# 1991 NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

## JOHN F. KENNEDY SPACE CENTER
## UNIVERSITY OF CENTRAL FLORIDA

# PRECISION CLEANING VERIFICATION OF NONVOLATILE RESIDUES BY USING WATER, ULTRASONICS AND TURBIDITY ANALYSES


| | |
|---|---|
| PREPARED BY: | Dr. S. Balloû Skinner |
| ACADEMIC RANK: | Professor |
| UNIVERSITY AND DEPARTMENT: | The University of South Carolina<br>Coastal Carolina College<br>Physics Department |
| NASA/KSC | |
| DIVISION: | Materials Science Laboratory |
| BRANCH: | |
| NASA COLLEAGUE: | Mr. Charles W. Hoppesch |
| DATE: | July 19, 1991 |
| CONTRACT NUMBER: | University of Central Florida<br>NASA-NGT-60002 Supplement: 6 |

ACKNOWLEDGMENT

I am grateful to the NASA/ASEE Summer Faculty Fellowship Program and to Mr. Charles W. Hoppesch, Chief of the Materials Science Laboratory of the Engineering Development Directorate at the Kennedy Space Center (KSC), for the opportunity of spending an enjoyable, productive and rewarding summer verifying precision cleaning of nonvolatile residues by using water, ultrasonics and turbidity analyses.

There are many people who assisted me in the research project. First and foremost was Mr. Charlie Hoppesch whose consultation, guidance and advice was most valuable. I greatly valued the helpfulness of Mr. Ed Dumas for the preparation of graphs and figures. I am also grateful to Mr. Billy Dearing for his assistance and advice throughout the project.

I further acknowledge the generous assistance provided by Mr. Jim Jones, Chief of the Microchemical Analysis Branch, Messrs. Lee Underhill and Charlie Bassett and Ms. Martha Williams.

Also, appreciation goes to Mr. Mitchell Buckely for his help in sample preparation and testing and Ms. Gayle Krisingha for typing this paper.

The expertise and kindness of the program director, Dr. Ray Hosler, is also gladly acknowledged.

ABSTRACT

Chlorofluorocarbons (CFC's) in the atmosphere are believed to present a major environmental problem because they are able to interact with and deplete the ozone layer. NASA has been mandated to replace chlorinated solvents in precision cleaning, cleanliness verification and degreasing of aerospace fluid systems hardware and ground support equipment. The Kennedy Space Center has a CFC phase-out plan which provides for the elimination of over 90% of the CFC and halon use by 1995.

The Materials Science Laboratory at the Kennedy Space Center is evaluating four analytical methods for the determination of nonvolatile residues removal by water: (1) Infrared analyses using an Attenuated Total Reflectance, (2) Surface Tension analyses, (3) Total Organic Content analyses, and (4) Turbidity analyses.

This research project examined the ultrasonic-turbidity responses for 22 hydrocarbons in an effort to determine (1) if ultrasonics in heated water (70°C) will clean hydrocarbons (oils, greases, gels and fluids) from aerospace hardware, (2) if the cleaning process by ultrasonics will simultaneously emulsify the removed hydrocarbons in the water, and (3) if a turbidimeter can be used successfully as an analytical instrument for quantifying the removal of the hydrocarbons.

Sixteen of the 22 hydrocarbons tested showed that ultrasonics would remove at least 90% of the contaminated hydrocarbon from the hardware in 10 minutes or less giving a good ultrasonic-turbidity response. Six hydrocarbons had a lower percentage removal, a slower removal rate and a marginal ultrasonic-turbidity response.

TABLE OF CONTENTS


| SECTION | TITLE |
|---|---|
| I. | **Introduction** |
| | 1.1 Background Information<br>1.2 Purpose of the Research |
| II. | **Instrumentation** |
| | 2.1 Ultrasonic Cleaning with Water<br>2.2 Turbidimetric Analyses |
| III. | **Criteria for Acceptance Standards** |
| IV. | **Design of the Experiment** |
| V. | **Results and Analysis** |
| VI. | **Conclusions and Recommendations** |
| VII. | **References** |

## List of Illustrations


| Figure | Title |
|---|---|
| 1 | Ultrasonic Cleaner |
| 2 | Fitting |
| 3 | Turbidimeter |
| 4 | Sonic Dismembrator |
| 5 | Virtis Emulsifier and Hand Mixer |
| 6 | Hydrocarbons Tested |
| 7-9 | Ultrasonic - Turbidity Response |
| 10 | Data Sheet |

## List of Tables


| Table | Title |
|---|---|
| 1 | List of Hydrocarbons Tested |
| 2-3 | Turbidity Response to Weight Removed |

# I. Introduction

## 1.1 Background Information

Chlorofluorocarbons (CFC's) in the atmosphere are believed to present a major environmental problem because they are able to interact with and deplete the ozone layer. As the ozone layer deteriorates, more ultraviolet radiation reaches the Earth's surface, causing skin cancer, eye cataracts and immune deficiencies in people, reducing crop yields and wreaking havoc on other life forms.

In accordance with the NASA Headquarters policy letter on the use of CFC and halon compounds (dated June 26, 1990), Kennedy Space Center (KSC) has developed a CFC and halon phase-out plan to comply with the established requirements. Annual KSC use of CFC and halons was 450,000 lbs. in 1989. About 70% of this usage was for solvent and cleaning operations. Approximately 25% was refrigerant make-up for facility and ground support equipment in heating, ventilation, air conditioning and refrigerant operations. The phase-out plan provides for the elimination of over 90% of the CFC and halon use at KSC by 1995.

At KSC, the Wiltech cleaning facility is responsible for precision cleaning, cleanliness verification and degreasing of fluid systems hardware and ground support equipment used in the Space Shuttle launch operations. The KSC precision cleaning specifications require a cleanliness inspection in which 1,1,2-trichlorotrifluoroethane (CFC-113) is used as the verification fluid for gravimetric nonvolatile residue (NVR) analysis. The cleaned parts/components are rinsed with the verification fluid and NVR is defined as the nonvolatile material remaining after the filtration and evaporation of a volatile solvent (verification fluid, CFC-113).

## 1.2 Purpose of the Research

In an effort to convert from a CFC system (pre-clean and cleanroom) to a totally aqueous system, water is being evaluated as a precision cleaning verification fluid.

There are four analytical methods being evaluated in the Materials Science Laboratory at KSC for the determination of nonvolatile residues removal by water: (1) Infrared analyses using an Attenuated Total Reflectance (ATR), (2) Surface Tension analyses, (3) Total Organic Content (TOC) analyses, and (4) Turbidity analyses.

My research employed the turbidity analyses. The research design addressed the following questions:

1. Will ultrasonics in heated water (70°C) clean hydrocarbons (oils, greases, gels and fluids) from aerospace hardware?

2. Will the cleaning process by ultrasonics simultaneously emulsify the removed hydrocarbons in the water?

3. Can the turbidimeter be used successfully as an analytical instrument for quantifying the removal of the nonvolatile residues (hydrocarbons) from the hardware in the heated water via ultrasonic cleaning?

## II. Instrumentation

### 2.1 Ultrasonic Cleaning with Water

The ultrasonic cleaner used in this research to remove hydrocarbons from aerospace hardware is a Branson 521 ultrasonic cleaner (Figure 1). The tank size is 12"L X 10.5"W X 8"D. It has four bottom mount piezoelectric transducers which operate at a frequency of 40 kilohertz and 200 watts power. Seventy degree centigrade (70°C) demineralized water is used as the liquid cleaning solution.

A 3/8 inch fitting (Figure 2) is the hardware on which the hydrocarbon contaminant is deposited. The fitting is placed in a 1000 ml beaker holding 500 ml of water. The beaker is suspended in a 70°C water bath for ultrasonic cleaning.

### 2.2 Turbidimetric Analyses

The turbidimeter used in this research is a DRT-100B (H.F. Scientific, Inc.) (Figure 3). It is a direct reading Nephelometric Instrument which measures scattered light from colloidal suspensions (or from particles in suspension) and direct light passing through a liquid. The ratioed optical signal which results is stabilized and amplified to energize a meter. The turbidimeter provides a linear display of turbidity in nephelometric turbidity units (NTU's).

Turbidity is an expression of the optical properties that cause light to be scattered or absorbed through a liquid sample and is largely a function of the refractive index, the size and shape of the particles suspended in the solution. As a result, turbidimeters do not produce an "absolute" measurement, but one that is "relative" to the optical nature of the solids suspended in a solution. Formazin polymer is accepted as the turbidity standard because when carefully prepared, it is uniform in number, size and shape of its particles.

## III. Criteria for Acceptance Standards

The standard for precision cleaning at Wiltech states that if more than one milligram of the nonvolatile residue (in 500 milliliters of a verification fluid) is removed from one square foot of hardware, the cleanliness of the hardware is considered nonacceptable and must be recycled in the precision cleaning process.

## IV. Design of the Experiment

Over 120 tests were conducted in order to answer the following questions regarding hydrocarbon response to ultrasonic cleaning-turbidity reading:

1. Which is the better remover of hydrocarbons from the fittings: the ultrasonic cleaner or the sonic dismembrator (Figure 4)?

2. Which is the better remover of hydrocarbons from the fittings: ambient water (25°C) or hot water (70°C)?

3. Will ultrasonics emulsify the hydrocarbons in water or will a virtis emulsifier or hand mixer (Figure 5) be needed?

4. Will ultrasonics remove the hydrocarbons no matter how or where they are located on the fitting?

5. Will ultrasonics remove the hydrocarbons from the fittings (percentage removed) and how long does it take for this removal (removal rate)? In other words, is ultrasonic cleaning effective on all hydrocarbons? Will we see a good ultrasonic-turbidity response for all the hydrocarbons?

## V. Results and Analysis

Test results from the questions proposed in Part IV are discussed below:

1. The analysis of 10 tests revealed that the ultrasonic cleaner was better than the sonic dismembrator at removing the hydrocarbon from the fittings. Therefore, all tests were conducted with the ultrasonic cleaner. The testing procedure called for placing a fitting contaminated with a hydrocarbon into 500 ml of water in a 1000 ml polyethylene beaker and ultrasounding for 2 minute intervals up to 10 minutes. If less than 75% of the hydrocarbon has been removed after 10 minutes, the fitting is further ultrasounded for 5 minute intervals up to 40 minutes or until more than 75% of the hydrocarbon is removed. Turbidity readings in NTU's are displayed by a turbidimeter and recorded at the end of each time interval (Figure 10).

2. The analysis of 8 tests showed that hot water (70°C) on an average would give a three-fold increase in removal rate of hydrocarbons from the fittings compared to ambient water (25°C). This research convinced me that it is crucial to keep the water in the beaker and the water in the ultrasonic bath at 70°C throughout the testing for optimum cleaning.

3. The research indicated that the ultrasonics in the heated water (70°C) were successful in emulsifying the removed hydrocarbons. Further testing revealed that the use of a hand mixer or a virtis emulsifier added very little to the total emulsification as shown by the turbidity responses.

4. A limited number of tests showed that ultrasonics were successful in removing the hydrocarbons no matter where or how they were located on the fitting, i.e., on the top, down in the hole, on the threads, in a glob, or spread out uniformly. However, more tests probably need to be run to substantiate this claim.

5. A list of 22 hydrocarbons tested (Figure 6) with their generic name, chemistry, percent and time for ultrasonic removal of one milligram and ultrasonic turbidity (NTU) is given in Table 1.

Table 1 shows that Krytox 240AC (77% removal, 40 min., 0.6 turbidity), DS-FS-1265 (75% removal, 30 min., 0.7 turbidity), Titan-Lube (68% removal, 40 min., 0.8 turbidity), Halovac 100 (100% removal, 35 min., 0.5 turbidity), DC-200 (100% removal, 25 min., 1.0 turbidity) and Dri-Tube (85% removal, 40 min., 0.9 turbidity) are the hydrocarbons with marginal ultrasonic-turbidity response at the 1 mg level. Additional tests using 5 mg and 10 mg samples for 10 minute ultrasonics will be run in the future to determine if an acceptable ultrasonic-turbidity response can be seen for these marginal hydrocarbons at these higher contamination levels.

Tables 2 and 3 depict each of the 22 hydrocarbons with the weight of the hydrocarbon removed from the fitting via ultrasonics along with corresponding turbidity readings. The data in Tables 2 and 3 is displayed in graphical form in Figures 7, 8 and 9.

Figures 7, 8 and 9 show that there is a direct relationship between turbidity and the hydrocarbon emulsified in the 500 ml of water for all 22 hydrocarbons. There is a linear relationship between ultrasonic removal of hydrocarbon and turbidity response at the 1/2 mg, 1 mg and 2 mg levels for all 22 hydrocarbons. It further shows clearly that six hydrocarbons (Krytox 240AC, DS-FS-1265, Titan-Tube, Halovac 100, DC-200 and Dri-Lube) have marginal ultrasonic-turbidity responses while 16 other hydrocarbons have good responses.

The slope of the lines in Figures 7, 8 and 9 is an indicator of the emulsion taking place and the capability of the hydrocarbon to remain in emulsion. The lines which are almost parallel (near "zero" slope) and close to the X-axis are those hydrocarbons which give marginal ultrasonic-turbidity responses. These are the problem hydrocarbons. The lines which are high above the X-axis and have large slopes are those hydrocarbons which have good ultrasonic-turbidity responses. These hydrocarbons present no problems in the verification of precision cleaning.

## VI. Conclusions and Recommendations

Approximately three quarter of the 22 hydrocarbons tested showed that ultrasonics would remove at least 90% of the contaminant from the fitting in 10 minutes or less. The hydrocarbons giving low percentage removal over long times of ultrasonics with low turbidity readings were two silicones, a fluorosilicone, a fluorinated polyether, a PCTFE and an Isobutylene.

This research project shows that hot water (70°C), ultrasonics and turbidity analyses can be used for precision cleaning verification of most nonvolatile residues. For the marginal ultrasonic-turbidity response hydrocarbons, better cleaning methods for removing hydrocarbons need to be found and other analytical methods may be needed in conjunction with the ultrasonics-turbidity analyses (e.g., infrared analyses using an attenuated total reflectance, surface tension analyses, total organic carbon analyses, fluorescence/scatter analyses, or some method to be determined) to completely solve the problem of quantifying the removal of nonvolatile residues by water.

## VII . References


1. "Encyclopedia of Chemical Technology", Vol. 8, 1978, New York, John Wiley and Sons, 900-930.

2. "Encyclopedia of Chemical Technology", Vol. 22, 1978, New York, John Wiley and Sons, 332-347.

3. Halbut, Jim, "Ultrasonic Cleaning with Water, Sonic Report No. SR1641", Delta Sonic, Inc., 1987.

4. Instruction Manual, DRT-100B and DRT-100B Research Turbidimeters, July 1990, Published by H.F. Scientific, Inc., Fort Myers, Florida.

5. Kashkoush, I. and Busnaina, A., "Submicron Particle Removal from Surfaces Using Acoustic Streaming", 1991 Proceedings, Institute of Environmental Sciences, 861-867.

6. Law, R. J., "Analytical Methods and Their Problems in the Analysis of Oil in Water", 1990 Seminar Proceedings, Ministry of Agriculture, Fisheries and Food, Buraham-on-Cronch, UK.

7. Sherman, Alan and Sherman, Sharon J., "Chemistry and Our Changing World", Second Edition, 1989, McGraw-Hill Publishing Company, New York, NY, 462-471.

| HYDROCARBON | GENERIC | CHEMISTRY | ULTRASONIC REMOVAL (1MG) PERCENT TIME | ULTRASONIC TURBIDITY (NTV) |
|---|---|---|---|---|
| DC-200 | FLUID | SILICONE | 100 (25M) | 1.0 |
| HOUGHTON SAFE 1055 | FLUID | PHOSPHATE ESTER BASED HYROCARBON | 98 (10M) | 2.9 |
| MOBIL JET II | FLUID | ESTER BASED HYDROCARBON | 100 (10M) | 2.5 |
| AMOCO - RYKON #2 | GREASE | HYDROCARBON | 100 (16M) | 2.8 |
| MOBIL - MOBILUX 2 | GREASE | HYDROCARBON | 100 (6M) | 2.8 |
| CHEVRON SRI | GREASE | HYDROCARBON | 100 (8M) | 3.0 |
| SHELL TELLUS - 32 | FLUID | HYDROCARBON | 100 (8M) | 2.4 |
| MIL-G-8188C | FLUID | ESTER BASED HYDROCARBON | 100 (4M) | 2.0 |
| MIL-G-5606 | FLUID | HYDROCARBON | 100 (6M) | 1.7 |
| CASTROL MOTOR OIL | FLUID | HYDROCARBON | 100 (10M) | 2.1 |
| DC-55M | GREASE | SILICONE | 100 (10M) | 1.3 |
| DRILUBE - TYPE 822 | GREASE | SILICONE | 85 (40M) | 0.9 |
| MIL-H-83282 | FLUID | ESTER BASED HYDROCARBON | 100 (10M) | 2.3 |
| MIL-G-3545C | GREASE | HYDROCARBON, SOAP ADDITIVE | 90 (10M) | 2.4 |
| DC-44 | GREASE | SILICONE | 91 (10M) | 2.8 |
| KRYTOX 240AC | GREASE | FLUORINATED POLYETHER | 77 (40M) | 0.6 |
| DC-33 | GREASE | SILICONE | 90 (8M) | 1.1 |
| HALOVAC 100 SB | FLUID | PCTFE | 100 (35M) | 0.5 |
| DC FS-1265 | FLUID | FLUOROSILICONE | 75 (30M) | 0.7 |
| MIL-G-23549C | GREASE | HYDROCARBON GREASE CONTAINING MOLYB-DENUM DISULFIDE | 54 (35M) | 1.6 |
| MINERAL OIL | FLUID | HYDROCARBON | 91 (10M) | 1.2 |
| TITAN LUBE | FLUID | ISOBUTYLENE | 68 (40M) | 0.8 |

TABLE 1 - LIST OF HYDROCARBONS TESTED

| HYDROCARBON | WEIGHT OF HYDROCARBON REMOVED FROM FITTING (Mg) | TURBIDITY (NTU) |
|---|---|---|
| DC-200 | 0.52 | 0.4 |
| | 0.83 | 0.7 |
| | 0.94 | 1.0 |
| | 1.68 | 1.3 |
| HOUGHTON-SAFE 1055 | 0.26 | 0.8 |
| | 1.08 | 2.9 |
| | 2.06 | 3.5 |
| MOBIL JET II | 0.34 | 1.1 |
| | 0.93 | 2.5 |
| | 1.50 | 2.8 |
| AMOCO-RYKON #2 | 0.45 | 0.9 |
| | 0.80 | 1.5 |
| | 0.96 | 2.8 |
| MOBIL-MOBILUX 2 | 0.51 | 1.9 |
| | 1.06 | 2.8 |
| | 2.09 | 4.8 |
| CHEVRON SRI | 0.48 | 0.9 |
| | 1.00 | 3.0 |
| | 1.96 | 6.2 |
| SHELL TELLUS-32 | 0.60 | 1.4 |
| | 1.04 | 2.4 |
| | 1.95 | 4.8 |
| MIL-G-8188C | 0.47 | 1.1 |
| | 0.96 | 2.0 |
| | 2.18 | 3.8 |
| MIL-G-5606 | 0.55 | 1.0 |
| | 1.09 | 1.7 |
| | 2.22 | 3.7 |
| TITAN LUBE | 0.35 | 0.6 |
| | 0.67 | 0.8 |
| | 1.36 | 0.9 |
| CASTROL MOTOR OIL | 0.62 | 1.3 |
| | 0.97 | 2.1 |
| | 2.09 | 4.4 |

TABLE 2 - TURBIDITY RESPONSE TO WEIGHT REMOVED

| HYDROCARBON | WEIGHT OF HYDROCARBON REMOVED FROM FITTING (Mg) | TURBIDITY (NTU) |
|---|---|---|
| DC-55M | 0.48 | 0.7 |
| | 0.92 | 1.3 |
| | 2.00 | 2.4 |
| DRILUBE-TYPE 822 | 0.38 | 0.3 |
| | 0.94 | 0.9 |
| | 1.29 | 1.3 |
| MIL-H-83282 | 0.55 | 1.3 |
| | 1.29 | 2.3 |
| | 2.18 | 4.0 |
| MIL-G-3545C | 0.46 | 1.8 |
| | 0.94 | 2.4 |
| | 2.08 | 5.5 |
| DC-44 | 0.52 | 0.9 |
| | 0.99 | 2.8 |
| | 1.30 | 3.4 |
| KRYTOX 240 AC | 0.32 | 0.2 |
| | 0.73 | 0.5 |
| | 0.77 | 0.6 |
| DC-33 | 0.43 | 0.3 |
| | 0.94 | 1.1 |
| | 2.00 | 2.0 |
| HALOVAC 100 SB | 0.56 | 0.3 |
| | 0.97 | 0.5 |
| | 0.98 | 0.5 |
| DC-FS-1265 | 0.22 | 0.5 |
| | 0.66 | 0.7 |
| | 0.88 | 0.7 |
| MIL-G-23549C | 0.31 | 1.2 |
| | 0.77 | 1.6 |
| | 1.17 | 2.2 |
| MINERAL OIL | 0.49 | 0.6 |
| | 0.95 | 1.2 |
| | 1.52 | 1.7 |

TABLE 3 - TURBIDITY RESPONSE TO WEIGHT REMOVED

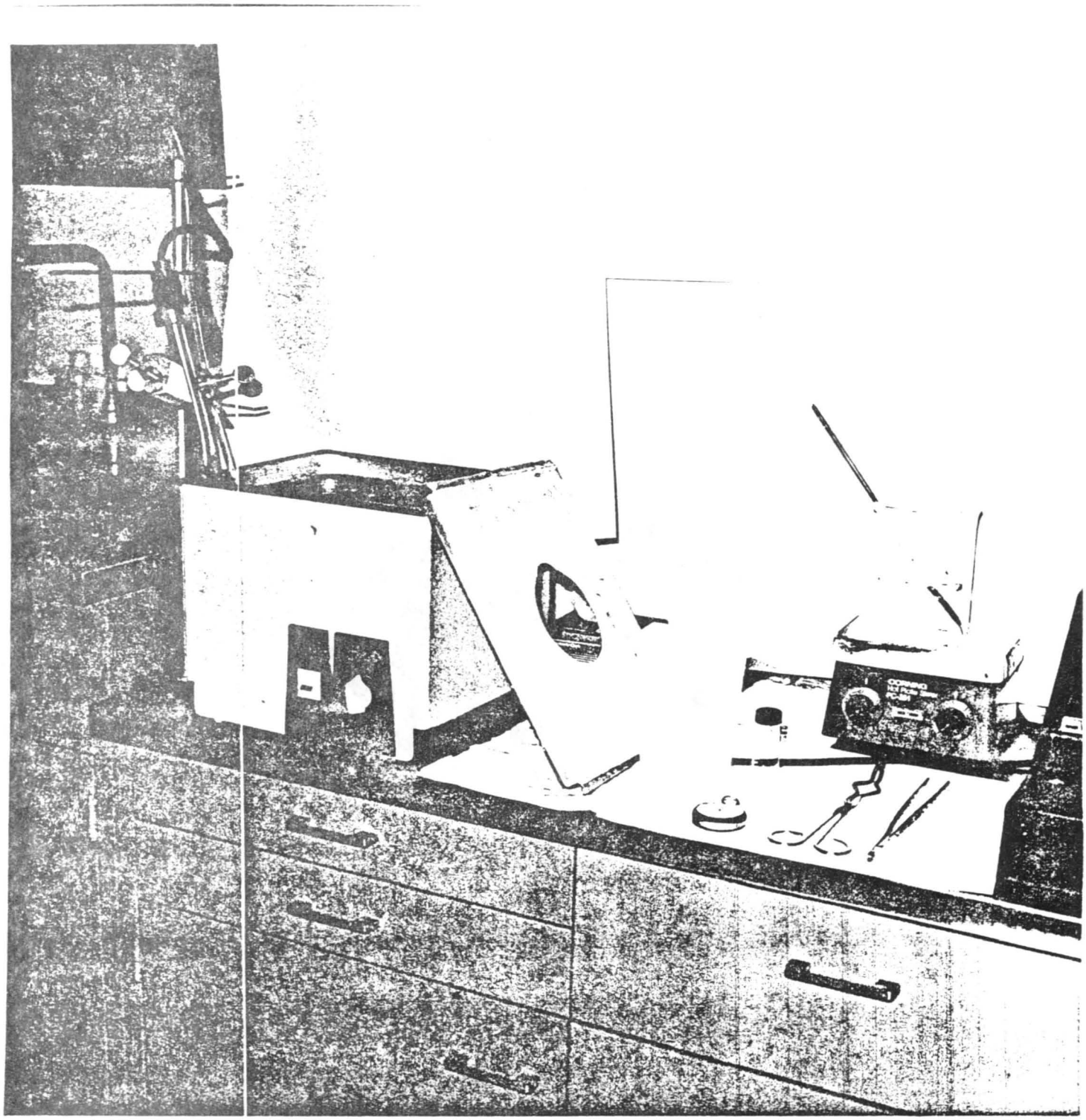

Figure 1. Ultrasonic Cleaner

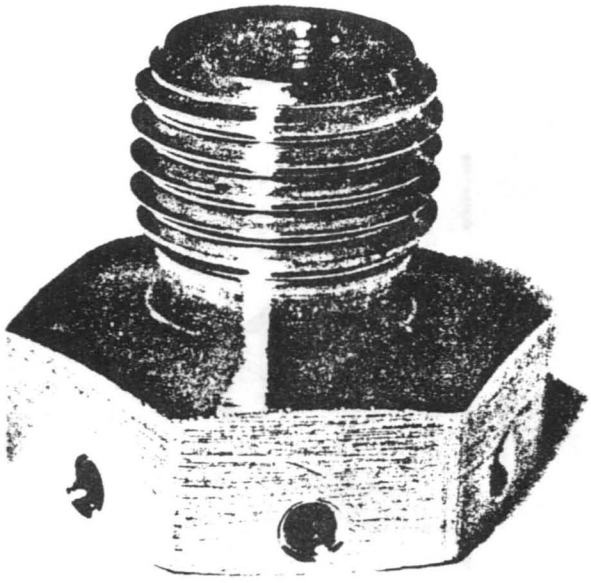

Figure 2. Fitting

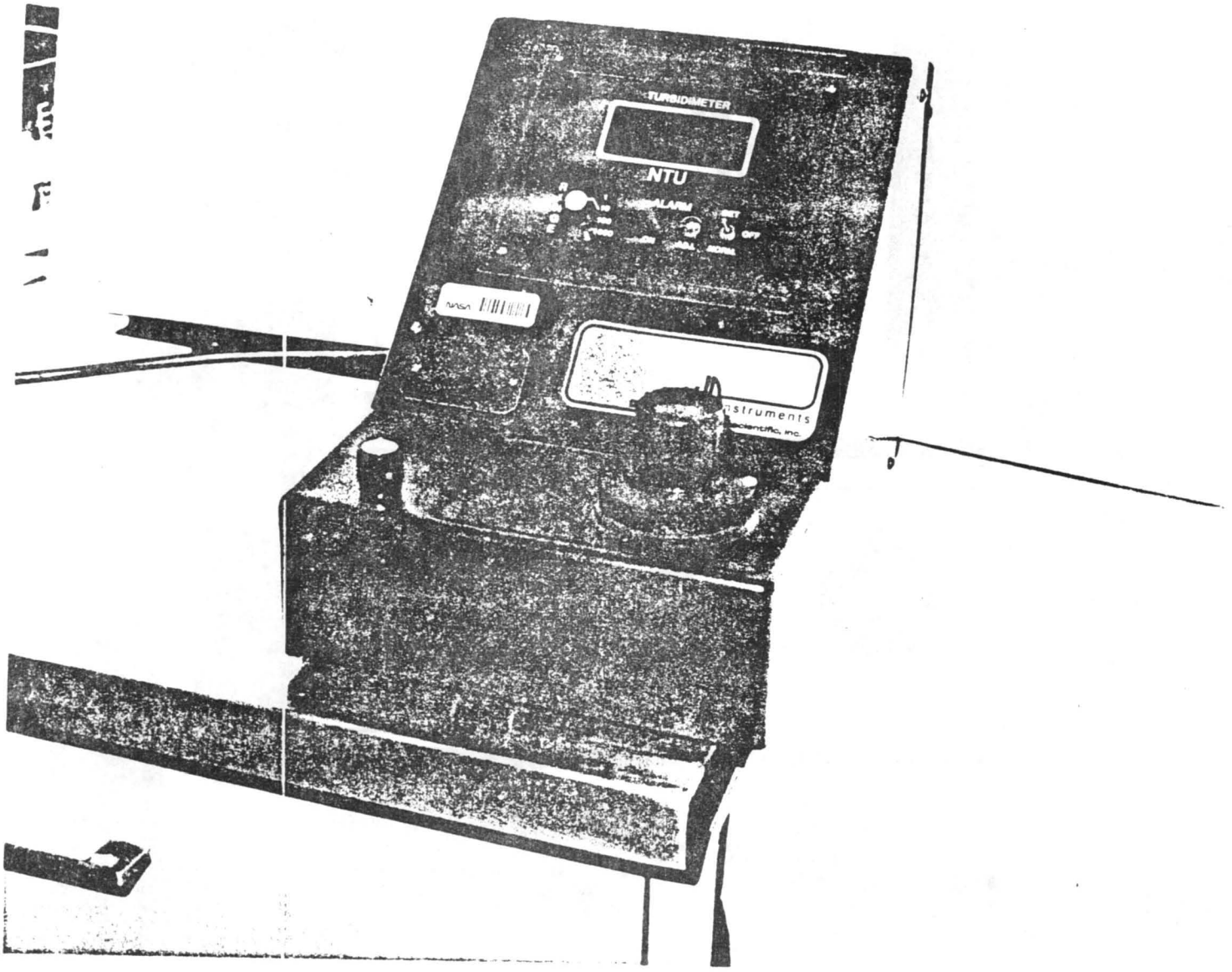


Figure 3. Turbidimeter

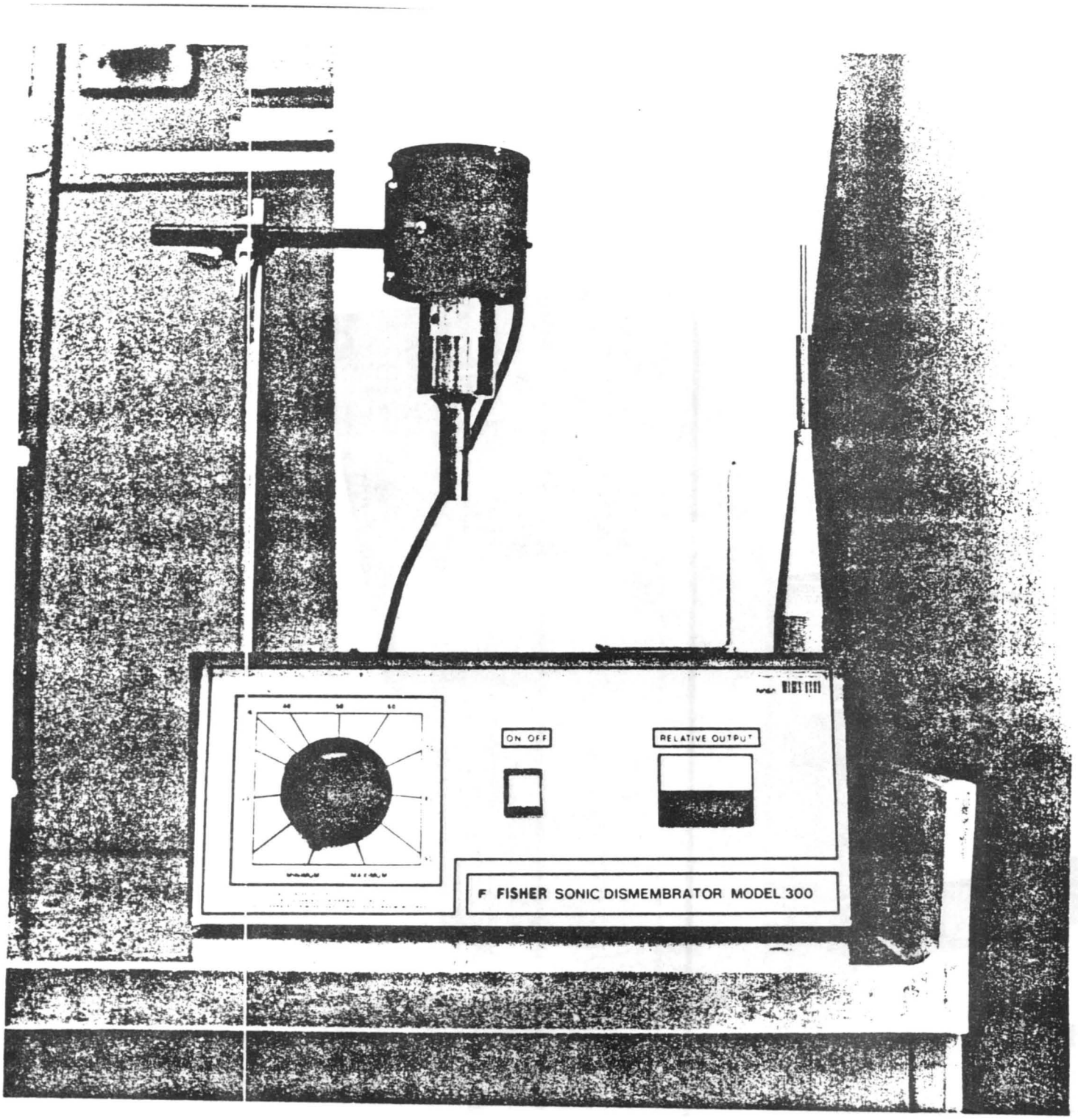


Figure 4. Sonic Dismembrator

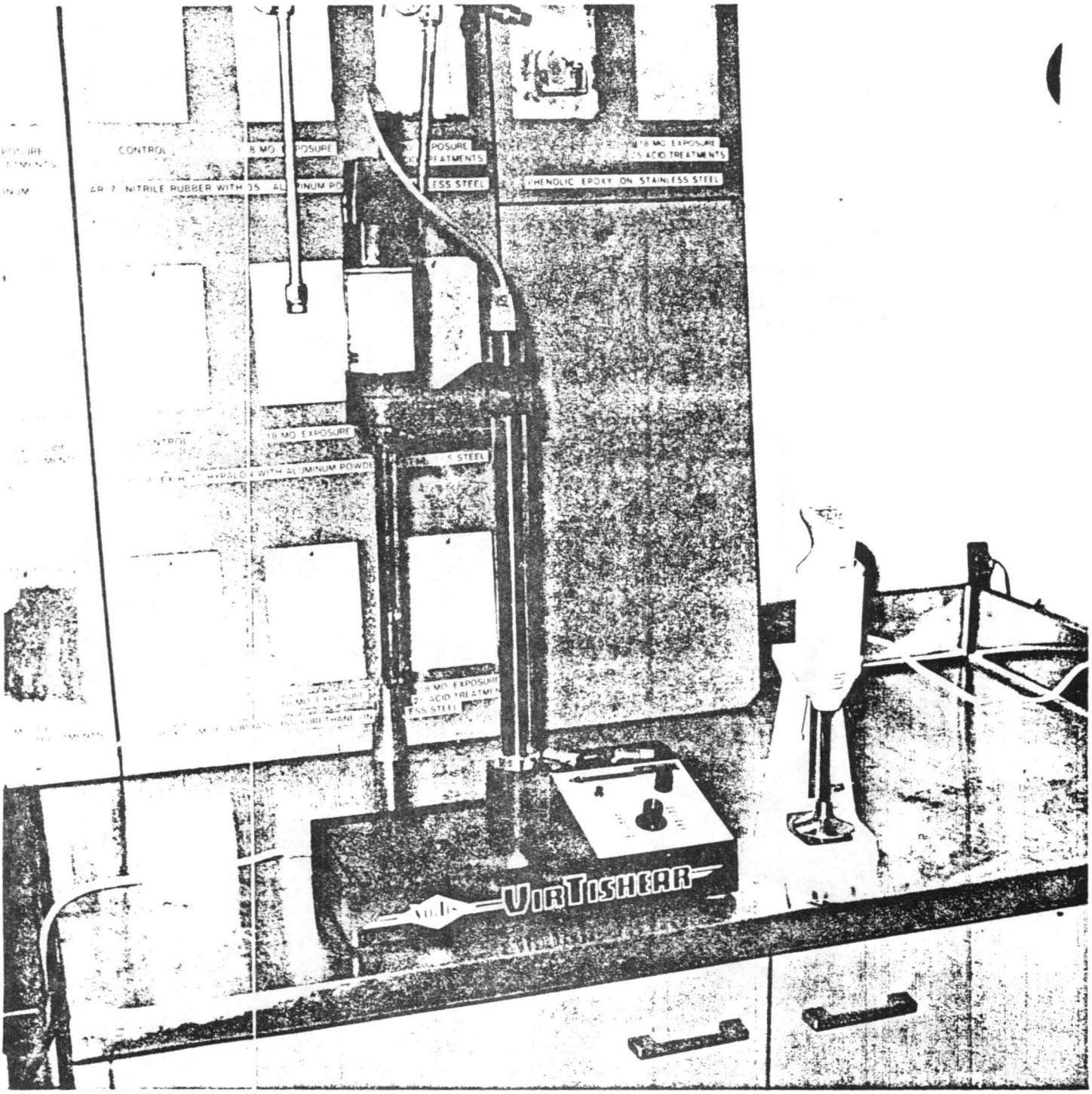


Figure 5. Virtis Emulsifier And Hand Mixer

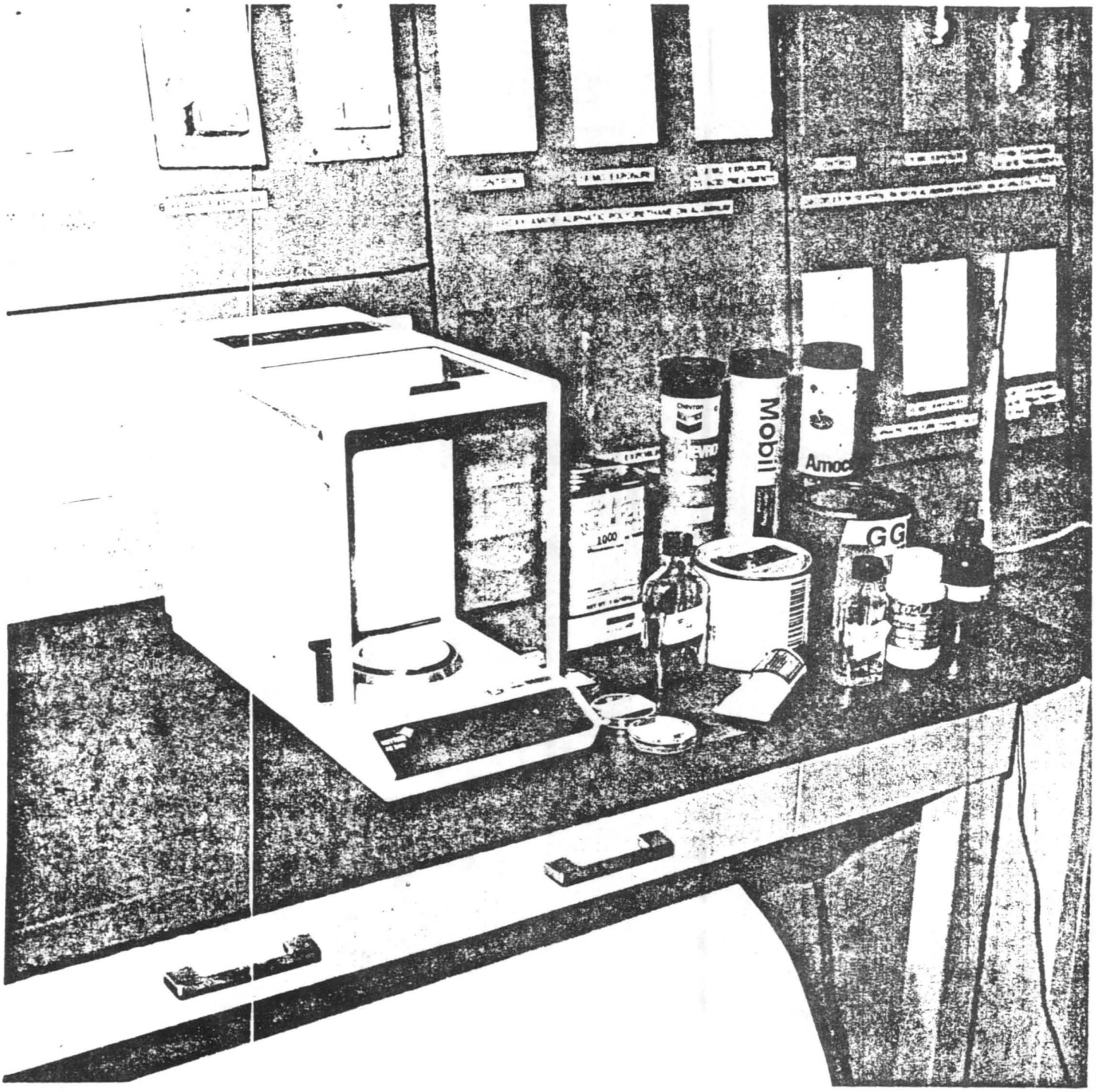


Figure 6. Hydrocarbons Tested

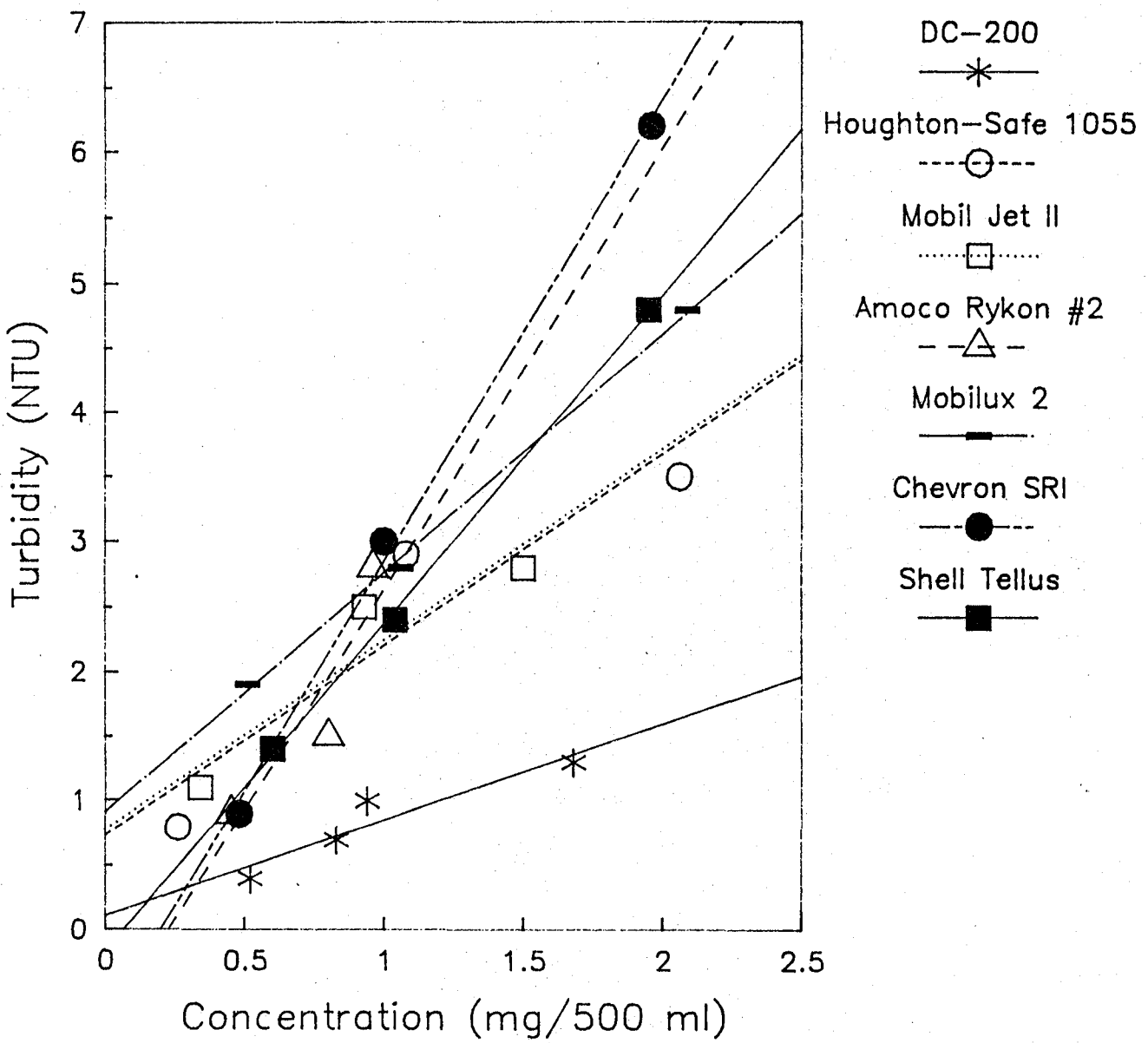


Figure 7. Ultrasonic – Turbidity Response

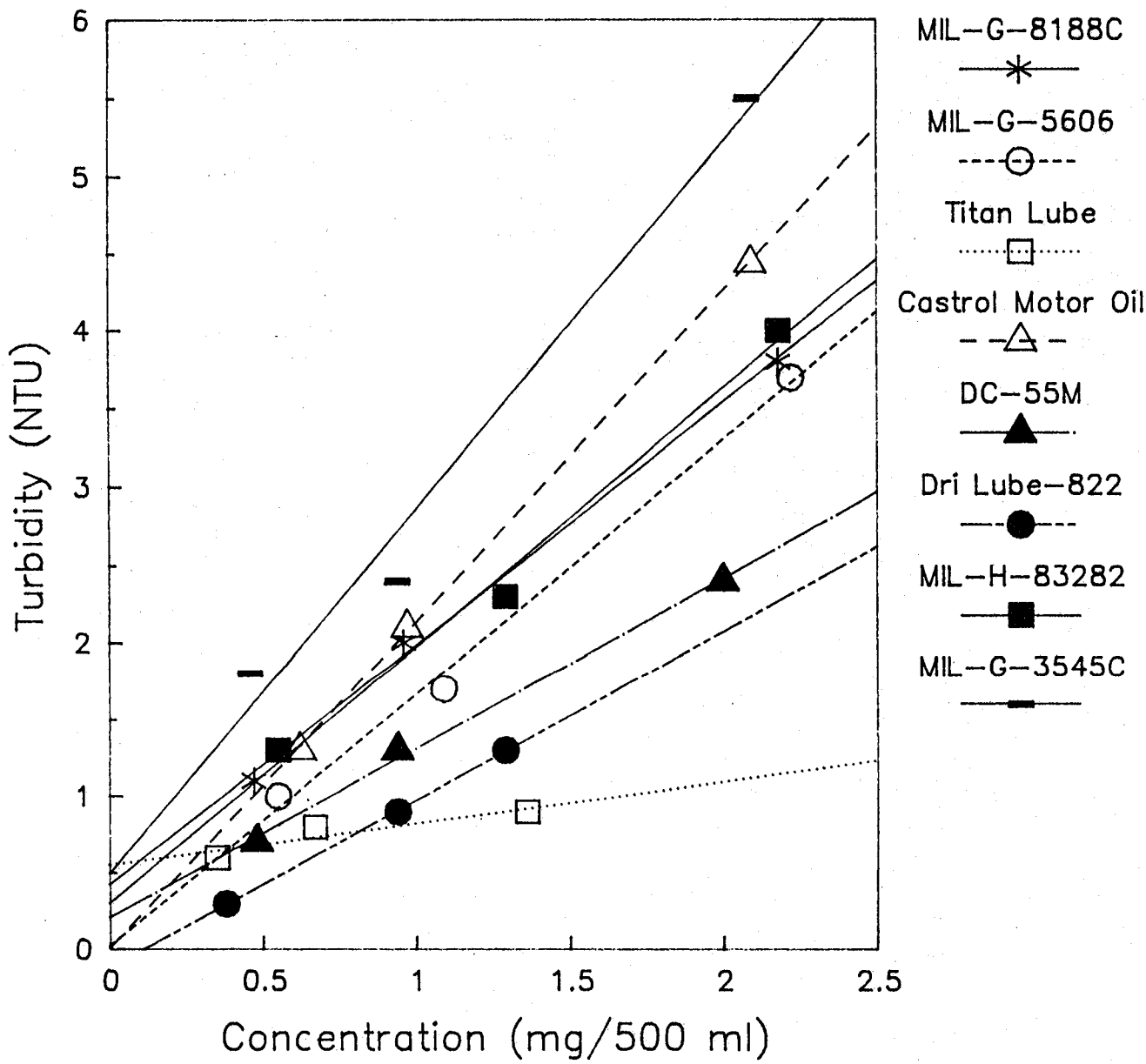


Figure 8. Ultrasonic – Turbidity Response

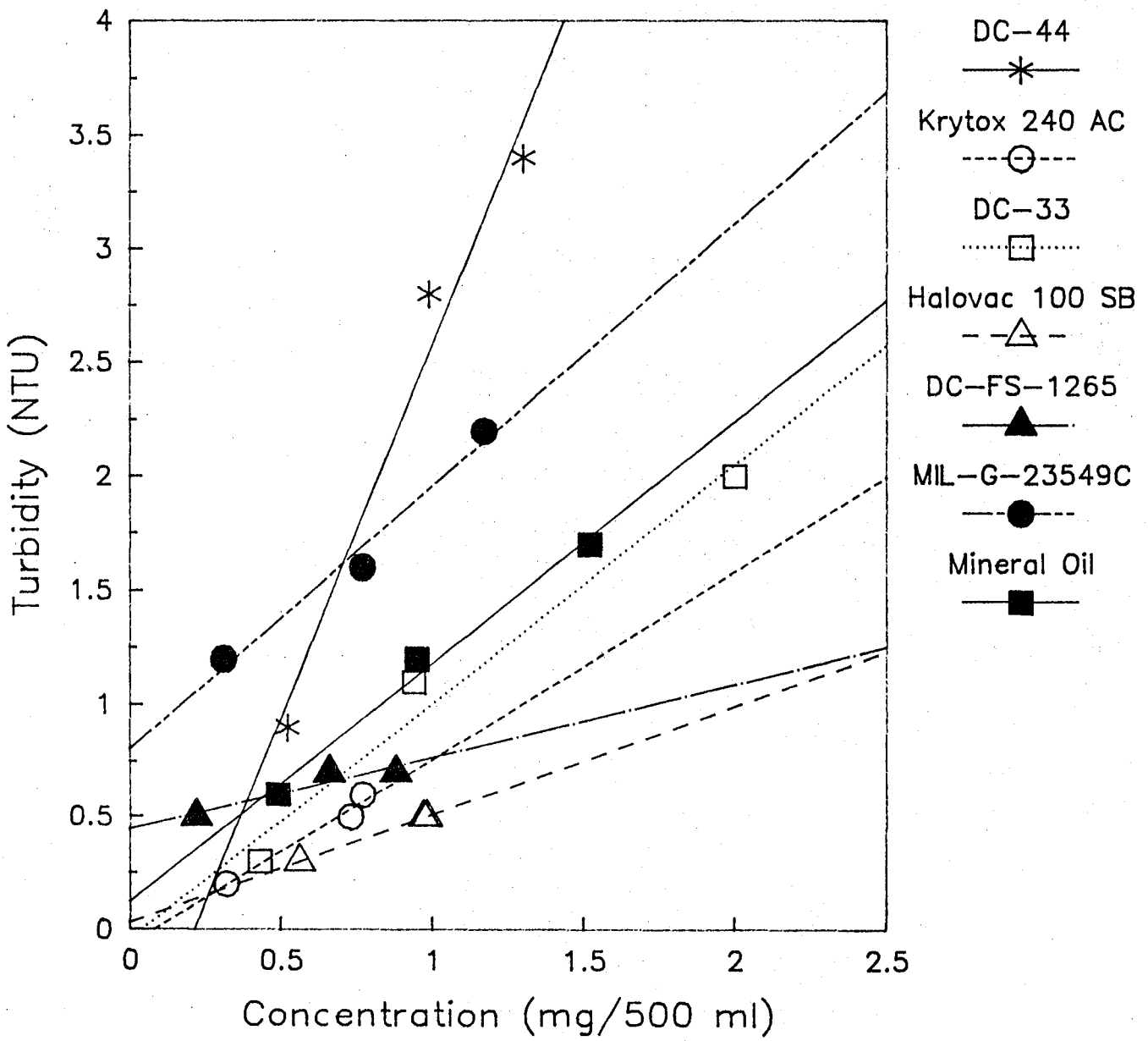


Figure 9. Ultrasonic – Turbidity Response

RESEARCHER:
DATE:

TEST #:
DESCRIPTION:

CLEAN BEAKER
CLEAN FITTING

WEIGHT OF FITTING & CONTAMINANT: _____

WEIGHT OF FITTING: _____

WEIGHT OF CONTAMINANT: _____

| TIME (MIN) | 0 | 2 | 4 | 6 | 8 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TURBIDITY READING | | | | | | | | | | | | |

EMULSIFY

WEIGHT OF FITTING & CONTAMINANT BEFORE US _____

WEIGHT OF FITTING & CONTAMINANT AFTER US _____

WEIGHT OF CONTAMINANT REMOVED _____

% REMOVAL = [ % ]

FIGURE 10 - DATA SHEET