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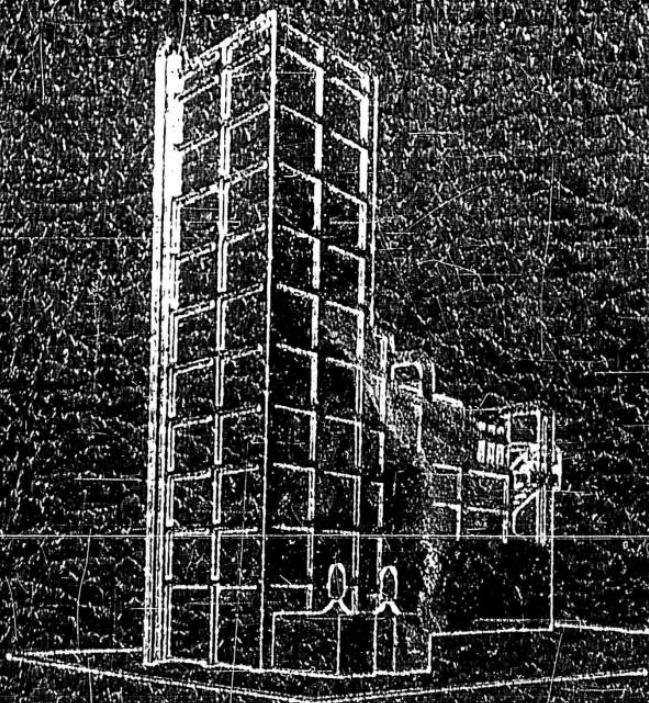
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STUDY OF
LIQUID OXYGEN CONTAMINATION

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XEROX

R. H. Foster, W. vanGelder, E. Kehat

AIR PRODUCTS, INCORPORATED

Allentown, Pennsylvania

A. P. I. Research Project No. 03-9-2881

Contract No. AF 33(616)-6730

October 1960



Directorate of Rocket Propulsion
AIR FORCE FLIGHT TEST CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
Edwards Air Force Base, California

Copy No. 27

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Progress Report No. 5

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ABSTRACT

The objective of this program is the recommendation of realistic specifications for procurement and use of liquid oxygen for rocket propellant supply systems, including standards for cleanliness, monitoring for cleanliness and contaminants, and recommendations of design criteria for reduction of contaminants and for increased safety.

This progress report discusses the experimental work done under this contract on the filtration of solid carbon dioxide (CO₂) from liquid oxygen and on hydrocarbon film ignition in gaseous oxygen. The equipment and methods used in the experiments are shown and described and the results obtained to date are discussed. It has become obvious that complete filtration of CO₂ "snow" from liquid oxygen is difficult and extensive work may be required to provide an adequate basis for the recommendation of filter design.

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I. SUMMARY

In July, 1959, Air Products entered into a contract with the Air Force to conduct a research study on contamination in missile liquid oxygen. Reports of this work [1, 2, 3, 4, & 5] discussed the many sources of contaminants to be found in liquid oxygen and the changing quality of liquid oxygen resulting from its continuous vaporization in storage and handling operations. Recommended procurement and use specifications for missile oxygen are presented with consideration given to all factors.

In May, 1960, Supplement A to the contract was written to extend the work to cover the following items:

- Phase IV. Sources and mechanisms for ignition.
- Phase V. Factors relating to solid contaminants.
- Phase VI. Cleaning and purification.
- Phase VII. Safety standards for handling of high pressure gases.

This report is the first in a series which will describe work done under Supplement No. 1 of the subject contract.

Under Phase IV, an investigation of hydrocarbon film ignition was started. N-hexadecane was deposited on films of different thicknesses from a CCl_4 solution upon the inner wall of a section of 1 inch stainless steel pipe. Ignition was attempted with an electric spark and duPont electric match. The latter method, however, introduced foreign materials into the system on firing and caused false results. The spark method proved more favorable. Tentative results from these first series of tests point to a safe upper limit for hydrocarbon film thickness greater than the 4000 micrograms per square foot which is in effect at the various missile sites (7).

Under Phase V, a program was initiated for determining the filtration characteristics of solid carbon dioxide (CO_2) from liquid oxygen. As pointed out in the previous reports [1, 2, 3, 4, & 5], CO_2 "snow" has existed in varying quantities at all times in the missile liquid oxygen, but has not been included in the missile liquid oxygen specifications.

A system of liquefaction, filtration, and analysis of liquid oxygen has been set up and test runs have been started. The data show an apparent effect of the Reynolds Number (effectively - liquid velocity) of the liquid at the surface of the filtering medium. The concentration of the CO_2 in the filtrate tends to rise with an increase in filtering rate. In all cases, some CO_2 remains in the filtrate. This amount, approximately the solubility limit, will precipitate out of solution as the liquid oxygen is handled further or vaporized while in storage.

In both cases, experimental work will continue and efforts will be made to improve techniques in order to reduce the spread of the data.

II. INTRODUCTION

Due to the interest of the Air Force in obtaining more information on commercial missile liquid oxygen and the oxygen produced in the Air Force's own plants, a contract was awarded in July, 1959, to Air Products, Incorporated, for a "Study of Liquid Oxygen Contamination". Under this contract, AF 33(616)-6730, Air Products, Incorporated, produced information concerning the possible sources of contaminants and a study of design concepts of the equipment for handling liquid oxygen wherein such contaminants could be introduced and/or concentrated. The reports of this work [1, 2, 3, 4, & 5] also presented a set of procurement and use specifications for missile liquid oxygen which considered the changing quality of liquid oxygen during production, transfer, transit, storage, and use at the missile launch site. This work was completed by July, 1960, and has been fully reported [1, 2, 3, 4, & 5].

In May, 1960, Air Products, Incorporated, was awarded Supplemental Agreement No. 1 to this contract. This authorized additional work is outlined in the following excerpts from the work statement in that supplemental agreement:

"Phase IV - Sources and Mechanisms for Ignition

"The Contractor shall conduct an experimental program to study the phenomenon of static electricity in liquid oxygen systems. This shall include investigation of such variables as rates of charge build up, system geometry, and dynamics and the nature and amount of impurities which are likely to be present. Other possible sources and mechanisms for ignition which might exist in oxygen systems will also be studied. Primary effort shall be placed on the analytical aspect.

"Phase V - Factors Related to Solid Contaminants

"The Contractor shall determine the effects of solid matter in liquid oxygen as it pertains to the use in missile systems. This phase shall include the following areas:

1. Determination of the factors relating to the agglomeration of small crystals or particles of insoluble contaminants such as carbon dioxide and the heavier hydrocarbons.

2. Determination of the effect of solid particles (rust, sand, lint, etc.) on oxygen systems, and recommend limits for various operating conditions. Particle size and quantity are to be considered.
3. Recommendations of proper operational conditions to reduce or eliminate all solid material shall be made.
4. Using the data obtained from paragraphs 1 through 3 above, recommend specification limits for the various contaminants, and suitable quality assurance provisions (See Phase III).
5. Conduction of a thorough investigation to determine the relative merits of the different types of filters for removing all types of solid material (crystal, agglomerated particles, granular and fibrous matter) from liquid oxygen. Specific filters shall be recommended. If commercially available equipment is not suitable, design criteria shall be developed.

"Phase VI - Cleaning and Purification

"During the various handling and transfer operations, clean liquid oxygen can become contaminated because of dirty equipment. To assure proper maintenance of oxygen quality, the Contractor shall:

1. Develop uniform cleanliness standards for oxygen equipment. (Development of cleaning agents, equipment and techniques are beyond the scope of this contract.)
2. Develop and recommend suitable means of inspection and surveillance of oxygen systems to assure proper cleanliness is maintained.
3. Study methods of removing contamination from liquid oxygen at the storage site, and make recommendations to the use of such techniques to reduce the disposal of contaminated oxygen, and to reduce the need for stringent cleaning requirements of oxygen systems.

"Phase VII - Safety Standards for Use of High Pressure Gases

"The Contractor shall prepare a document covering the safe handling, storage, shipping, and use of high pressure gases. The format shall

conform to that of the "Liquid Propellant Safety Manual", published by the Liquid Propellant Information Agency for the Office of the Assistant Secretary of Defense (R&E). The gases to be considered are:

1. Oxygen
2. Nitrogen
3. Helium
4. Other gases as mutually agreed upon by AFFTC and Air Products, Incorporated. "

This is the first report covering work done under Supplemental Agreement No. 1. It discusses:

1. Solid carbon dioxide, or CO_2 "snow" (as the trade knows it) as a contaminant in missile liquid oxygen and its response to filtration attempts.
2. Hydrocarbon film ignition studies, wherein an attempt is being made to find a satisfactory replacement for the 4000 micrograms per square foot concentration specification now in force at the various missile bases [7].

III. DISCUSSION

A. Filtration of Solid Carbon Dioxide from Liquid Oxygen

1. General

The average carbon dioxide (CO_2) concentration in the atmosphere is approximately 320 ppm. In the commercial low temperature air separation processes by which liquid oxygen is produced in the United States, this is reduced to a concentration of the order of 1 to 5 ppm by one of two methods: by scrubbing the air with a caustic solution which combines with the CO_2 to form an insoluble carbonate; by solidification and subsequent filtration. In either case, because of the solubility of CO_2 in liquid air, essentially all CO_2 which enters the cold section of the liquid oxygen producing equipment becomes concentrated in the liquid phase. During the processing of this liquid, it is passed through mechanical filters which are designed to remove the last traces of solid CO_2 . However, it has been the experience of these vendors that not all of the CO_2 is retained by the filters and some is withdrawn in the product.

Few users of commercial oxygen are concerned about the presence of small quantities of solid carbon dioxide. In fact, few commercial users apply liquid oxygen directly. In most cases, the liquid oxygen is vaporized and super-heated to ambient temperatures in the facilities supplied by the customer or vendor. Under these conditions, the solid CO_2 is also vaporized and becomes an unnoticeable contaminant in the usable gas. The storage and rapid turnover characteristics of commercial users preclude concentration of solid CO_2 over periods of weeks to years.

The missile industry alone is faced with the problems of long-term liquid oxygen storage, concentration of CO_2 by vaporization, and by frequent handlings between vendor, tank truck, launch site storage, and return from missile. Therefore, the relatively new and unexplored field of removal of the last vestiges of solid CO_2 which do remain in the commercial oxygen product part has become of greater importance. The reason is that the solid CO_2 will agglomerate where conditions are static, as found in storage vessel and in the launch pad storage tank. These larger particles may not be broken down during subsequent agitation and may possibly create a blockage in some missile LOX system.

Under the subject contract an investigation was undertaken to study the means and problems of removing the last remaining solid CO_2 . This problem can be divided into two phases: (1) the removal of solid CO_2 from liquid oxygen at the producer's plant site upon or before delivery to the customer, and (2) subsequent removal of CO_2 which may have been in solution in the liquid oxygen as produced by the vendor, but which by reason of handling, long term storage, or involvement in missile operations has been concentrated to the point where the CO_2 has exceeded the solubility limit in liquid oxygen and has begun to precipitate. At this point, the mechanical considerations are given essentially the same as those at the producers' sites. The obvious means of removing solid particles from a liquid is by filtration. In this process the solid-bearing liquid is passed through a medium which contains openings smaller than the smallest desired particles to be left remaining in the solution. These particles are retained on the upstream side of the filter element and at intervals the particles are removed.

This leads directly into a study of the factors involved in satisfactorily filtering solid CO_2 from liquid oxygen. The agglomeration of these particles previous to filtering is of prime importance. This operation is best carried out in a quiescent pool of liquid since turbulence of the mixture tends to break up the particles of solid CO_2 . The factor of particle break-up has been seen to operate on relatively large particles already formed. Although these particles appear to be solid, they break into many small pieces upon agitation of the liquid.

Complicating this situation is the nature of CO_2 particles. These particles cannot be analyzed by the normal screening procedures because of this break-up tendency and because the CO_2 particles exist only at low temperatures and not at room temperatures where normal screening processes are conducted. Under approximately 40 microns in diameter, a particle is not visible to the naked eye. Although the filtrate may appear clear, this same liquid, vaporized and heated to room temperature and passed through a CO_2 analyzer, will reveal the presence of CO_2 .

2. Equipment Description

Figure 1 presents a schematic flow diagram of the equipment used in the tests. The equipment is also shown in detail in Figures 2

through 8. This diagram is referenced in subsection 3 - Test Procedure. During a test run, CO_2 -contaminated liquid oxygen is transferred from vessel 1 through Filter 4 and sample coil 5 to vent through V_6 . In order to take a sample, valves V_6 and V_2 are closed, V_7 is opened and the liquid is transferred into the sample bottle 2 where it is vaporized for analysis. Figure 2 shows the equipment in operating position without the Dewars in place.

The identifying numbers on the succeeding photographs are as shown in Figure 1. After 5 runs, filter house (4) was replaced with a Lucite plastic unit so that the filtering process could be visually inspected. Sight glass and scale (6) were used to measure throughput during a test by the liquid level difference. Figure 3 illustrates the plastic filter house (4) and storage vessel (1) immersed in the Dewar flask (3) full of liquid nitrogen. The sample coil (5) and sample bottle (2) are not visible. At first the manometer was used to measure pressure drop across the filter; however, the pressure lines created an uneven boiling in the process stream, and the manometer had to be removed.

Figure 4, which shows the equipment of Figure 3 removed from the Dewar flask, enables one to see the sight glass and scale (6) more easily. Figure 5 shows a second generation plastic filter house in a close-up view. The operation of this model is the same as the previous one with the exception of the side outlet in the center of the photograph. During the test, the flow enters at the opening at the bottom of the photograph and is split in the filter house. The excess liquid which measures the turbulence leaves by the side opening while the filtered liquid leaves by the connection at the top.

Figure 6 shows the assembly in Figure 5 disassembled for examination. The filter is a 10-micron nominal pore size sintered stainless steel unit purchased as a laboratory item from the Purolator Company. It is approximately 1-1/4" long by 9/16" O.D. Teflon gaskets are used to seal the flange joint. The flow through this filter is from outside to inward.

Figures 7 and 8 schematically show the principle of operation of the test filter unit.

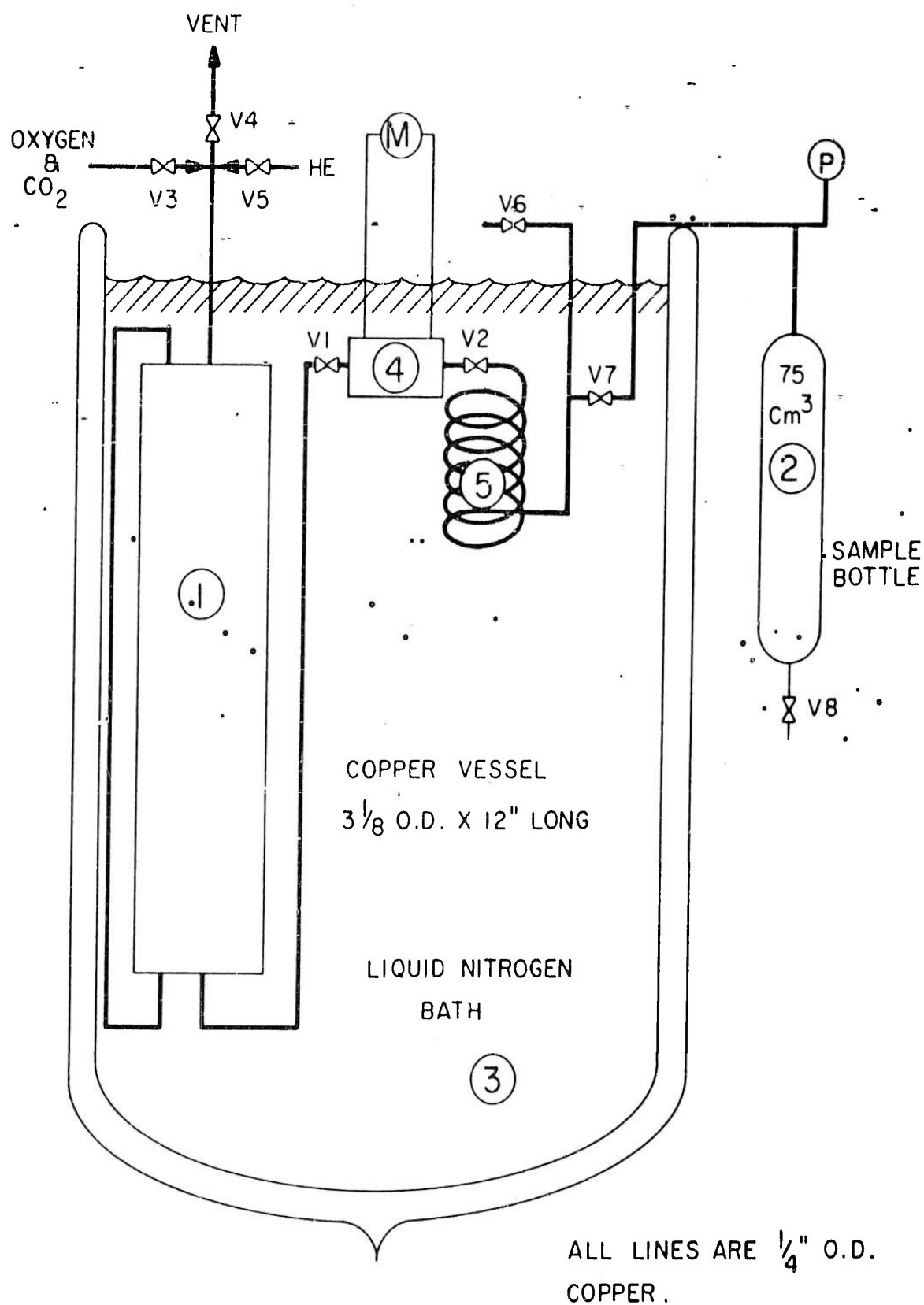


Figure 1
 APPARATUS FOR EXAMINATION OF SOLID
 CO₂ FILTERING PHENOMENON

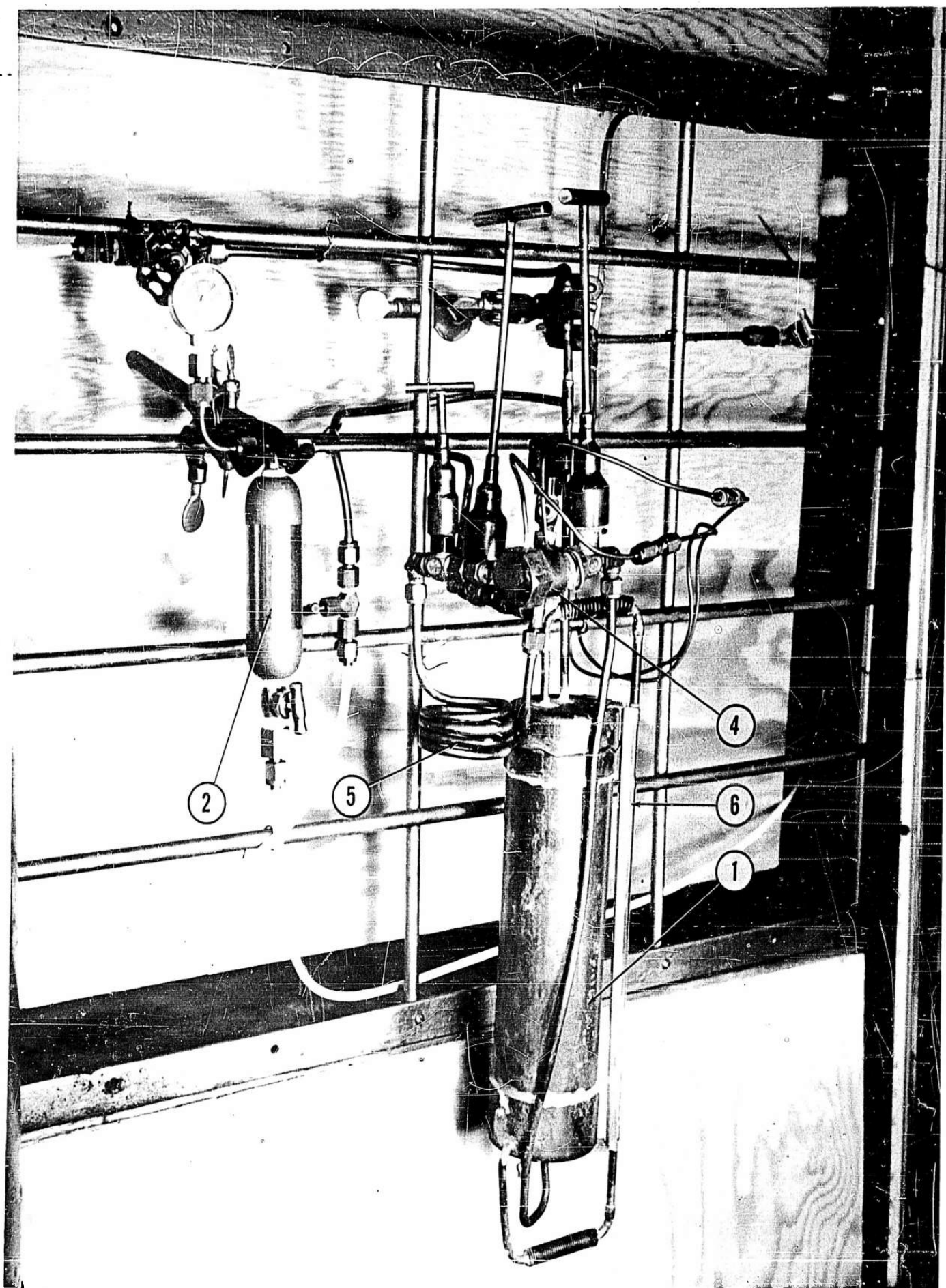


Figure 2. Equipment for Examination of the CO₂ Filtration Equipment

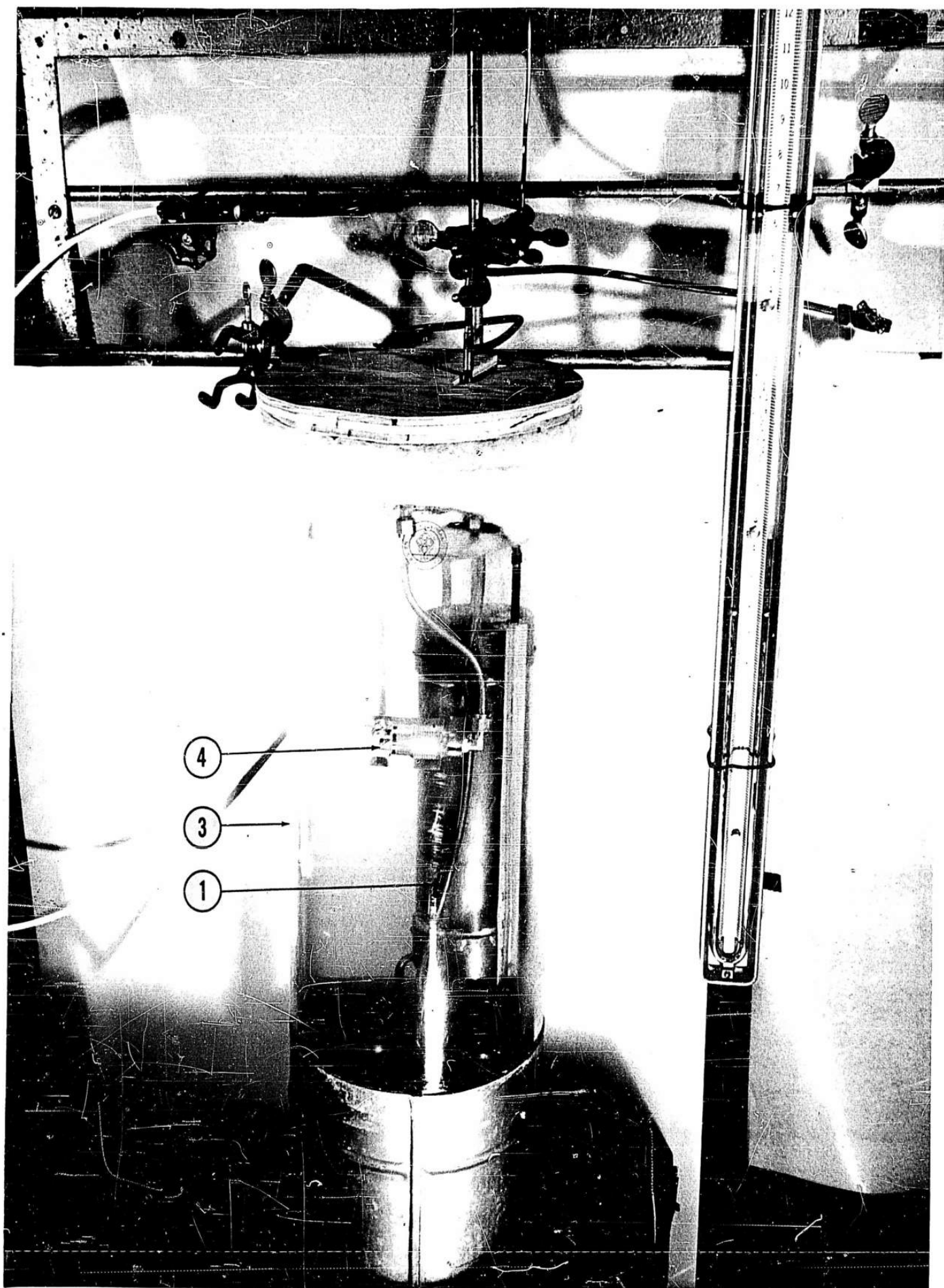


Figure 3. CO₂ Filtration Equipment in Action

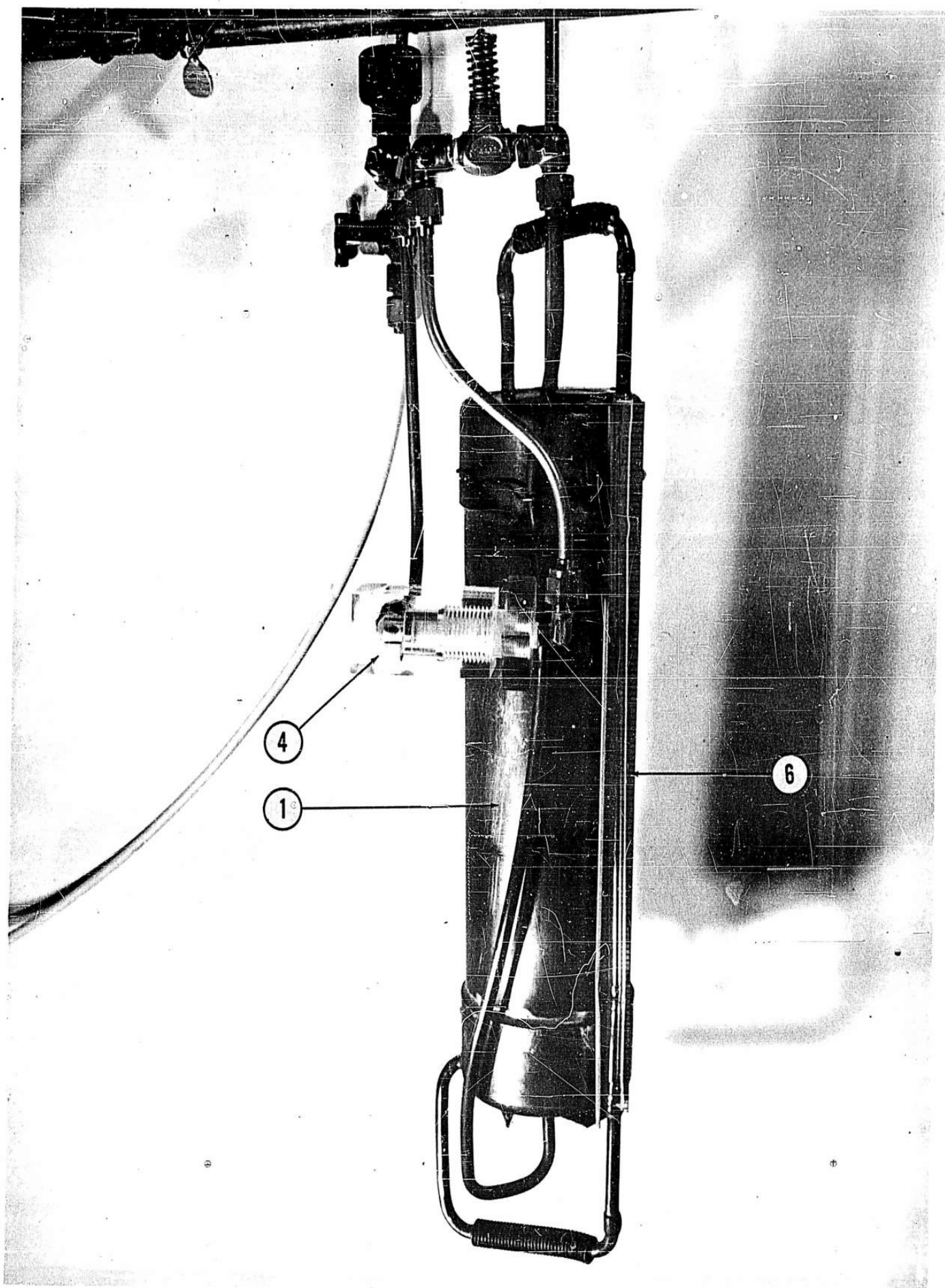


Figure 4. Revised Filtration Study Intervals

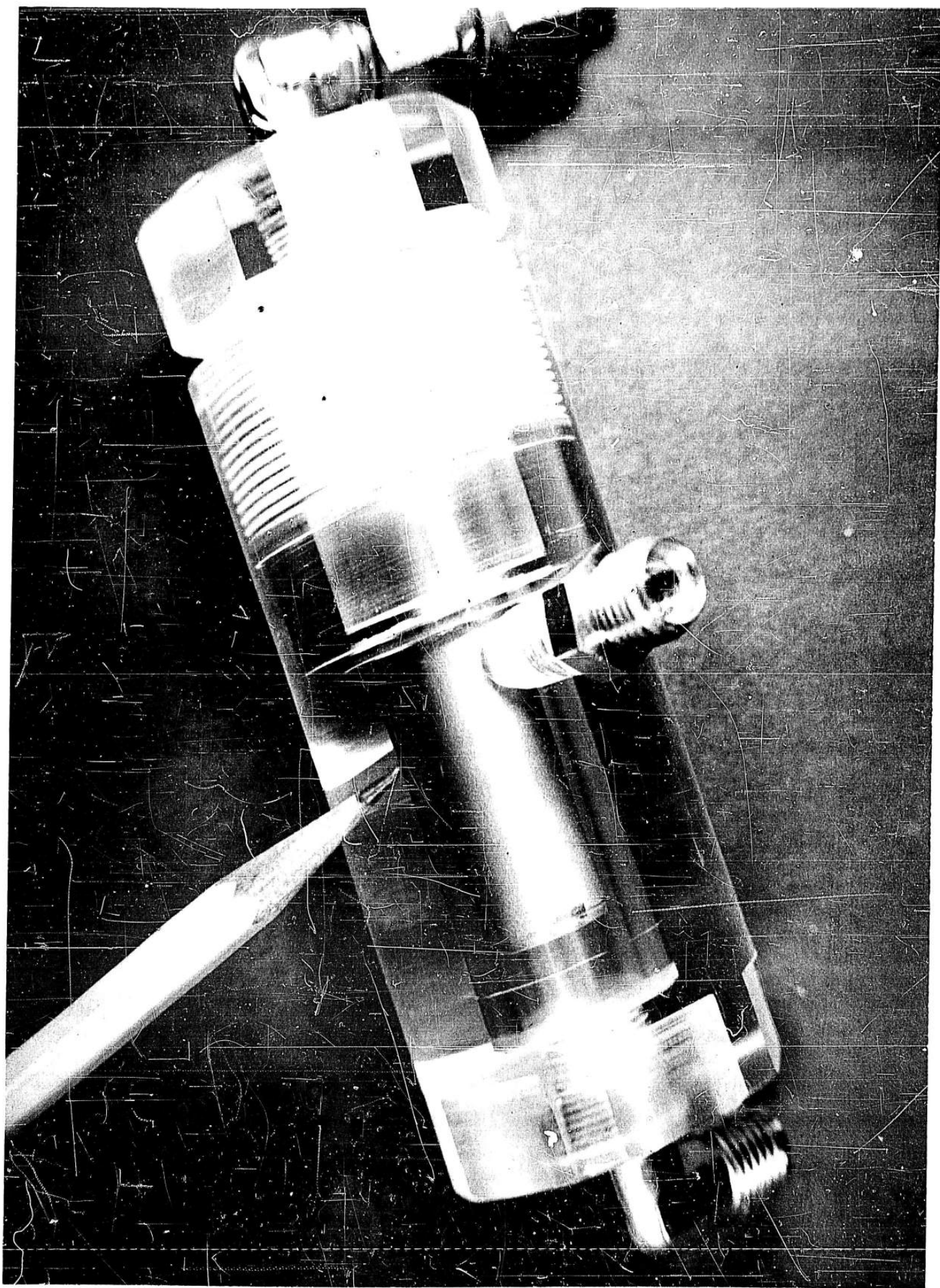


Figure 5. New Filter Assembly with Side Tap

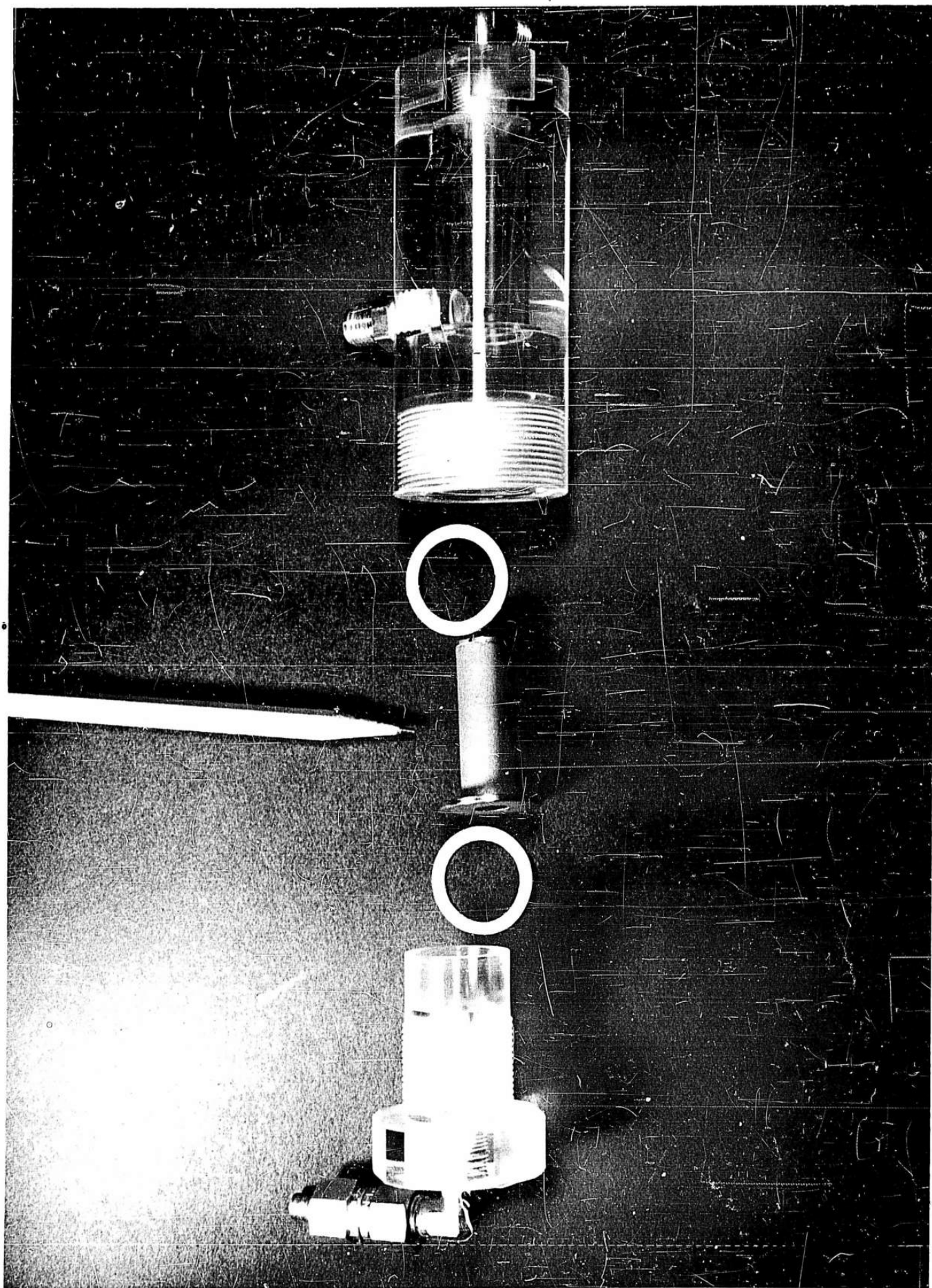


Figure 6. Dissassembled Filter

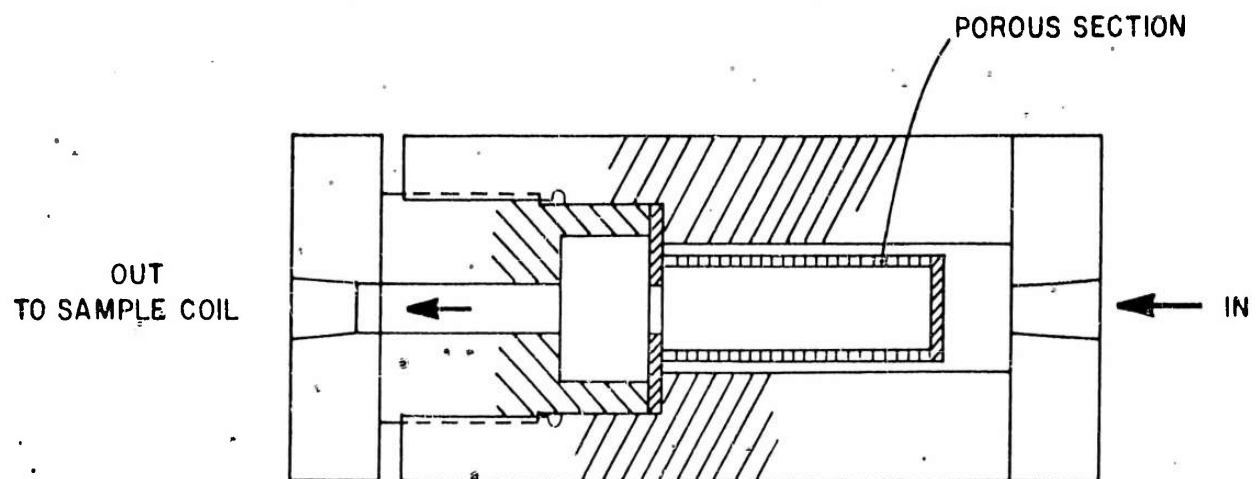


Figure 7
PLASTIC FILTER ASSEMBLY WITH CYLINDRICAL
FILTER ELEMENT. (FULL SIZE)

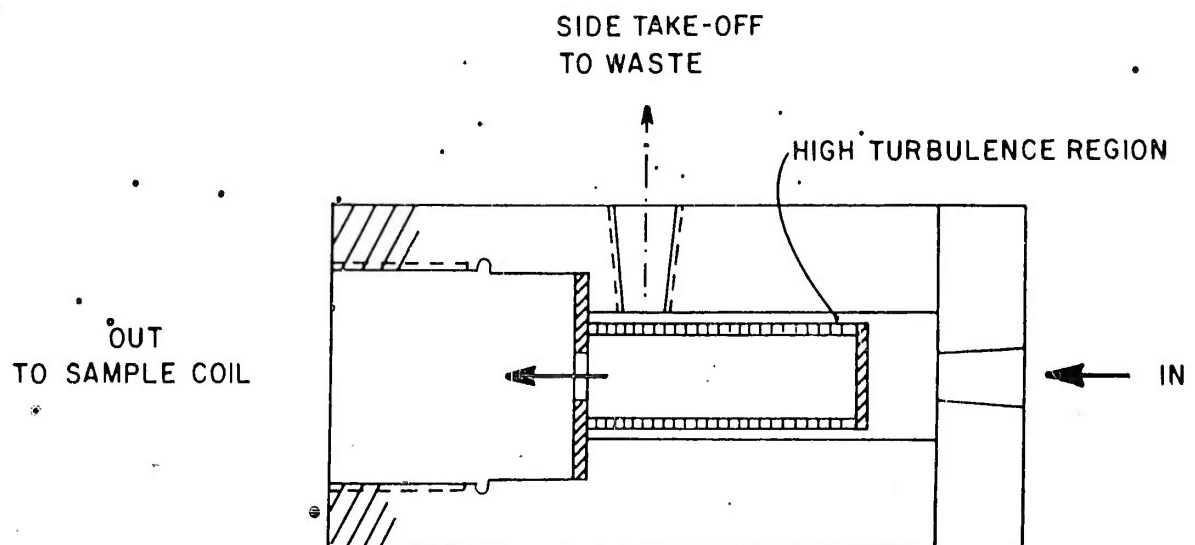


Figure 8
FILTER ASSEMBLY AS MODIFIED WITH
SIDE TAKE-OFF FOR HIGH REYNOLDS
NUMBER. (FULL SIZE)

3. Test Procedure

The Dewar flask (3) is first filled with liquid nitrogen. Valve V_3 is opened, allowing liquefaction of oxygen containing a known concentration of solid CO_2 into vessel (2). A regulated supply of helium is then connected into the system through valve V_5 to apply a steady pressure on the liquid oxygen in vessel A. to establish the flow rate through the filter assembly. After steady transfer conditions have been obtained, valves V_6 and V_2 are closed (V_7 had been closed), trapping a sample filter liquid in the sample coil. Valve V_7 is opened and the sample is transferred to vessel B by warming the coil to room temperature and cooling vessel B in liquid nitrogen. Valve V_7 is closed; the sample bottle is detached, warmed, and analyzed for CO_2 . This procedure is used with all samples where subcooled liquid is filtered.

The same arrangement of the test apparatus is used when boiling liquid is filtered, except a small heat exchanger is inserted immediately before valve V_1 . This exchanger introduces heat into the contaminated liquid oxygen to the point that approximately 50% gas volume can be observed in the filter house during the filtering procedure. All other parts of the procedure remain the same.

For the runs where a high flow rate was attempted, the 3-1/8" O.D. storage vessel was changed to one 6-1/8" O.D.; the larger storage volume was required in order to make a run for a reasonable time period.

4. Results

During this report period, 43 runs were made under several different conditions using the equipment illustrated. Results of these runs are shown in Table I. Two phenomena have begun to show even though there is considerable spread in the recorded data due to difficulties in handling the O_2 - CO_2 mixture in small equipment. One difficulty is the passage of visible CO_2 from the exit of the filter element during and immediately after times when the elements have been vibrated mechanically. The filter element was one having 10-micron rating. Since the lower limit of visibility is about 40 microns in diameter, we must assume that this cloud is due to a large quantity of individually invisible particles. It has become apparent during this experiment that the actual filtering medium

TABLE I.

RESULTS OF CO₂ FILTRATION RUNS

<u>Run No.</u>	<u>Filter Type</u>	<u>Reynolds Number</u>	<u>CO₂ in Filtrate (ppm)</u>	<u>Remarks</u>
1.	5 micron disc	105	4	
2.	5 micron disc	367	5	
3.	5 micron disc	483	5	
4.	5 micron disc	13,900	2	Blank run.
5.	10 micron disc	364	65	
6.	10 micron disc	538	22	
7.	10 micron disc	229	102	Manometer unsteady.
8.	10 micron disc	150	10	Manometer steady.
9.	10 micron disc	244	82	Manometer unsteady.
10.	10 micron disc	717	121	Manometer unsteady.
11.	10 micron disc	336	301	Manometer unsteady.
12.	10 micron disc	347	218	New sample coil.
13.	10 micron disc	92	3	Pressure tap removed.

TABLE I (Cont'd)

<u>Run No.</u>	<u>Filter Type</u>	<u>Reynolds Number</u>	<u>CO₂ in Filtrate (ppm)</u>	<u>Remarks</u>
14.	DISCARDED - leaky valve			
15.	DISCARDED - leaky valve			
16.	10 micron disc	2950	44	Filter vibrated before taking sample.
17.	10 micron disc	1434	68	Filter vibrated before taking sample.
18.	10 micron disc	93	3.5	Quiet.
19.	10 micron disc	25	2	Quiet.
20.	10 micron disc	390	21	Filter tapped continuously.
21.	10 micron disc	403	27	Filter tapped continuously
22.	5 micron disc	35	1	No tapping.
23.	5 micron disc	885	21	Tapped continuously.
24.	5 micron disc	1210	15	Tapped continuously.
25.	5 micron disc	-	-	Blank run - no sample taken.
26.	5 micron disc	383	27	First test with Lucite filterhouse.
27.	5 micron disc	640	-	Blank run - no sample taken.

TABLE I (Cont'd)

Run No.	Filter Type	Reynolds Number	CO ₂ in Filtrate (ppm)	Remarks
28.	5 micron disc	50	-	Blank run - no sample taken.
29.	2 micron woven stainless mesh	24	3	Quiet
30.	2 micron woven stainless mesh	22	-	Tapped - filtrate cloudy - no sample.
31.	5 micron woven mesh	2420	160	Continuous tapping.
32.	5 micron woven mesh	3290	120	Continuous tapping.
33.	5 micron woven mesh	3300	25	Continuous tapping.
34.	2 micron woven mesh	74	-	No sample taken.
35.	MSA Fibreglass	11.5	4.5	Continuous tapping.
36.	MSA Fibreglass	7.2	(7)	Discarded - leaky valve.
37.	1 micron ceramic	7.5	0.3	Continuous tapping.
38.	1 micron ceramic	10.8	0.5	Continuous tapping.
39.	1 micron ceramic	7	0.9	Continuous tapping.
40.	Micro-Metallic H	1095	50	Continuous tapping.
41.	Alofrite No. 2	3540	-	All CO ₂ went through.
42.	5 micron ceramic	188	73	Continuous tapping.

TABLE I (Cont'd)

<u>Run No.</u>	<u>Filter Type</u>	<u>Reynolds Number</u>	<u>CO₂ in Filtrate (ppm)</u>	<u>Remarks</u>
43.	5 micron ceramic	104	127	Continuous tapping.
44.	5 micron ceramic	75	0.4	Quiet, subcooled.
45.	7 micron ceramic	147	0.4	Quiet, subcooled.

is the cake which is being built up on the outside of the filter element rather than the filter element itself. In other words, the filter element is simply forming a base for the actual filtering medium. Upon agitation, the CO₂ cake is broken up into smaller particles. Some particles immediately pass through the filter element. Obviously, in a plant with moving machinery such a condition may exist at all times in the actual production filter house.

The second phenomenon is that the concentration of CO₂ in the filtrate seems to vary in a pattern with the Reynolds number of the liquid in the filter house at the surface of the filter cake. Figure 9 shows the data on concentration of CO₂ in the filtrate plotted against Reynolds number before a 10 micron absolute filter. Figure 10 shows the results from the same filter with a vibration applied to the filter. Figure 11 represents the results of all runs plotted on one chart, with a proposed correlation of these points. The Reynolds number is a flow correlation of

$$Re = \frac{4w D_h}{A \mu}$$

where: w = Flow rate, lb/hr

D_h = hydraulic diameter, feet

A = crosssectional area, sq ft

μ = viscosity, lb/ft sec

As stated previously in this report, the CO₂ particles will agglomerate if the liquid is allowed to stand quietly for a period of time. These agglomerations are known to break up if the quiescent pool is agitated by mechanical means or simply by boiling the liquid. This agitation also occurs during the transfer and filtration of the liquid in the test apparatus. Figure 9 shows an increase in CO₂ concentration in the filtrate with an increase in filtering rate. This figure illustrates that the agglomerated CO₂ in the storage vessel (1) has broken down into increasingly larger numbers of small particles as the agitation of the filtration increased. With

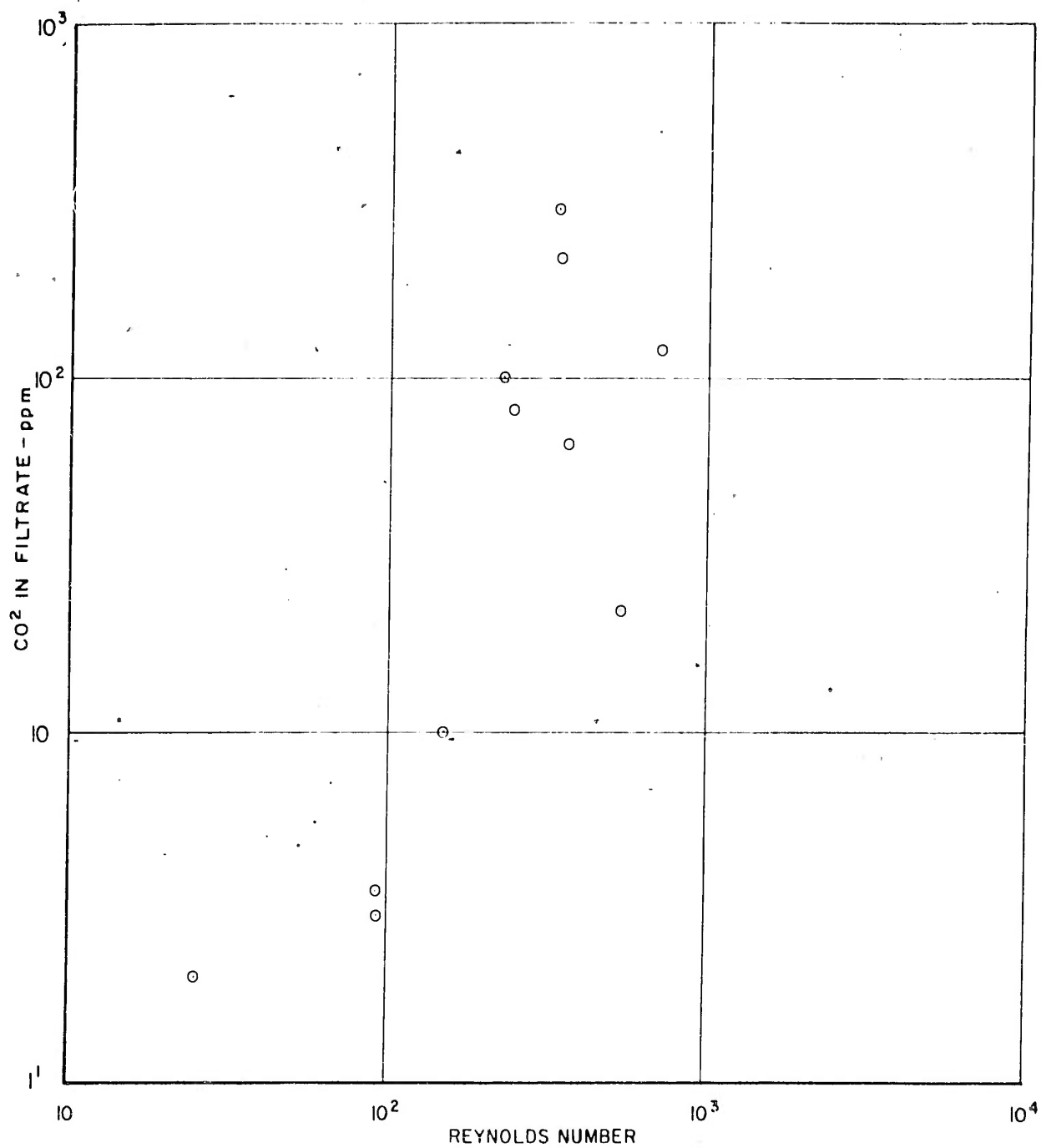


Figure 9
REYNOLDS NUMBER BEFORE FILTER
(10 MICRON PORE SIZE)
QUIESCENT STATE

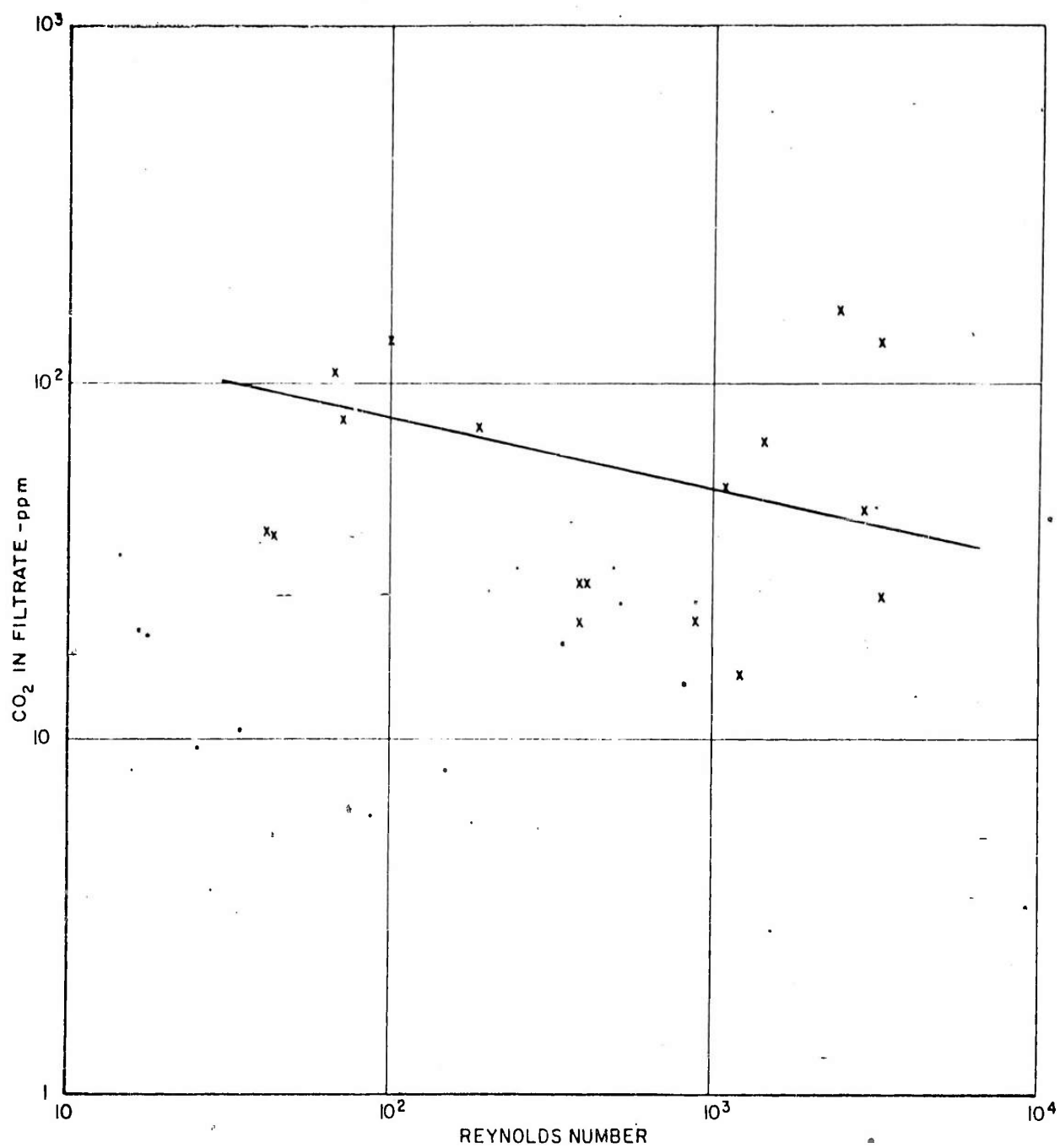


Figure 10
REYNOLDS NUMBER BEFORE FILTER
(10 MICRON PORE SIZE)
VIBRATED FILTER

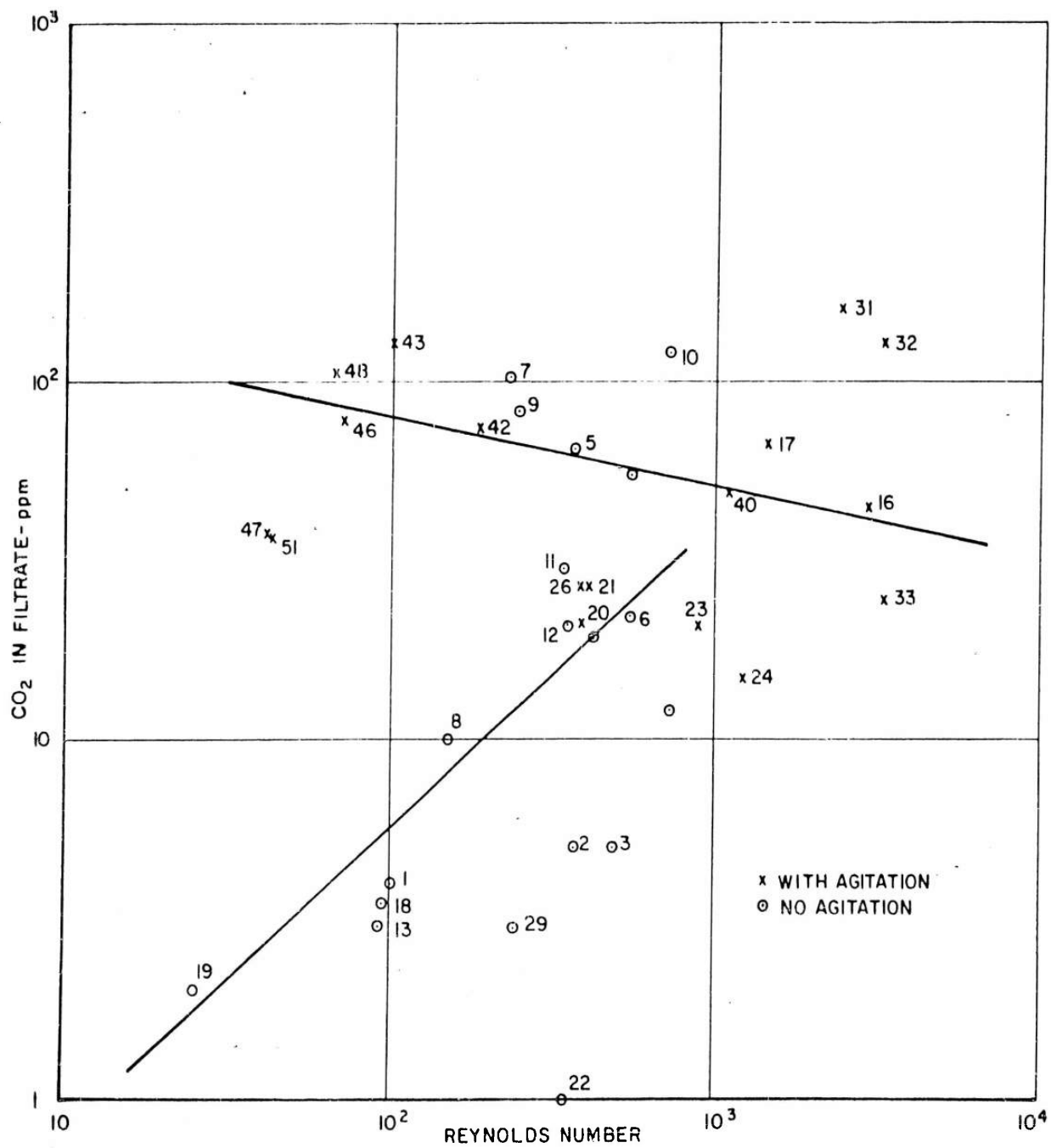


Figure II
REYNOLDS NUMBER BEFORE FILTER

sufficient agitation, the filtering efficiency of the unit is poor regardless of the rate of flow (see Figure 10).

Operation of small-scale equipment for handling liquid oxygen, or any other liquid with a boiling point far below ambient temperature is very delicate. The liquid exhibits a natural tendency to boil at the most inopportune times. The simple operation of throttling the liquid to control flow creates a two-phase system due to flash-off caused by the expansion through a valve. The equipment and procedures for these tests were revised several times.

The procedure of obtaining representative samples from a liquid oxygen stream carrying suspended solid CO_2 is another critical operation. If sampling is done by a single tap into the stream, the solids will flow past rather than into the side arm which produces a low value. Unless the CO_2 -bearing liquid oxygen is flash-vaporized in a heater whose surfaces are warmer than the sublimation point of CO_2 , the CO_2 will concentrate in the boiling liquid and the resultant analysis will be low. If the tubing carrying the mixture passes through a warm area, the CO_2 will tend to deposit out on the walls of the tube. If the sample is throttled, the CO_2 will tend to deposit out on the valve seal or disc. This difficulty in properly sampling from solid CO_2 -liquid created many problems in test equipment design before productive experimental work could be initiated.

5. Future Work

Additional experimental data will be obtained to corroborate the apparent existence of the trend shown in Figure 11. The experimental procedures are being reviewed and revised to narrow the spread of the recorded data.

B. Hydrocarbon Film Ignition Tests

1. General

Phase IV, of Exhibit A-1 of the Subject Contract entitled "Sources of Mechanisms for Ignition" includes a study of the ignition and explosion which might exist in oxygen systems. Under present study is the possibility of ignition of hydrocarbon film existing on the wall of piping for vessels in gaseous oxygen service. This effort is

pointed toward the determination of a reasonable safety limit for the concentration of hydrocarbons on the surface of such equipment or piping to be used in lieu of the 4000 microgram per square foot (mcg/sq ft) standard developed by LeSuer and William [6] in their standard report. This level of contamination was based on tests run at CCMTC using RP-1 as the contaminant. This material is highly combustible and promoted a safe upper limit which may be excessively low when a normal lubricant is considered. A 4000 mcg/sq ft concentration is a clean dry surface. A literature search has revealed only one previously reported study done in 1952 by Palmer [7]. These tests were performed with an oil concentration of about 20,000 milligrams per square foot and a long (200 to 300 ft.) pipe under 100 psig air pressure. This combination ruptured the pipe. Therefore, the area of present interest is between 4 mg/sq ft and 20,000 mg/sq ft.

2. Equipment Description

Figure 12 shows the test vessel being used for these experiments. It is a 2-foot section of 1-inch stainless steel pipe with two 6-inch long 1/2-inch diameter sections at each end which have provisions for the introduction of a solution of hydrocarbon (n-hexadecane) in carbon tetrachloride. The ignition is provided by either a spark coil connected to the electrode or by an electric match inserted at the center of the pipe. N-hexadecane was chosen because it is a common component of lubricating oils and because a single hydrocarbon is more easily analyzed than a mixture.

3. Test Procedure

The n-hexadecane was applied to the surface in a solution of carbon tetrachloride which was evaporated in a hot water bath, while rotating the pipe section, to achieve uniformity of the hydrocarbon film on the surface. The amount of the hydrocarbon deposited on the surface was controlled by the amount and concentration of the feed solution.

After the film was applied, the pipe section was cooled to room temperature and the igniter and oxygen line were connected. The pipe was purged with dry oxygen for 5 minutes to remove the last traces of the solvent. All connections were tightened, the pipe was pressurized with oxygen, and ignition was applied. This resulted in a spark of about 20,000 volts for 10 seconds.

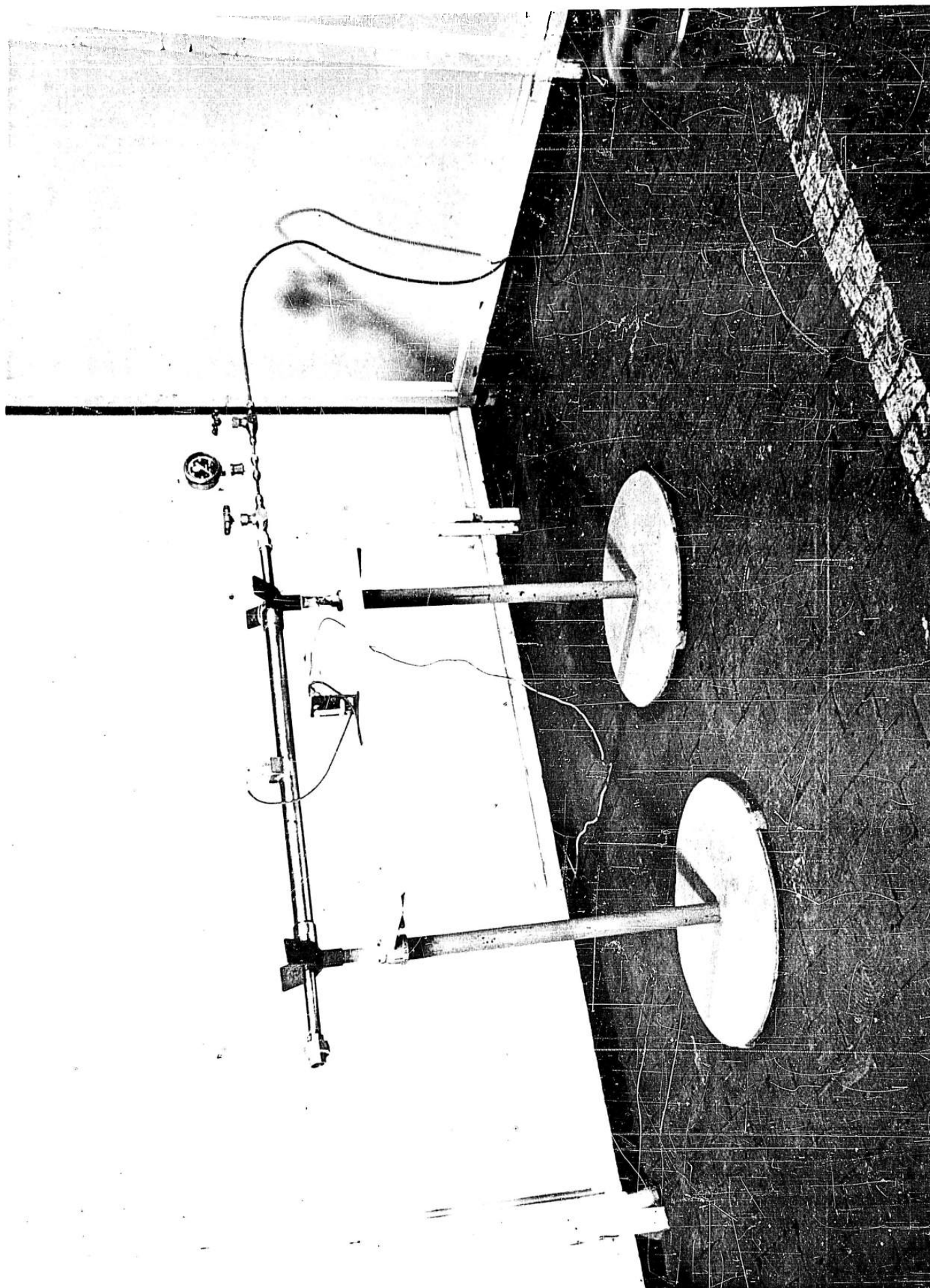


Figure 12. Film Ignition Equipment

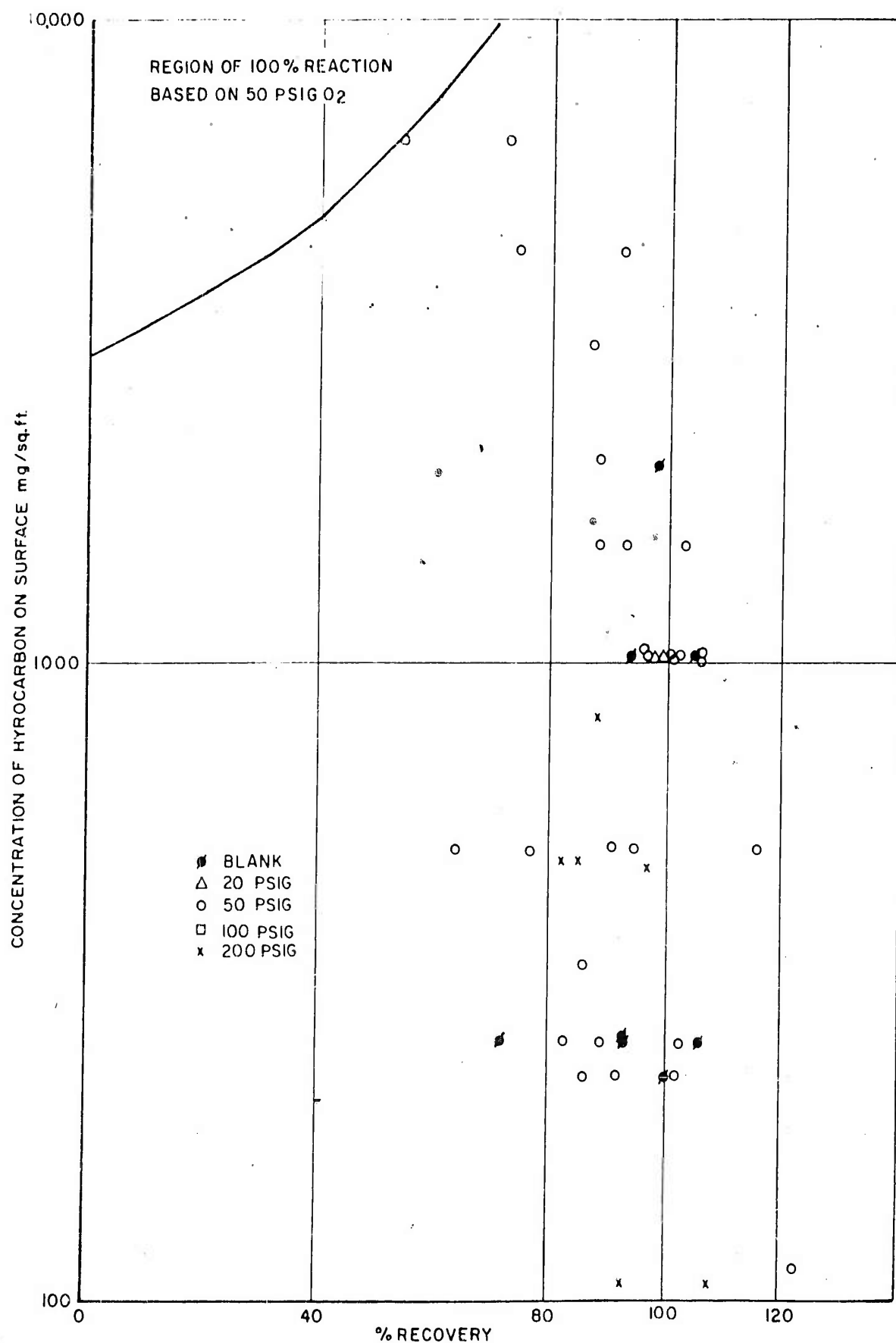


Figure 13.
PERCENT RECOVERY OF HEXADECANE
AFTER SPARK IGNITION

TABLE II.
RECOVERY OF N-HEXADECANE FROM IGNITION TESTS

Surface Concentration mg/sq. ft.	Oxygen Phase	Pressure psig	Igniter	No. of Runs	Recovery Percent	95% Confidence Level for Recovery
145	Gas	50	Blank	2	100, 119	109 + 19
240	Gas	50	Blank	4	100, 93, 93, 106	98 + 6
290	Gas	50	Blank	3	103, 82, 97	94 + 12
1050	Gas	50	Blank	2	94, 105	99 + 11
110	Gas	200	Spark	2	93, 108	108 + 17
110	Gas	50	Spark	1	123	---
145	Gas	50	Spark	4	80, 111, 80, 100	93 + 15
240	Gas	50	Spark	6	86, 92, 102, 83, 89, 103	92 + 8
290	Gas	50	Spark	6	122, 90, 112, 86, 89, 109	101 + 12
500	Gas	200	Spark	3	82, 85, 97	88 + 10
500	Gas	50	Spark	6	86, 64, 77, 91, 95, 116	---
580	Gas	50	Spark	5	93, 85, 100, 92, 97	93 + 5
1050	Gas	200	Spark	1	83	99 + 3
1050	Gas	100	Spark	4	100, 5, 101, 5	---
1050	Gas	50	Spark	5	96, 97, 100, 106, 106	---
1050	Gas	20	Spark	2	98, 99	---
1050	Gas	1500	Spark	10	Original data accidentally destroyed.	83 + 6
1520	Gas	50	Spark	3	88, 93, 103	95 + 9
4400	Gas	50 ^a	Spark	2	74, 92	83 + 18
6500	Gas	50 ^b	Spark	2	53, 72	62 + 19
28	Gas	200	Electric Match	5	61, 70, 84, 108, 143	93 + 28
110	Gas	200	Electric Match	2	99, 127	113 + 28
220	Gas	200	Electric Match	1	99	---

TABLE II (Cont'd)

Surface Concentration mg/sq. ft.	Oxygen Phase	Pressure psig	Igniter	No. Runs	Recovery Percent	95% Confidence Level for Recovery
450	Gas	200	Electric Match	2	70, 74	72 + 4
800	Gas	200	Electric Match	1	88	-----
274	Liquid	-	Blank	1	106	-----
584	Liquid	-	Blank	2	113, 129	121 + 16
1096	Liquid	-	Blank	4	76, 61, 94, 63	74 + 15
274	Liquid	-	Spark	5	123, 143, 101, 120, 85	115 + 20
584	Liquid	-	Spark	4	72, 81, 99, 113, 99	93 + 14
1096	Liquid	-	Spark	5	85, 55, 48, 54, 89	66 + 17

The pipe section was disconnected and opened. The remaining film was dissolved in two 125 cc. batches of fresh carbon tetrachloride. This solution was concentrated by evaporation of most of the solvent in a standard Pyrex evaporation unit, and the n-hexadecane in the concentrate was determined.

4. Discussion

Figure 13 is a plot of the results of 45 tests including 8 control blanks in which concentrations of n-hexadecane ranging from 250 to 6000 mg/sq ft were exploded by spark ignition. (See Table II) Apparently, in the concentration range above 1,000 mg/sq ft of n-hexadecane, ignition and subsequent burning occurred only in the immediate area, while below the range of 1,000 mg/sq ft no detectable reaction took place.

Some runs were made using DuPont Electric Squibs having an energy rating of 6 cal/sec for about one second. However, insufficient work has been done on this phase to make available data which may be analyzed for conclusions. The runs with the electric match showed wide variations in hydrocarbon recovery which was attributed to some materials burning off the match itself.

The points at lower concentrations indicating more than 100% recovery of n-hexadecane, are due to variations in the mechanical handling of the equipment and are due to the incomplete washing-out of the lubricant from the previous test. The spread of data is partly due to techniques which needed revising.

The results of these tests (Figure 13) indicate that a safe load of n-hexadecane film thickness is perhaps 100 mg/sq ft rather than the 4 mg/sq ft. A higher concentration could have been chosen except for mechanical reasons. A film thickness of 250 mg/sq. ft. of n-hexadecane created an oily surface, and 500 mg/sq. ft. produced a film having definite flow characteristics. This latter condition should never be tolerated in any LOX system because films which are thick enough to flow are capable of accumulating in puddles.

5. Future Work

These tests will be continued with particular attention given to technique so that the spread of values may be decreased. Tests will also be run with liquid oxygen to verify that the safety level is not lower than with gaseous oxygen.

BIBLIOGRAPHY

1. Bailey, B. M. and Vignale, V. J. : "Study of Liquid Oxygen Contamination", Progress Report No. 1, dated October 1959, Air Force Contract No. AF 33(616)-6730. Air Products, Incorporated, Allentown, Pennsylvania.
2. Bailey, B. M. and Vignale, V. J. : "Study of Liquid Oxygen Contamination", Progress Report No. 2, dated January 1960, Air Force Contract No. AF 33(616)-6730. Air Products, Incorporated, Allentown, Pennsylvania.
3. Bailey, B. M. and Vignale, V. J. : "Study of Liquid Oxygen Contamination", Progress Report No. 3, dated April 1960, Air Force Contract No. AF 33(616)-6730. Air Products, Incorporated, Allentown, Pennsylvania.
4. Bailey, B. M., Sterner, C. J. and Vignale, V. J. : "Study of Liquid Oxygen Contamination", Progress Report No. 4, dated July 1960, Air Force Contract AF 33(616)-6730. Air Products, Incorporated, Allentown, Pennsylvania.
5. Ent, W. L. : "Sampling and Analysis of Liquid Oxygen", Supplement to Summary Progress Report No. 4, Air Force Contract No. AF 33(616)-6730. Air Products, Incorporated, Allentown, Pennsylvania.
6. LeSuer, J. C. and Williams, C. L. : "Interim Standards for Liquid Oxygen Systems", STL/BMD, AFMTC, May 8, 1959.
7. Palmer, K. N. : "Selected Aspects of Gas and Vapor Explosions", Progress Report No. 38, Jour. Inst. Fuel 29, 293, 1956.

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