
	too high									

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Mixing Parameters				Particle Count and Distribution					
	Date	Agitation*	RPM	Time Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$
<u>Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)</u>										
Fresh Distilled Water Comments: Cell cleaned with hexane, air, water	10/22	---	---	---	---	2004	618	90	14	4
Fresh Distilled Water Comments: Cell probed with shimstock, flushed with detergent	10/24	---	---	---	---	532	48	4	1	0
Kuwait Crude Comments: Instrument could not count particles, emulsion was too opaque	10/25	A3 B1	---	10 25	---	---	---	---	---	---

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Mixing Parameters				Particle Count and Distribution				
	Agitation*	RPM	Time Minutes	Time After Mixing	Counts/ 5 ml, less background				
<u>Oil injected into the test tube containing the small aliquot of water while subjected to ultra sonic agitation: (step A) Mixture then injected thru #20 needle to intake side of mixer in mixing (step B).</u>	A3	---	10	10	32096	18135	4443	993	180
	B1	2000	25						
Comments: Count rate too high, counts monitored to 45 min.									
South Louisiana Crude: 500 and Aerosol C-61 50	A3	---	10	10	22185	23582	17445	9522	2192
	B1	2000	75						
Comments: count rate too high, counts monitored to 45 minutes.									

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	Mixing Parameters				Particle Count and Distribution				
		Agitation *	RPM	Time	Seconds	Time After Mixing	2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$
<u>Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)</u>										
Lub. Oil 9250	11/5	A3 B1	---	10 25	10	32400	21237	7417	1679	153
Comments: Counts monitored up to 45 minutes; count rate too high.										
South Louisiana Crude and Product BC0	11/6	A3 B1	---	10 25	10	17020	21141	19082	14790	4961
Comments: Counts monitored up to 45 minutes; count rate too high.										
Lub. Oil 9250 and Product BC0	11/7	A3 B1	---	10 25	10	29121	17334	5860	2497	705
Comments: Counts monitored up to 45 minutes; count rate too high.										
MarineDiesel	11/11	A3 B1	---	45 25	---	---	---	---	---	---
Comments: Cell and Sensor blocked; was sent to manufacturer for cleaning and repairs. When the sensor and cell was returned, the original emulsions were diluted before taking data to avoid accumulation of detergent films or oils in the cell, and prevent instrumental saturation from high count rates. The data thus obtained follows in this appendix.										

PARAMETERS AND DATA OF PRELIMINARY INVESTIGATIONS FOR DEVELOPMENT OF EXPERIMENTAL TECHNIQUES

Oil Type and Concentration PPM	Date	* Agitation		RPM	Time Seconds	Time After Mixing	Particle Count and Distribution							
		A3	B1				2-4 $\mu$	4-7 $\mu$	7-10 $\mu$	10-15 $\mu$	15-25 $\mu$			
Oil, Water plus Detergent Added to Test Tube Which Then was Subjected to Sonification (Step A); Mixture then Injected thru #20 Needle to Intake Side of Mixer in Mixing (Step B)														
South Louisiana Crude and Aerosol C-61	10/30	A3	B1	--- 2000	10 25	10	17445	22224	21755	17260	5150			
Comments: Count rate too high, count monitored to 45 minutes.														
South Louisiana Crude and Pluradot HA-510	10/30	A3	B1	--- 2000	10 25	10	16869	22907	24030	21224	6817			
Comments: Count rate too high, count monitored to 45 minutes.														
South Louisiana Crude and Triton X-100	10/31	A3	B1	--- 2000	10 25	10	13132	18190	18694	18262	8859			
Comments: Count rate too high, counts monitored to 45 Minutes.														
Kuwait Crude	11/1	A3	B1	--- 2000	10 25	10	19914	5306	1370	647	230			
Comments: Counts monitored up to 45 minutes.														
Kuwait Crude and Aerosol C-61	11/1	A3	B1	--- 2000	10 25	10	27553	24446	13942	9873	5206			
Comments: Counts monitored up to 45 minutes, count rate too high.														
2190 TEP and Triton X-100	11/1	A3	B1	--- 2000	10 25	5	13982	15506	12723	9812	4235			
Comments: Counts monitored up to 45 minutes, count rate too high.														

Particle Size Distributions Obtained, With Coulter Counter, Model TA

Coulter Test Run	Volume % in Diameters:					Oil; Detergent	Sec. of Ultra sonic agitation time	No. of min. after mixing data taken:
	3.17-4.00 u	8.00-16.0u	12.7-25.4u	20.2-40.3u	40.3-50.8u			
1	1.8	3.5	6.0	8.0	20.0	2190-TEP; 50 ppm Klearfac AB-270	45	2
2	0.8	1.9	4.5	6.0	21.0	2190-TEP; 50 ppm Klearfac AB-270	45	13
3	5.3	7.3	9.0	8.7	15.0	Hydraulic; 25 ppm Klearfac AB-270	45	2
4	3.5	5.0	9.0	8.3	9.3	Hydraulic; 25 ppm Klearfac AB-270	45	10
5	5.0	5.0	8.0	11.9	13.0	So. Louis. Crude; 50 ppm Aerosol C-61	10	2
6	2.9	5.0	9.8	7.9	7.3	So. Louis. Crude; 50 ppm Aerosol C-61	10	10
7	1.0	2.8	7.2	12.0	24.8	So. Louis. Crude; 100 ppm Span 80	45	2
8	2.0	5.9	13.5	16.5	7.3	So. Louis. Crude; 100 ppm Span 80	45	10
9	3.0	5.9	8.6	10.0	16.3	Navy Sp Fuel Oil; 100 ppm Aerosol OT-75	45	2
10	5.7	5.9	8.7	9.0	13.9	Navy Sp Fuel Oil; 100 ppm Aerosol OT-75	45	10
11	0.5	2.0	4.0	5.2	7.8	Lub. Oil 9250; 100 ppm Aerosol OT-75	45	2
12	0.8	2.4	6.0	9.3	14.9	Lub. Oil 9250; 50 ppm Klearfac AB-270	45	2
13	0.8	2.0	4.0	6.8	20.0	Lub. Oil 9250; 50 ppm Klearfac AB-270	45	10
14	1.0	3.7	7.3	11.2	13.0	Lub. Oil 9250; 50 ppm Klearfac AB-270	45	13
15	1.0	3.0	6.0	8.0	15.0	Kuwait Crude; 50 ppm Alkano1 189-S	45	2

\*all input oil concentrations - 500 ppm  
(Emulsification Technique as outlined previously)

RAW DATA<sup>1</sup> FOR TABLE 4.1 AND TABLE 4.2

(see Matrix for Oil and Detergent/Concentration Code designation)

<u>Oil Code</u>	<u>Diameter, in microns</u>				
	<u>2-4<math>\mu</math></u>	<u>4-7<math>\mu</math></u>	<u>7-10<math>\mu</math></u>	<u>10-15<math>\mu</math></u>	<u>15-60<math>\mu</math></u>
C	1092	482	72	30	6
D	2048	689	82	21	5
A	28,438	8318	879	199	21
H	2826	658	92	26	9
E	1290	197	44	22	11
F	2156	859	151	81	19
B	2044	253	13	17	5
G	4295	690	50	20	2

---

<sup>1</sup>Particle count in 5 ml of 1:60 dilution of original dispersion, minus background counts  
5 min. after final mixing

RAW DATA<sup>1</sup> FOR TABLE 4.3

(DISPERSED OIL CONCENTRATION, ppm, WITH NON-IONIC DETERGENTS)

<u>Oil-Det. Code</u>	<u>Diameter, microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
C-25	8679	5018	1257	514	147
C-26	11,378	9337	2733	1195	141
C-27	6523	4455	1183	583	137
D-25	11,198	7171	1992	660	69
D-26	8089	4512	1285	610	123
D-27	5825	3520	899	434	75
A-26	7502	2128	435	213	54
H-26	5605	2278	507	216	41
F-25	4935	721	101	44	9
F-26	3015	763	199	90	15
F-27	2653	594	115	42	11
G-25	6319	4035	877	304	36
G-26	5411	3195	705	304	73
G-27	7826	2073	225	70	20
E-26	14,205	3398	480	208	80
D-22	9827	5269	1661	884	248
D-23	5460	2814	550	256	55
D-24	9401	6733	1828	909	175
A-22	15,023	5547	975	354	115
A-23	10,487	3293	400	113	28
A-24	13,343	3833	561	231	66
H-22	6337	2485	534	203	95
H-23	4966	2425	518	287	90
H-24	6591	2589	594	331	106
B-22	3727	1271	247	116	26
B-23	4091	1791	244	70	22
B-24	4264	1102	169	51	14
F-22	6627	1916	359	102	29
F-23	3591	915	171	61	19

(cont'd)

<sup>1</sup>Particle counts in 5 ml of 1:60 dilution minus background counts.  
5 min. after final mixing

RAW DATA FOR TABLE 4.3 (cont'd)

<u>Oil-Det. Code</u>	<u>Diameter, microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
F-24	6119	1230	205	71	22
G-22	8129	2670	463	187	56
G-23	1,1572	4151	499	188	63
G-24	8134	2926	434	130	43
C-19	2416	853	154	54	12
C-20	17,802	8255	1463	396	50
C-21	1360	491	97	53	6
D-19	3581	2013	446	234	45
D-20	3155	1580	316	133	8
D-21	9299	4366	707	334	48
A-19	14,507	2669	244	81	18
A-20	5790	965	109	43	15
A-21	8623	2373	390	122	30
B-19	2149	683	205	57	15
B-20	1229	403	47	28	3
B-21	1360	491	97	53	6
F-19	2893	802	106	41	15
F-20	2663	818	109	29	20
F-21	2493	824	103	41	10
G-19	5223	1375	218	63	12
G-20	5449	1707	355	128	33
G-21	3396	999	159	63	9
E-20	3470	745	140	47	14

RAW DATA<sup>1</sup> FOR TABLE 4.4

(Dispersed oil concentration, ppm, with cationic detergents)

<u>Oil-Det. Code</u>	<u>Diameter, in microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
C-15	29775	15720	2597	847	122
D-13	22351	7187	1013	335	53
D-15	27532	11471	1879	302	70
B-13	11216	3095	358	123	25
B-14	8212	2437	350	124	33
B-15	9992	3016	392	120	7
F-14	4922	987	140	47	4
A-15	37135	14010	1455	303	14
C-17	27115	10886	1219	260	34
B-18	36230	13571	1359	320	49
F-17	2944	513	50	18	5
F-18	15624	4145	335	92	17
A-18	36230	13571	1359	320	49
H-17	21368	7744	916	212	23
G-17	19316	6402	819	148	20

(cont'd)

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<sup>1</sup>Particle counts in 5 ml of 1:60 Dilution of original dispersion minus background counts, 5 min. after final mixing.

RAW DATA<sup>1</sup> FOR TABLE 4.4 (cont'd.)

<u>Oil-Det. Code</u>	<u>Diameter, in microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
C-10	20161	8356	2008	730	117
C-11	27115	10886	1219	260	34
C-12	21918	6521	883	262	47
A-12	36230	13571	1359	320	49
H-12					
B-10	5081	959	97	31	4
B-11	5589	1173	120	50	16
B-12	9359	1690	442	66	11
F-11	2229	450	77	28	7
G-12	23480	8001	665	201	28

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RAW DATA<sup>1</sup> FOR TABLE 4.5

(Dispersed Oil Concentration, ppm, with Anionic Detergents)

<u>Oil-Det. Code</u>	<u>Diameter, in microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
C-9	3494	2159	647	277	62
D-8	4516	2538	612	282	44
A-7	18173	5431	760	312	92
A-8	17241	3907	332	94	12
A-9	7331	2259	364	172	41
H-7	5614	2322	544	186	68
H-9	4503	1991	389	176	38
B-7	1849	673	97	36	10
B-9	952	356	93	36	8
F-7	5380	1375	124	43	10
F-8	4492	896	90	32	8
F-9	1967	409	42	20	6
G-7	5617	1637	225	88	15
E-8	11270	3982	950	410	89
E-9	6320	946	97	62	18
C-2	5495	3313	658	334	91
C-3	4548	2390	475	207	22
D-3	5208	4264	1157	423	46

(cont'd.)

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<sup>1</sup> Particle counts in 5 ml of 1:60 dilution of original dispersion, minus background counts, 5 minutes after final mixing.

RAW DATA FOR TABLE 4.5 (cont'd.)

<u>Oil-Det. Code</u>	<u>Diameter, in microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
A-3	18124	4418	651	128	23
H-3	14116	5707	935	401	126
B-1	5706	851	116	45	8
B-2	3658	938	190	63	20
B-3	2876	523	69	26	8
F-2	7396	2444	378	138	57
F-3	3199	909	119	37	11
G-3	4838	2805	535	199	50
E-3	9852	1640	278	134	51
C-4	2017	1565	296	103	12
C-5	2280	1483	269	149	45
C-6	3764	1991	503	205	34
D-4	5208	3279	695	295	58
A-5	28549	9953	1762	401	65
H-5	3216	1437	259	95	33
B-4	220	116	29	22	2
B-5	586	713	51	11	1
B-6	548	231	58	11	3
F-4	1139	392	68	33	7
F-5	3800	1078	161	50	10
F-6	4490	1372	258	110	17
G-5	1456	778	148	60	5
G-6	1732	629	154	48	18
E-4	5236	1001	142	65	16
E-5	4121	666	85	27	19
E-6	2861	609	118	63	27

RAW DATA<sup>1</sup> FOR TABLE 4.6

(Dispersed Oil Concentration, ppm, with Commercial Detergents)

<u>Oil-Det. Code</u>	<u>Diameter, microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-60</u>
D-28	3992	1761	309	133	39
D-29	3211	1592	333	137	14
D-30	1943	1522	340	144	28
B-28	1924	323	49	22	—
B-29					
F-28	4904	1135	109	43	12
F-29	2571	496	70	26	3
F-30	864	45	66	31	6
D-32	6224	2438	422	237	64
D-33	4448	2053	394	210	77
E-31	8520	1432	220	72	16
E-33	6698	1440	266	75	25
F-31	1589	273	66	25	11
F-32	2347	549	75	38	9
F-33	927	785	52	12	1
G-31	9327	2838	237	76	11
G-32	5402	1769	193	75	9
G-33	7161	2107	231	83	19
D-34	2324	1146	305	130	30
D-35	2743	1224	268	124	30
F-35	1485	606	140	57	11
E-35	709	87	27	9	0

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<sup>1</sup>Particle Counts in 5 ml of 1:60 dilution of original dispersion,  
minus background counts, 5 min. after final mixing.

RAW DATA<sup>1</sup> FOR TABLE 4.7

(Dispersed Oil Concentration, ppm, with High Molecular Weight Polymers)

<u>Oil-Det. Code</u>	<u>Diameter, in microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-1</u>	<u>10-15</u>	<u>15-35</u>
F-43	7127	1195	111	43	6
F-44	4921	692	69	37	10
F-45	3216	626	39	13	2
B-37	4485	1227	251	105	26
B-38	7303	421	59	30	9
B-39	1423	355	36	20	4
A-40	13345	2738	458	249	66
A-41	16421	3480	391	164	29
A-42	11732	2125	216	64	18

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<sup>1</sup>Particle counts in 5 ml of 1:60 dilution of original dispersion, minus background counts, 5 min. after final mixing.

RAW DATA FOR TABLE 4.13

(Effect of Temperature on Dispersed Oil Concentration)

<u>Temp.</u>	<u>Oil-Det. Code</u>	<u>2-4</u>	<u>Diameter, in microns</u>			<u>15-35</u>
			<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	
120°F	F-21	3773	1105	92	24	3
120°F	F-5	1964	754	73	21	0
120°F	F-14	15770	5305	556	134	9
120°F	G-14	44144	15814	1149	124	0
120°F	G-7	3177	1101	160	29	3
120°F	G-23	8083	3093	471	168	36
40°F	G-5	4972	1471	145	53	19
120°F	B-3	2876	523	69	26	8
120°F	B-21	2785	783	88	21	0
120°F	D-12	17711	5661	441	46	0
120°F	D-21	3687	2175	448	130	23
120°F	D-3	8693	5143	664	98	0
120°F	H-3	31276	12980	1339	243	14
40°F	H-3	17550	5405	769	358	93
120°F	E-3	9291	2155	307	101	16
40°F	E-12	2247	400	53	18	5
120°F	C-16	23885	7294	503	58	3
120°F	A-14	43348	22211	2360	355	12
120°F	A-23	35585	13752	1625	313	31

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<sup>1</sup> Particle counts in 5 ml of 1:60 Dilution of original dispersion minus background counts 5 min. after final mixing.

RAW DATA<sup>1</sup> FOR TABLE 4.13

(Effect of pH on Dispersed Oil Concentration)

pH	Oil-Det. Code	Diameter, in microns				
		<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-35</u>
6	A-23	28720	14540	2624	892	217
8	A-2	25203	7379	752	208	57
6	A-2	13156	2259	367	135	42
6	C-2	5803	3501	798	412	97
6	C-27	6729	3933	870	471	80
6	C-19	4337	2887	787	438	94
6	C-22	9317	6907	1927	1203	424
6	C-11	17750	6328	876	333	78
6	B-2	7493	2527	329	120	23
6	B-18	6614	1476	135	37	14
6	B-11	4055	803	102	50	11
8	B-4	1057	404	75	27	5
8	B-27	5729	1550	216	98	11
6	B-23	4403	1522	247	117	23
6	F-19	3045	738	65	40	11
6	F-19	2632	831	122	44	10
6	F-11	8619	2499	307	112	34
6	F-2	9228	2143	185	50	7
6	F-23	4558	1552	248	90	30
6	G-2	12031	3878	353	110	17
8	G-11	10437	3326	374	136	20
8	G-4	4775	1744	246	105	34
8	G-23	13938	5156	712	240	46
6	G-23	8960	2096	245	97	19
6	G-11	16802	4743	404	101	8
6	D-23	21543	9352	1803	714	135
8	D-23	9337	5344	1275	543	117
6	D-2	6171	4565	1065	592	102
6	D-18	23693	7964	678	189	18
6	D-11	16352	4342	1013	405	80
6	H-2	5918	3188	531	242	43
6	H-11	27405	10922	1518	481	97
6	H-23	28720	14540	2624	892	217

<sup>1</sup>Particle counts for 5 ml of 1:60 dilution of original dispersion, minus background counts; 5 min. after final mixing.

RAW DATA<sup>1</sup> FOR TABLE 4.15

(Effect of Salinity on Dispersed Oil Concentration)  
- all values are for dispersions generated in water of 50% salinity-

<u>Oil-Det. Code</u>	<u>Diameter, in microns</u>				
	<u>2-4</u>	<u>4-7</u>	<u>7-10</u>	<u>10-15</u>	<u>15-35</u>
C-10	12570	6005	892	493	100
C-1	8122	2654	260	89	24
C-22	12399	9666	2670	1344	299
A-22	10720	2827	352	153	51
B-10	3501	1048	116	52	11
F-1	5972	1858	208	77	19
F-10	6662	1980	260	96	22
D-1	8956	5489	1358	719	128
D-10	11036	6573	1396	684	440

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<sup>1</sup>Particle counts in 5 ml of 1:60 dilution of original dispersion,  
minus background counts; 5 min. after mixing.

**RAW DATA<sup>1</sup> TABLE 4.16**

**(Dispersed Oil Present as Droplets Smaller than Ten Microns With High Detergent Concentration)**

Oil-Det. Code	Diameter, in microns				
	2-4	4-7	7-10	10-15	15-35
C-46	7604	3496	874	245	37
P(I) <sup>2</sup>	8.9	33.1	54.6	74.0	100.0
C-47	5479	3903	1264	435	67
P(I)	4.4	22.9	44.2	67.7	100.0
C-48	5134	2908	848	309	54
P(i)	5.5	23.9	43.0	65.3	100.0
C-49	8099	5499	2073	916	230
P(I)	2.8	14.2	29.6	51.3	100.0
C-50	7572	6137	2168	1087	210
P(I)	2.6	15.2	31.0	56.3	100.0
C-51	6107	4643	1516	658	155
P(I)	3.0	16.6	32.2	54.1	100.0
C-52	7342	6010	2208	1054	192
P(I)	2.6	15.6	32.4	58.1	100.0
C-53	8834	5523	1606	816	136
P(I)	4.1	19.6	35.5	61.4	100.0
C-54	5851	3152	808	331	86
P(I)	5.0	21.2	35.9	55.2	100.0
B-46	2819	842	158	65	20
P(I)	10.2	28.3	40.4	56.3	100.0
B-47	3641	895	136	50	21
P(I)	13.0	32.1	42.4	54.6	100.0
B-48	1065	413	81	37	10
P(I)	7.7	25.6	38.0	56.2	100.0
B-49	3775	1946	525	244	59
P(I)	4.8	19.6	33.6	54.7	100.0
B-50	3592	1572	329	185	43
P(I)	6.1	22.2	34.1	55.5	100.0
B-51	2343	831	194	100	28
P(I)	6.7	20.8	32.4	51.8	100.0
B-52	6118	1822	307	145	30
P(I)	11.9	33.0	45.6	64.7	100.0
B-53	3192	762	114	60	5
P(I)	18.5	44.9	58.9	82.5	100.0
B-54	6591	1285	152	49	15
P(I)	22.1	47.8	58.5	69.6	100.0

<sup>1</sup>Particle counts for 5 ml of 1:60 dilution of original dispersion.  
<sup>2</sup>P(I) - Computer-calculated cumulative volume percent.

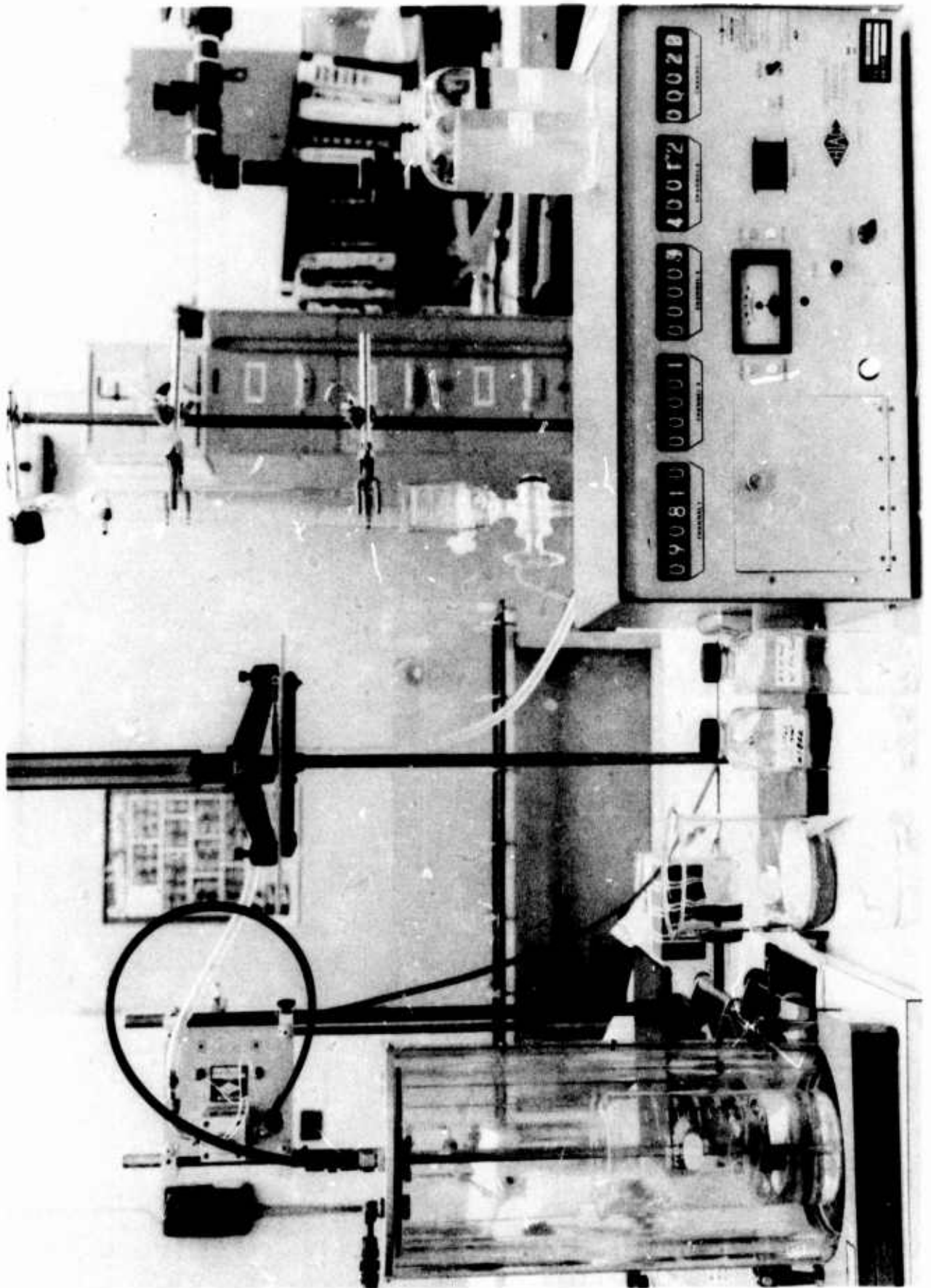


Fig. 1 - HIAC Counter, HIAC Bottle Sampler AB-11

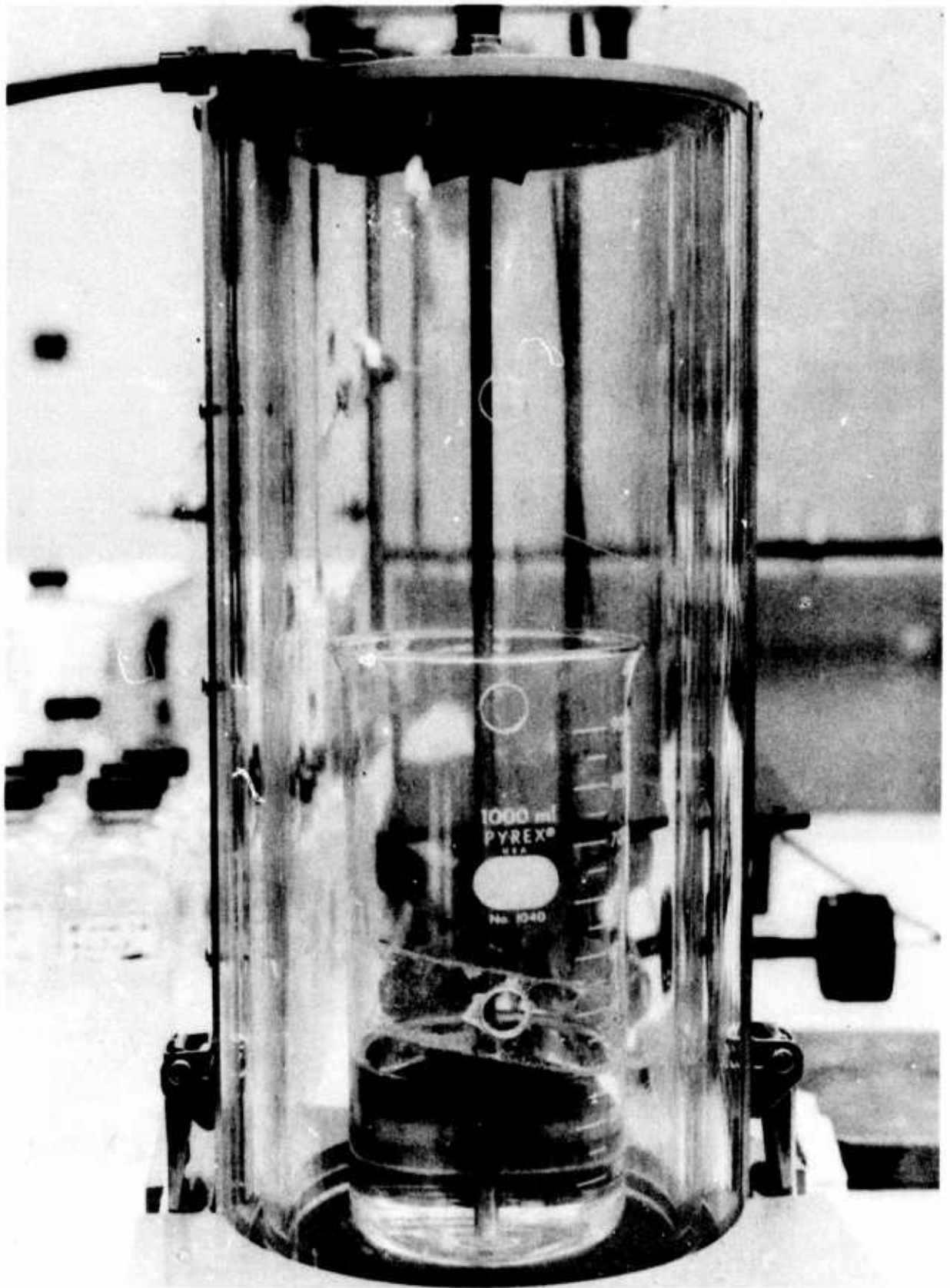


Fig. 2 - Sample in HIAC Bottle Sampler AB-110

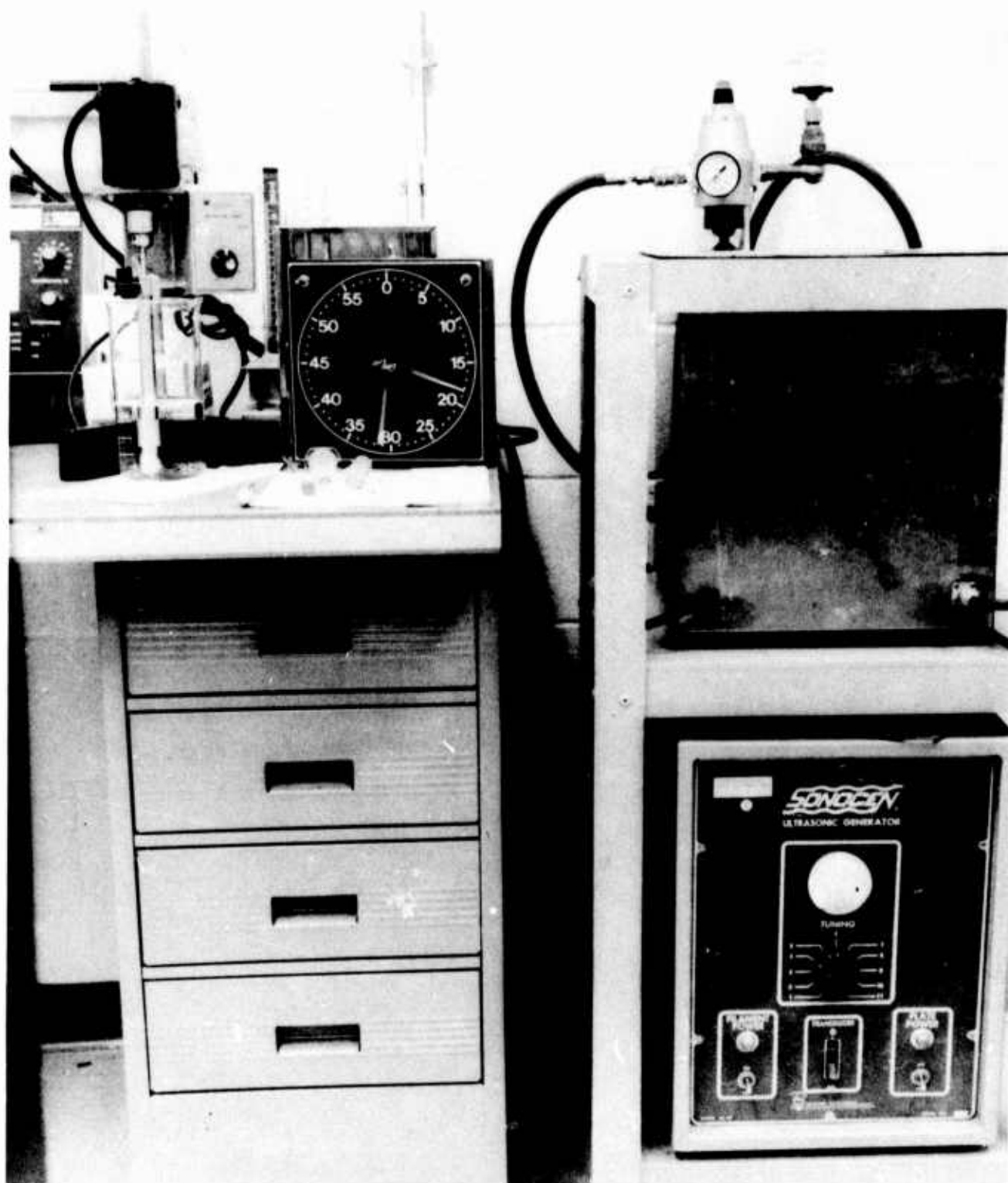


Fig. 3 - Ultrasonic Bath, Syringes, Timer, and Non-Aerating Dispersator, Model S-25

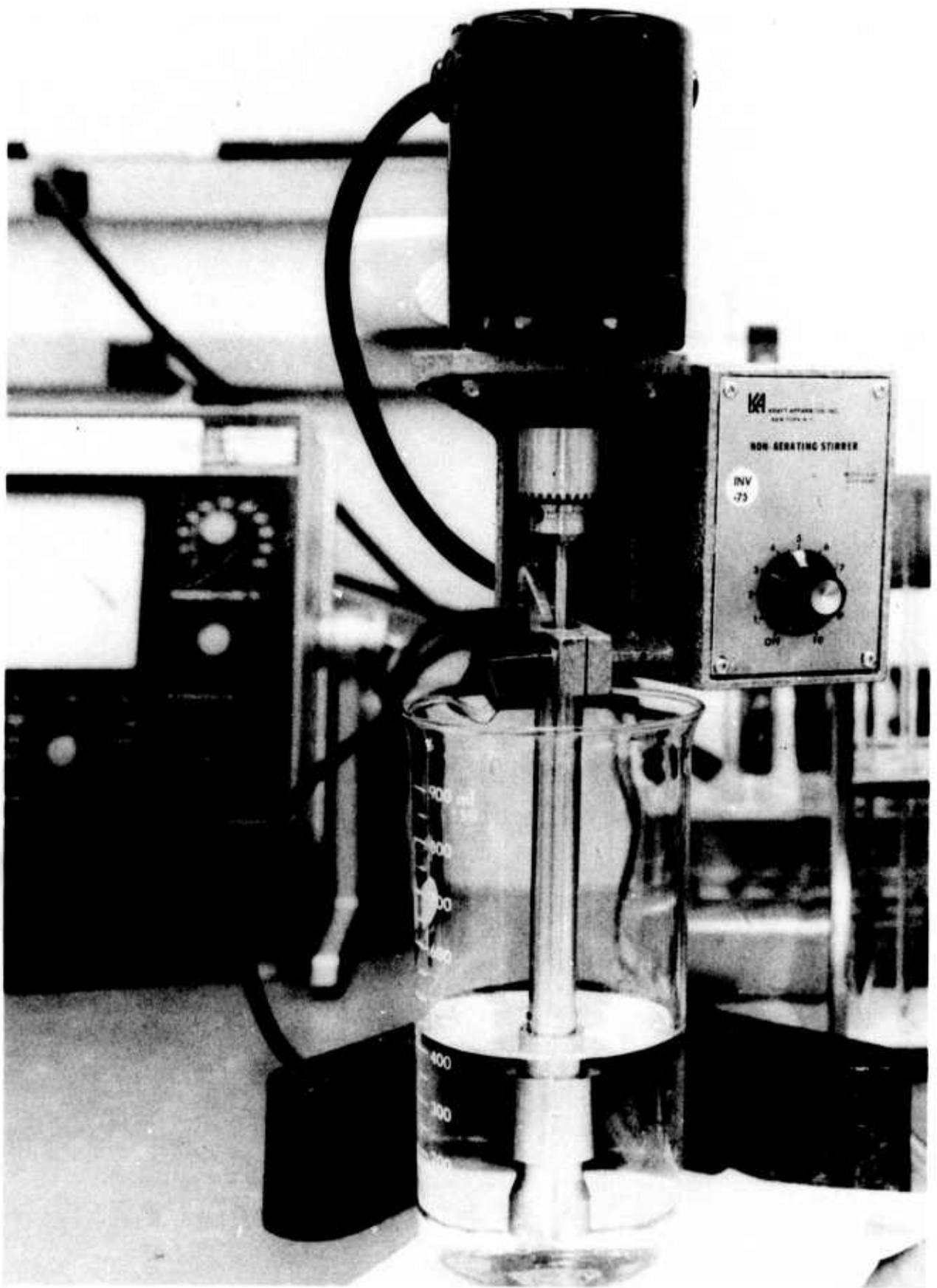


Fig. 4 - Kraft Non-Aerating Dispersator, Model S-25