3057

NATIONAL BUREAU OF STANDARDS REPORT

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Performance of Drifreez Driers in a Freon-12 Refrigerating System

by

Minoru Fujii
Albert W. Diniak
Ernest E. Hughes
C. W. Phillips
P. R. Achenbach

Report to

The Office of The Quartermaster General
Department of the Army

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

U. S. DEPARTMENT OF COMMERCE
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Heating and Air Conditioning Section
Gas Chemistry Section

to

The Office of The Quartermaster General
Department of the Army

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PERFORMANCE OF DRIFREEZ DRIERS IN A FREON-12 REFRIGERATING SYSTEM

by

Minoru Fujii, Albert W. Diniak, Ernest E. Hughes,
C. W. Phillips, and P. R. Achenbach

ABSTRACT

An investigation of the performance of Drifreez driers for removing moisture from a Freon-12 refrigerating system and the possible attendant hazards from pulverization of the calcium carbide desiccant and the circulation of acetylene in the refrigerant circuit was made for the Office of The Quartermaster General. The drying characteristics of the Drifreez drier were compared with those of a silica gel drier intended for the same purpose and for systems of similar size. The test results showed that the Drifreez drier was superior to the silica gel drier in the amount of water that could be removed with equal values of end dryness up to 40 ppm or conversely the Drifreez drier was superior in that it could produce a lower end dryness than a silica gel drier for equal water removal in the range from 5 to 20 grams of water. The Drifreez drier was shown to have a lower drying rate than the silica gel drier. The hazard tests showed that the highly-explosive material, copper acetylide, was formed in the refrigerating system by the reaction of acetylene with the copper tubing and that a mild explosion could be initiated by cutting the tubing with a hacksaw after removing the refrigerant. Another hazard was shown to be possible if a Drifreez drier or any other drier using calcium carbide as the desiccant was employed to remove moisture from a closed system in which air alone was being circulated. Vibration tests showed that the calcium carbide in the Drifreez drier pulverized to some extent but the particles leaving the drier were too small to clog strainers and would probably not score compressor cylinder walls.

I. INTRODUCTION

In response to a request from the Office of The Quartermaster General, dated May 27, 1952, an investigation of the performance of certain Drifreez driers manufactured by Berna Corporation, Richmond Hill, N.Y., was undertaken as a basis for determining the desirability of using these or other driers employing calcium carbide as the desiccant in Quartermaster refrigeration units. The investigation was divided into three main parts, as follows: (A) Tests to determine the effectiveness of the Drifreez driers in removing water in a Freon-12 refrigerating system with respect to speed of drying, total capacity for water absorption, and end dryness of the system, (B) tests to determine whether or not any hazards would result from the presence of acetylene gas in the system, produced from the reaction of calcium carbide and water, and (C) tests to determine whether the calcium carbide granules would pulverize under vibration and contribute foreign matter in a solid state to the remainder of the refrigerant system. The description of the apparatus, test procedure, and results for the three parts of the investigation are presented separately under the following headings:

Part A	Drying Tests
Part B	Hazard Tests
Part C	Vibration Tests

An overall evaluation of the Drifreez drier is made at the end of the report.

PART A. DRYING TESTS

I. Introduction

The effectiveness of the Drifreez drier containing calcium carbide for removing moisture from circulation in a refrigerating system using dichlorodifluoromethane (Freon-12) was studied on request of The Office of the Quartermaster General. The performance of the specimen driers was studied with respect to end dryness, speed of drying, and total moisture removing capacity with some consideration being given to size, weight, and cost in comparison with other driers now being used. Tests of a silica gel drier were also made for comparison.

Some of the more desirable properties of a refrigerant drier are as follows:

1. Ability to produce a low final moisture content.
2. Non-deliquescent.
3. Non-frangible.
4. No corrosive or erosive end products.
5. Chemically inert with respect to refrigerant and oil.
6. The rate of moisture removal may be of importance for some applications.

Hitherto moisture determinations in refrigerating units depended on sampling a large quantity of refrigerant from the system and measuring the average moisture content of the entire sample. The inherent disadvantages of such methods can be eliminated by the application of an electrolytic method developed by E. R. Weaver at the National Bureau of Standards. This method of moisture measurement employing an electrolytic film permitted making observations in rapid succession at the inlet and outlet of the drier so that the drying process could be followed as it progressed.

II. Description of Specimens

Development of the Drifreez driers by the manufacturer was in progress during the course of the tests. Five different models were submitted at different times by the manufacturer. The several models differed primarily in the method of embedding the calcium carbide granules and in the number and kind of filter pads and screens used at the two ends of the drier. The vibration tests were made on the first model and drying tests were made with specimens of the second, third and fourth models.

The specimens were identified as follows:

DRIFREEZ CARTRIDGE

Berna Corporation
Richmond Hill 18, N. Y.

1/3 to 1 horsepower
The nameplate carried the following information: "This cartridge removes all moisture occurring in refrigeration units using Methyl Chloride or Freon under all normal operating conditions. Do not install on Sulfur Dioxide or Ammonia Systems. Installation is directly into the liquid line before the expansion valve."

The dimensions of the cartridges were as follows:

Length from flare to flare	6-3/4 in.
Diameter, outside	1-5/16 in.
Weight, approximately	232 grams
3/8 in. flare connections	
6 cu. in. capacity	

The desiccant was described by the manufacturer as hard crystalline acetylenogens containing trace elements. This can be more simply described as impure calcium carbide. It was granular in form ranging from 0.4 in. to 8 mesh, approximately. About 43 grams of desiccant were used in each cartridge. Item 1, Fig. 1, is an exterior view of one of the Drifreez driers.

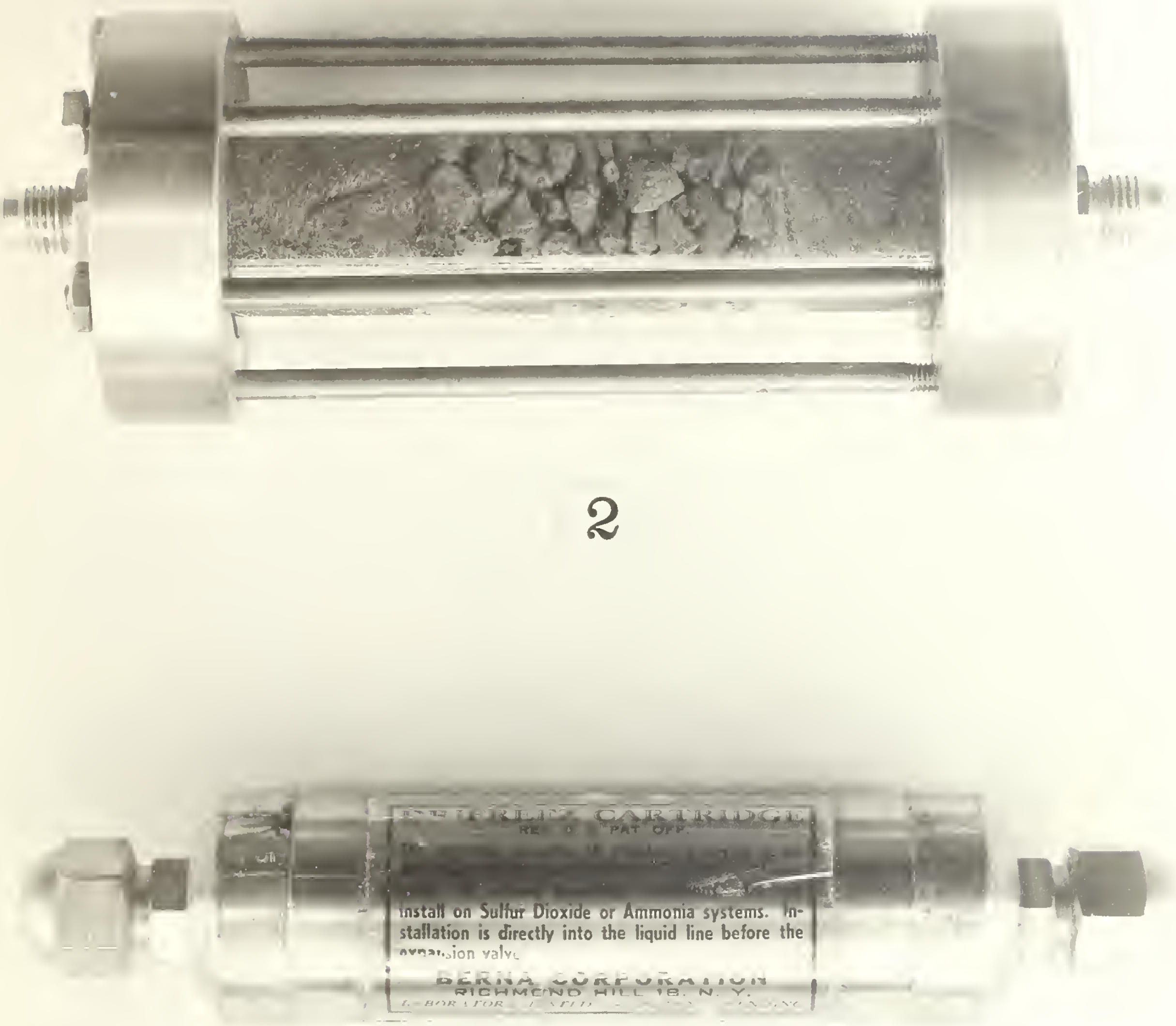

2
CARTRIDGE
PAT OFF
install on Sulfur Dioxide or Ammonia systems. Installation is directly into the liquid line before the expansion valve
RICHMOND HILL 18, N. Y.
1

Fig. 1

The second model submitted is shown disassembled as item 1 in Fig. 2. Calcium carbide granules, weighing approximately 43 grams but with slight variation in amount among several cartridges, were spread on a fine steel wool pad. This pad was rolled up for insertion into the cartridge as shown in Fig. 2. A steel wool pad was used at each end of the steel wool roll. On the outlet end of the drier two fine wire screens with a thin wool filter sandwiched between were used whereas a single fine wire screen was used on the inlet end. The screens were approximately 65 x 88 mesh and appeared to be made of bronze wire. The brass end-pieces were soft-soldered to the cylinder. A perforated baffle was placed between the wire screen and the brass end-piece on the outlet end.

The third model submitted is shown disassembled as item 2 in Fig. 2. In this model the calcium carbide granules were rolled up in a steel wool pad backed up by a pad of wool felt. The outlet edges of these pads were folded over the calcium carbide as shown in Fig. 2 before rolling them up. A single layer of screen was used at each end of the roll and there were no wool fiber or steel wool pads at either end. The end-piece and baffle features were identical to those on the first model tested.

The fourth model submitted had a cylindrical body of glass for observation purposes and was considered to be a demonstration unit. It is shown as item 2 in Fig. 1. The dimensions of this cartridge were about the same as those of the previous models except that the brass flanges were 2-7/16 inches in diameter and 3/4 in thick. The glass cylinder fitted against shoulders machined in the flanges and was sealed with a rubber gasket at either end. Six studs were used to draw the flanges snugly against the gaskets and the cylinder. The center portion of the cylinder was filled with granulated calcium carbide, and fine steel wool pads filled the remaining space at either end. A fine mesh screen was placed downstream of the steel wool pad within the cartridge on the outlet end. The entire specimen weighed 1134 grams at the end of the test. The original weight of the calcium carbide was reported by the manufacturer to be 43 grams whereas the weight of the mixture of calcium carbide and calcium hydroxide was 58 grams at the end of the test. The original weight of the calcium carbide could not readily be computed from the final weight of the mixture because of the impurities present.

The silica gel drier used for the test was identified as follows:

Mueller Brass Company
Maximum horsepower - 1

The dimensions of the cartridge were as follows:

Length from flare to flare	8 in.
Diameter, outside	1-15/16 in.
Weight	572 grams
3/8 in. flare connections	
12 cu. in. capacity	

The desiccant was granular silica gel weighing 116 grams. The desiccant filled the entire cylinder except for a flat screen at the inlet end and a cone-shaped screen at the outlet end. The brass end-pieces were screwed to the cylinder and soft-soldered.

III. Description of Apparatus

1. Refrigeration Unit - (See Figs. 3 and 4)

A 1/3-horsepower air-cooled condensing unit (R) with an evaporator (H) made of 3/8" copper tubing was employed. The system was charged with 4.5 pounds of Freon-12 at the beginning of the test. A heat load was imposed on the evaporator by passing electric current through nichrome wire wound around the evaporator coil which was insulated electrically from the heating element with asbestos. Current flow was adjusted by means of rheostat (M) to control the load. The thermostatic expansion valve was exchanged to an automatic expansion valve (G) during the course of testing to provide steadier operating temperatures and to avoid freeze-up at the valve due to hunting. An oil separator (N) was used to minimize the flow of oil through the evaporator portion of the system. A by-pass arrangement (C) was installed between the discharge drier downstream of the oil separator and the suction line for the purpose of introducing water into the system. The specimen drier (A) was installed in the liquid line in accordance with

FIG. 2

FIG.3

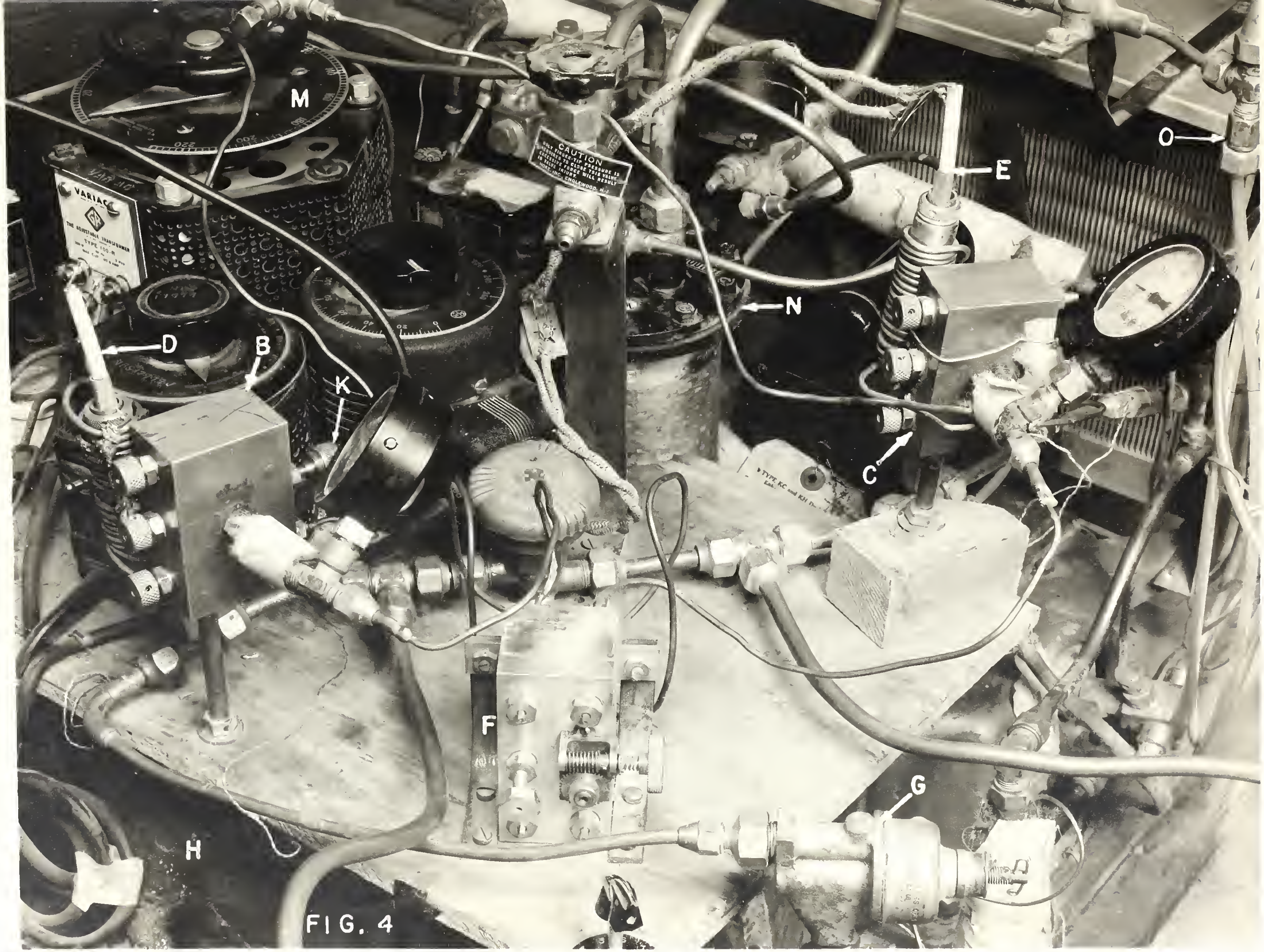


FIG. 4

the manufacturer's instructions. The overall view of the refrigeration unit and moisture measurement apparatus is shown in Fig. 3.

2. Moisture Measurement

The measurement of moisture in the refrigerant was made using a method developed by E. R. Weaver of the National Bureau of Standards in which a hygroscopic film of sulphuric-phosphoric acid mixture was applied to the surface of a detector exposed to the refrigerant gas and water vapor mixture in the refrigerating system. The film reached equilibrium with the water vapor in the refrigerant gas rapidly forming a solution, the electrical conductivity of which was a measure of the water content of the refrigerant vapor. Compressed air of known moisture content was used as a comparison gas to calibrate the film after each reading. By adjusting the pressure of the compressed air until the same conductivity was obtained, the two gases were made to have the same concentration of water. The unknown water content was then calculated from the two pressures and the known content of the compressed air from the following formula:

$$Wx = Wc \frac{Pc}{Px}$$

Where Wx = unknown water content in refrigerant at zero gage pressure.
Wc = known water content of comparison air at zero gage pressure.
Px = absolute pressure at which a conductivity reading was obtained on the unknown refrigerant gas.
Pc = absolute pressure of the comparison air at which the same conductivity reading was obtained as for the refrigerant gas.

Corrections were made for the deviation in behavior of all the gases involved, including water vapor, from the ideal gas laws. The compressed air used for comparison was saturated at between 1000 and 2000 pounds per square inch gage pressure and was permitted to expand to get a comparison reading. For very dry conditions in a refrigerating system, however, a secondary comparison air was sometimes used. This secondary supply of air is a cylinder of fairly dry air whose moisture content had been previously determined by comparison with the saturated air. For these tests the compressed air required for making all moisture determinations was obtained from a single cylinder by means of a parallel circuit with a saturator in one branch. Because of the pressure relationships involved, the electrical method could be used to make moisture measurements in refrigerant in the gaseous state only.

The sampling system is shown diagrammatically in Fig. 5 and certain components are identified by letter in Figs. 3, 4 and 6 also. Two sampling points, one on each side of the drier (A), were established on the liquid line. Two small bore tubes, each dipping into the main stream of liquid refrigerant at the sampling points, carried a portion of the liquid refrigerant to heaters (D, E) where it was completely vaporized. The heaters (D, E) consisted of the electric heating elements regulated by rheostats to supply the required amount of heat for complete vaporization of the liquid refrigerant. To attain an efficient vaporizing process, the refrigerant tubing was wrapped around the heaters in a spiral and was thermally insulated from the surrounding air. The vaporized refrigerant then flowed to specially-built, pressure-tight detector blocks (B, C) containing the detectors (K), (See Fig. 6) where the moisture determinations were made. By manipulating these control valves in the detector block, either refrigerant vapor or the compressed air used for comparison could be caused to flow past the hygroscopic film on the detector (K). After passing through the detector blocks (B, C) the refrigerant was returned to the suction line for recirculation. The flow through the sampling circuit was controlled by valves (F) so that very little refrigerant was permitted to bypass the evaporator (H). Compressed air used for comparison was exhausted to atmosphere. The piping circuits used for connecting the compressed air supply to the detector blocks are shown diagrammatically in Fig. 6. The gas connections were so arranged that the same cylinder of compressed air (I) supplied the "dry" comparison air directly and the "wet" comparison gas through saturator (J). As shown in Fig. 6, either of the two comparison gases could be directed to the two detector blocks (B, C).

The detectors (K) were connected to a Weston galvanometer (Q) (See Fig. 3) which served as a null point indicator. An Esterline-Angus time recorder (L) was used to record the net operating time of the refrigeration unit. A potentiometer (P) was used to measure the temperatures of detector blocks (B, C) and of the gas samples.

SAMPLING SYSTEM

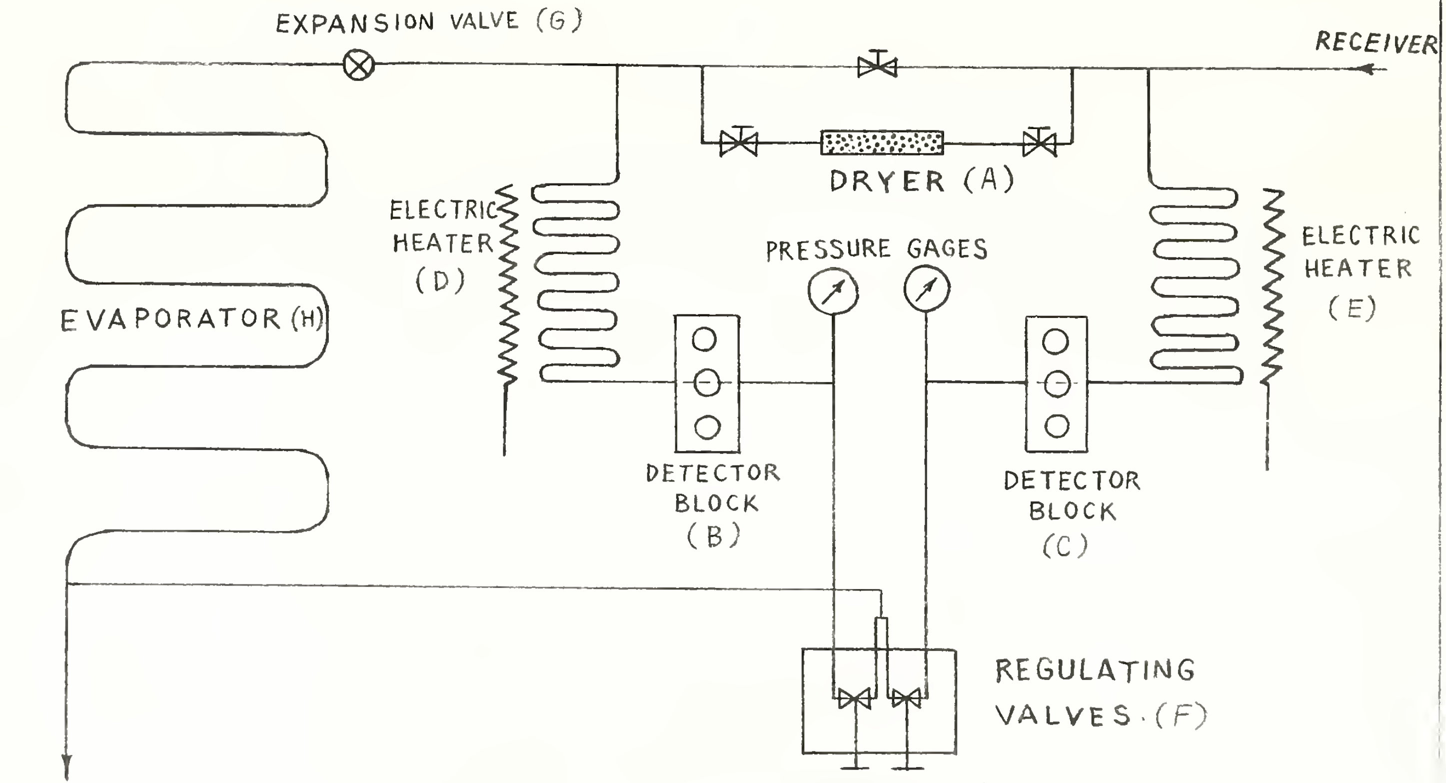


FIG. 5

NOTE: LETTERS IN PARENTHESIS CORRESPOND TO LETTERING IN FIG. 3 AND FIG. 4

GAS CONNECTIONS

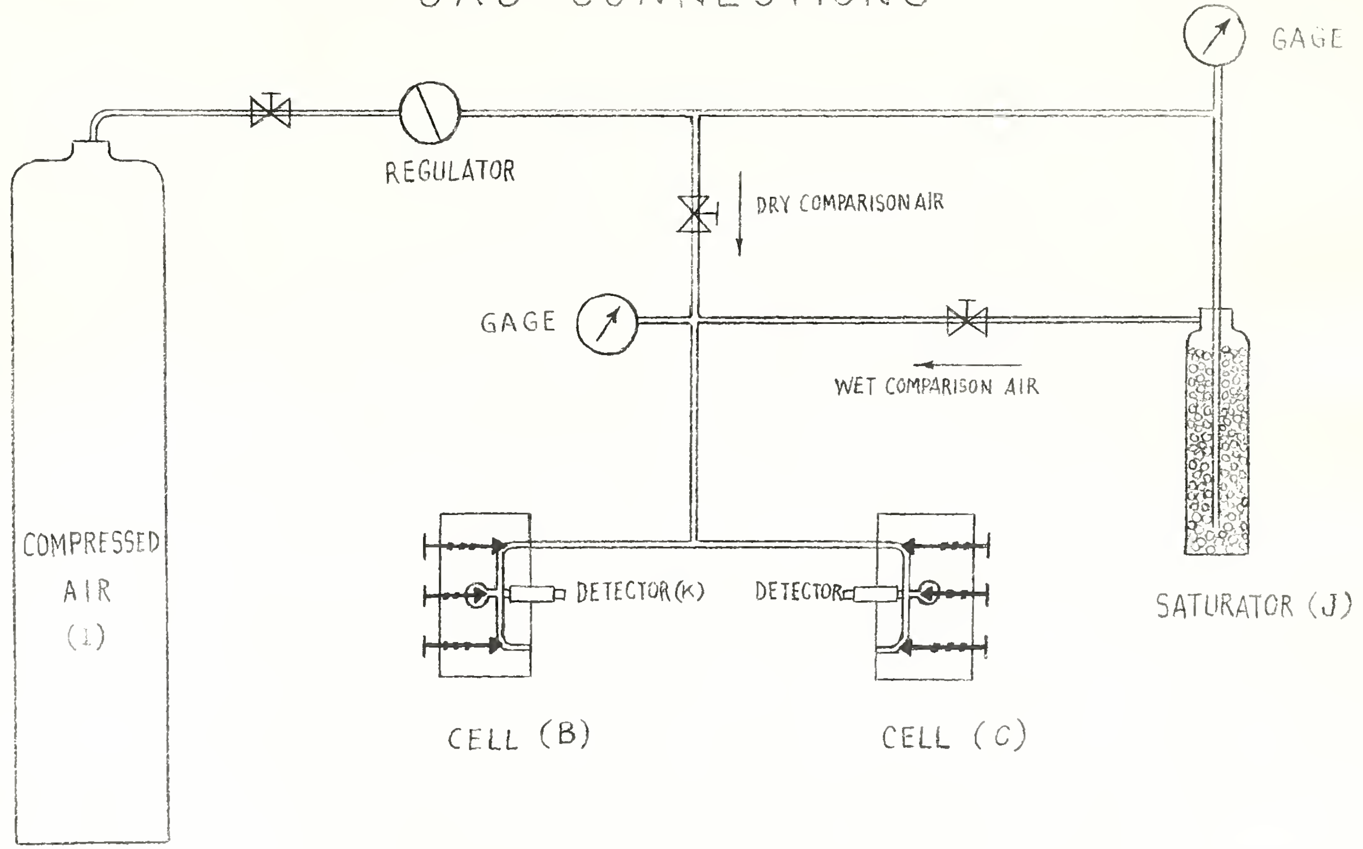


FIG. 6

NOTE: LETTERS IN [illegible] CORRESPOND TO LETTERS IN FIG. 3 AND FIG. 4

IV. Test Procedure

A total of seven series of tests were made to determine drying performance of three models of the Drifreez drier and one model of a silica gel drier. A fifth model of the Drifreez drier was not tested because the investigation was terminated.

Each drying test was begun with a new drier in a well-dried system. When initial wetness of the system was high, other spare driers were used to reduce the moisture content in the system. Known quantities of water were added in the suction line by means of the bypass between the discharge line and the suction line, utilizing the pressure difference across the compressor to inject the water. The quantity of water added at one time varied from 0.1 gram to 20 grams. With a refrigerant charge of 4.5 lb of Freon 12, 0.1 gram of water uniformly mixed in the system would produce a concentration of about 50 ppm by weight if the effect of the oil in the system is neglected. At first, smaller amounts of water were added and larger amounts were added later. The moisture content at the inlet and at the outlet of the specimen dryer was measured alternately as fast as the apparatus permitted.

The compressor served as a good means of mixing water in the refrigerant. Care was taken not to damage it by adding water too rapidly. The system was operated with an evaporator temperature above 32°F during most of the investigation to prevent freezing of water in the evaporator and at the expansion valve orifice.

V. Test Results

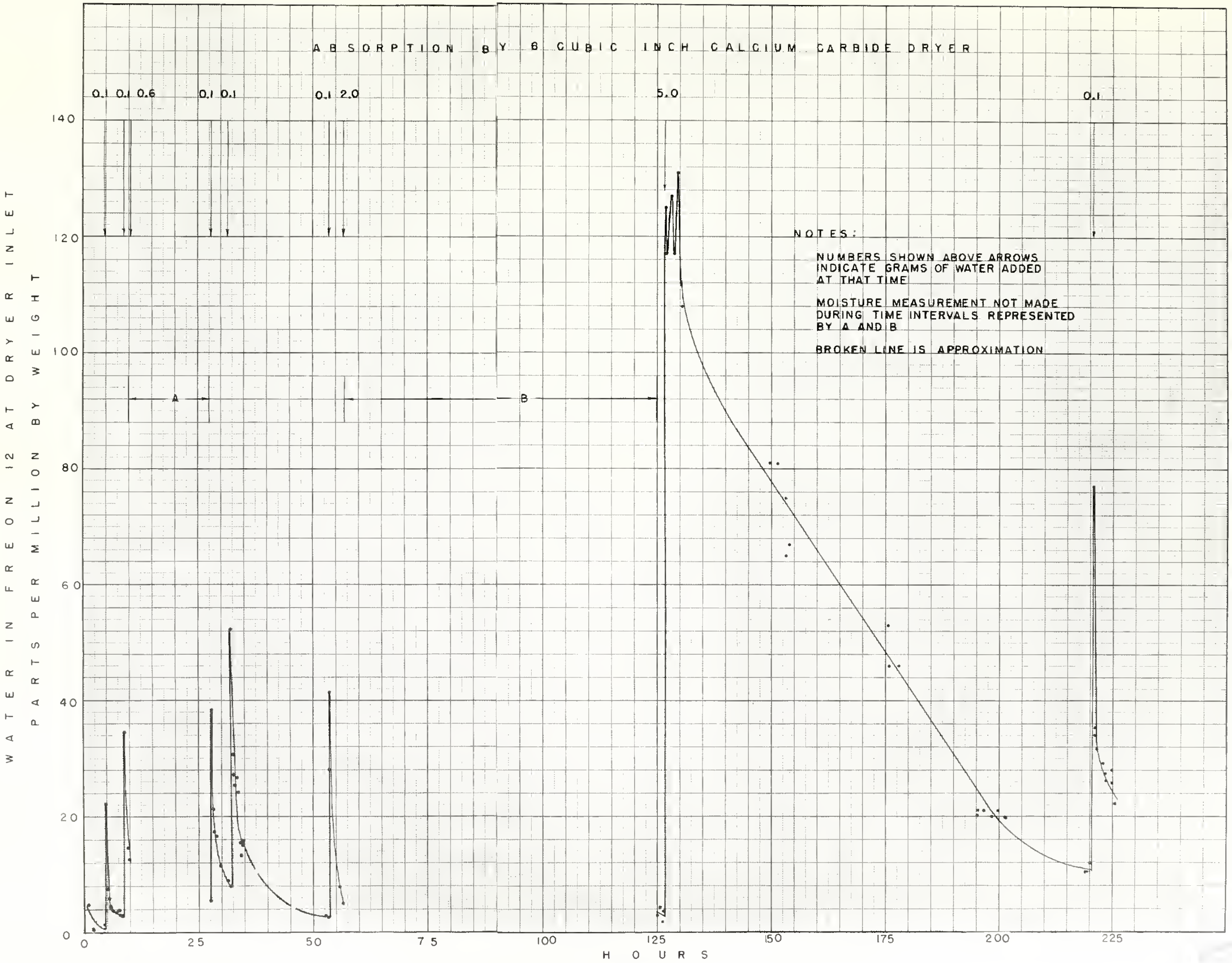
1. Drying Tests

Preliminary tests were made of two specimens of the second model of Drifreez cartridge. The results of these tests were not suitable for plotting in graphical form because of difficulties with the moisture measuring apparatus and freezing of the water at the expansion valve. These preliminary tests did indicate that a low end dryness could be obtained with the Drifreez driers.

Fig. 8, giving results of a different specimen of Drifreez drier also indicates that low end dryness was attained.

Tests were made of three specimens of the third model of the Drifreez driers submitted by the manufacturer. In this model the calcium carbide granules were rolled up in overlaid pads of steel wool and wool felt as shown in item 2 of Fig. 2. A total of 8.2 grams of water was introduced into the system during tests of the first specimen in 9 injections ranging in magnitude from 0.1 gram to 5 grams. The moisture content in parts per million at the inlet to the drier is plotted in Fig. 7 whereas that at the drier outlet is plotted in Fig. 8 for the 225 hours of the test. Moisture contents were observed just before and for several hours after 7 of the 9 injections. When a small amount of water (0.1 gram) was added, the system was dried to approximately the initial condition in 3 to 4 hours.

When 5.0 grams of water were added at one time over 90 hours were required to lower the moisture content of the system from the maximum value of 131 ppm to 10 ppm by weight. The moisture content remained reasonably steady at a value near 125 ppm for about 3.5 hours after injecting the 5 grams of water. This suggests that the amount of water added was more than could be dissolved in the entire refrigerant charge so there was probably free water floating on the liquid refrigerant in the receiver. The moisture content at the drier outlet was almost as high as at the drier inlet during this 90 hour period indicating that the moisture was absorbed very slowly by the drier. The close agreement in moisture content between the drier outlet and drier inlet was undoubtedly caused in part by the bypassing of moisture around the calcium carbide granules. Because a relatively small amount of calcium carbide was rolled up in steel wool and felt in the Drifreez cartridge, there would be many paths through the drier for which the moisture-laden refrigerant would not come in contact with the calcium carbide. Since the solubility of water in Freon-12 at 32°F is of the order of 25 ppm by weight, (A.S.R.E. Data Book, 7th Edition), free water was probably released in the evaporator of the refrigerating system for 50 or more hours after the injection of the 5 grams of water because the moisture content at the outlet of the drier exceeded this value. The moisture released in the evaporator would gradually be returned to the compressor by the refrigerant vapor as the system became dryer.


ABSORPTION BY 6 CUBIC INCH CALCIUM CARBIDE DRYER

NOTES:

NUMBERS SHOWN ABOVE ARROWS INDICATE GRAMS OF WATER ADDED AT THAT TIME

MOISTURE MEASUREMENT NOT MADE DURING TIME INTERVALS REPRESENTED BY A AND B

BROKEN LINE IS APPROXIMATION

FIG. 7

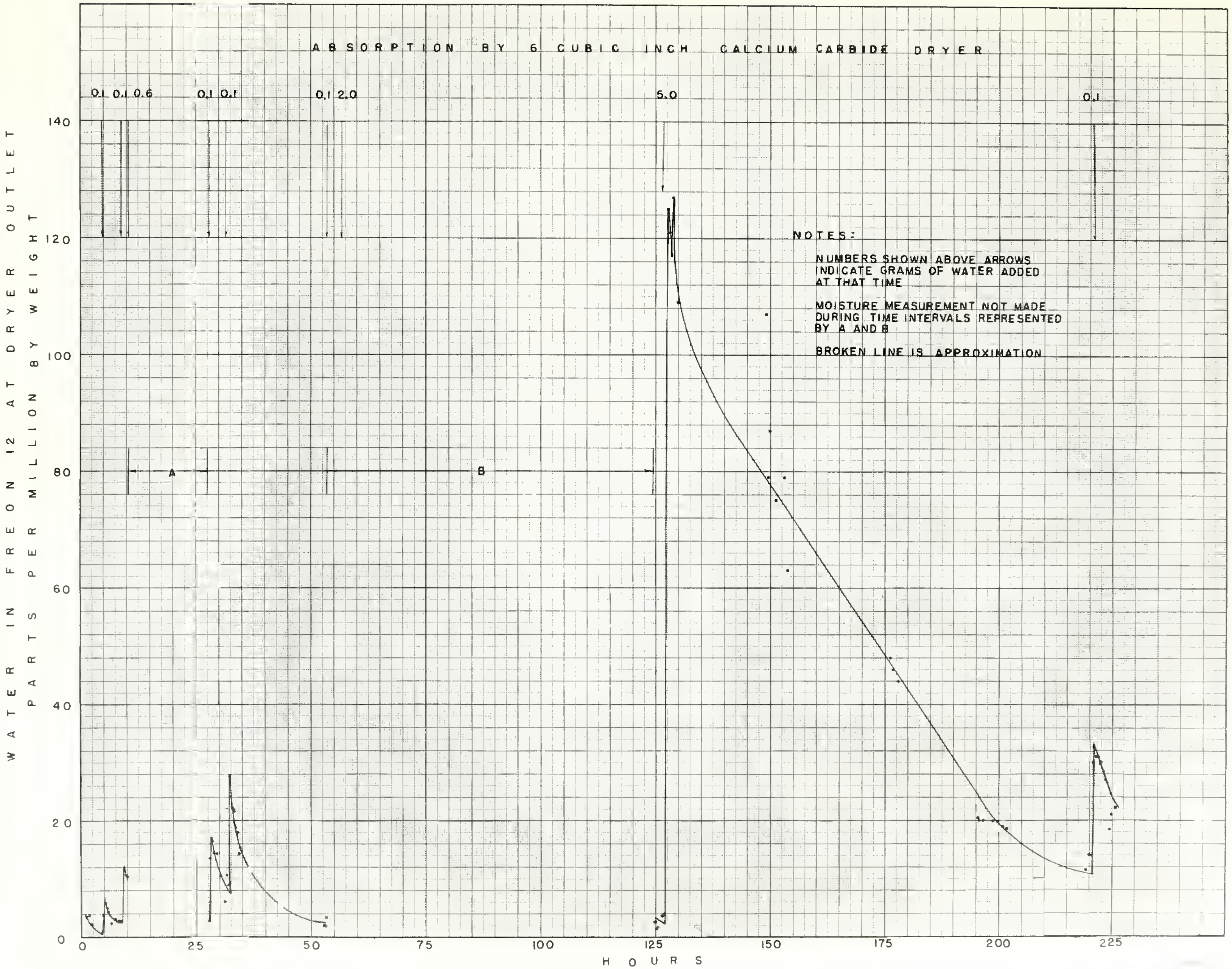

ABSORPTION BY 6 CUBIC INCH CALCIUM CARBIDE DRYER
0.1 0.1 0.6
0.1 0.1
0.1 2.0
5.0
0.1
A
B
NOTES:
NUMBERS SHOWN ABOVE ARROWS INDICATE GRAMS OF WATER ADDED AT THAT TIME
MOISTURE MEASUREMENT NOT MADE DURING TIME INTERVALS REPRESENTED BY A AND B
BROKEN LINE IS APPROXIMATION
WATER IN FREON 12 AT DRYER OUTLET
PARTS PER MILLION BY WEIGHT
0
20
40
60
80
100
120
140
0
25
50
75
100
125
150
175
200
225
HOURS

FIG. 8

During the tests of the second specimen of the third model of the Drifreez drier 20 grams of water were added to the system at one time to determine the capacity of the drier for absorbing water. With an initial moisture content of 16 ppm before injection of the water, the moisture content was reduced back down to 40 ppm after 7 days operation. An additional two days of operation did not reduce the moisture content below 40 ppm which is not dry enough to prevent freezing-out of free water at the expansion valve for suction pressures below freezing.

Calcium carbide reacts with water to form calcium hydroxide and acetylene in accordance with the following equation:

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2\uparrow$$

From the atomic weights of the several elements it can be shown that 43 grams of calcium carbide would react with about 24 grams of water to produce about 50 grams of calcium hydroxide and 17 grams of acetylene. The test of this second specimen indicated that 20 grams of water was somewhat in excess of the capacity of this drier when applied to a system operating at evaporator temperatures below 32°F, whereas the theoretical equation indicated a capacity of about 24 grams of water. The difference may be due to impurities in the calcium carbide.

A similar test was made of a third specimen of the third model of the Drifreez drier with 5 grams of water being added at three different times. The moisture content of the system was reduced to a low value with a spare drier before adding the first increment of 5 grams. Four days later the moisture content was 18 ppm at which time the second increment was added. In another four days of continuous operation the drier had reduced the moisture content to 22 ppm whereupon the third 5 gram injection was made. After the third injection of 5 grams 11 days were required to reduce the moisture content to 17 ppm.

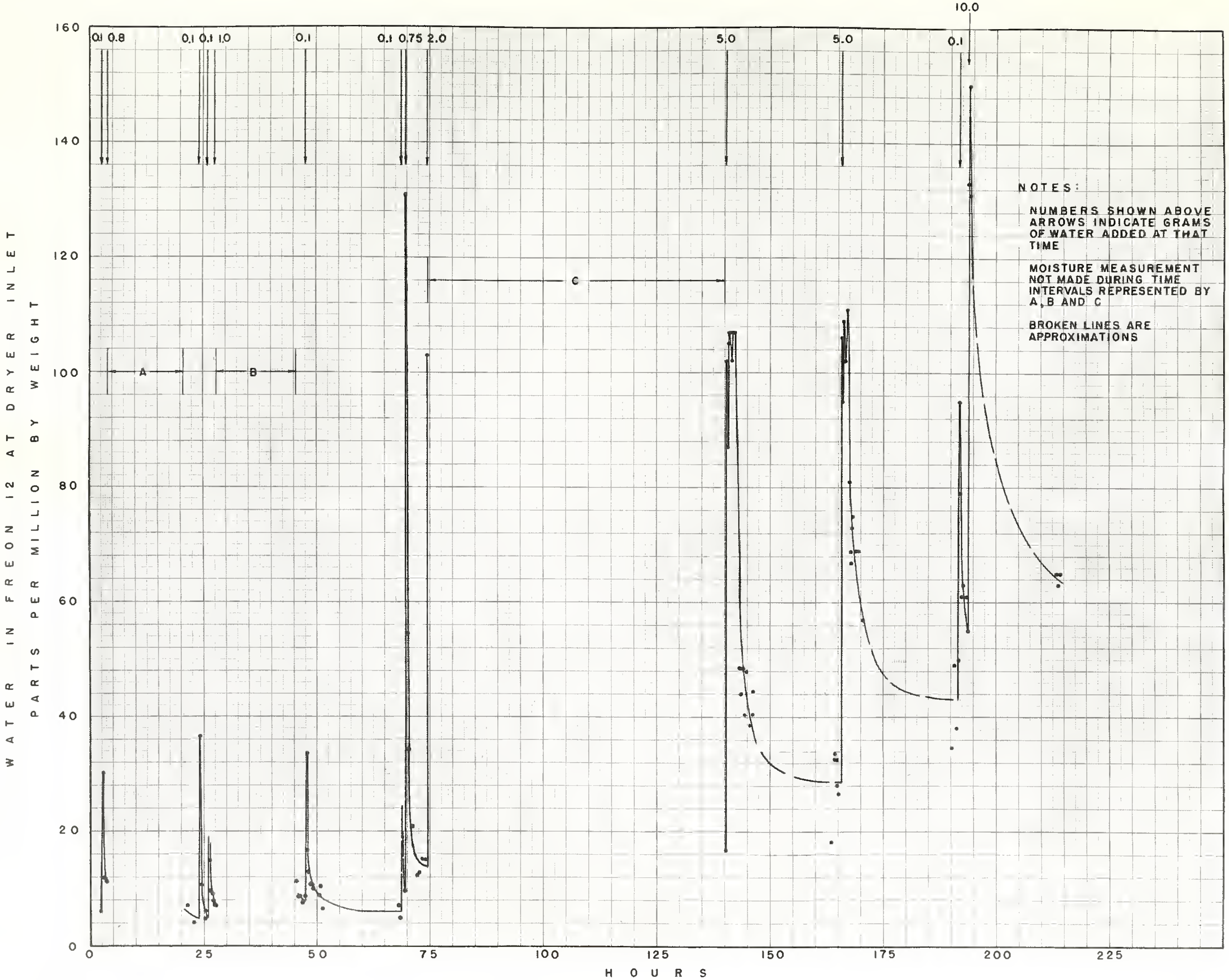
The results obtained with the latter two specimens indicated that the third model Drifreez cartridges had a useful moisture absorbing capacity between 15 and 20 grams of water when used in a Freon-12 system that is to be operated at evaporator temperatures a little below freezing.

One test was made with the fourth model of Drifreez drier - the demonstration model shown as item 2 of Fig. 1 with a cylindrical glass body. The test was started with an initial moisture content of 17 ppm and 10 grams of water were injected at one time. The drying curve is shown in Fig. 11 for the ensuing 60 hours during which the moisture content was reduced from a peak value of 150 ppm to a final value of about 30 ppm. There is a likelihood that the moisture content at the drier inlet remained near 150 ppm for three hours or more until all of the excess water in the receiver or in the compressor could be dissolved by the refrigerant passing through the system. Observations were taken for only about one hour immediately after injection of the water. Fig. 11 indicates that the moisture content varied somewhat for repetitive readings at close time intervals. This could be caused by random variations in the moisture content at the receiver outlet since the liquid refrigerant and water in the receiver would not necessarily remain well-mixed. The moisture content at the drier outlet averaged about 5 ppm lower than that at the drier inlet. A comparison of Fig. 11 with Fig. 7 and 8 shows that the fourth model Drifreez cartridge reduced the moisture content more rapidly than the third model even though more water was injected at one time in the fourth model. This difference is probably accounted for by the better contact between the desiccant and the moisture-laden refrigerant in the fourth model in which the calcium carbide granules filled the entire cross section of the cartridge in the center portion.

After the 60 hours operation illustrated in Fig. 11 an additional 5 grams of water were injected into the system. After about 5 days operation a pressure drop of 110 psig developed between the drier inlet and outlet indicating a stoppage. Inspection revealed that the stoppage was caused by the calcium hydroxide deposited in a pasty mass on the downstream side of the calcium carbide granules.

One test was made with a silica gel drier. A total of 25.15 grams of water was added to the system in 13 injections ranging in amount from 0.1 gram to 10 grams. Moisture observations were made at the inlet and outlet of the drier before and after 10 of the 13 injections of water. The results are plotted in Figs. 9 and 10 for the inlet and outlet of the drier, respectively.

ADSORPTION BY 12 CUBIC INCH SILICA GEL DRYER



NOTES:

NUMBERS SHOWN ABOVE ARROWS INDICATE GRAMS OF WATER ADDED AT THAT TIME

MOISTURE MEASUREMENT NOT MADE DURING TIME INTERVALS REPRESENTED BY A, B AND C

BROKEN LINES ARE APPROXIMATIONS

FIG. 9

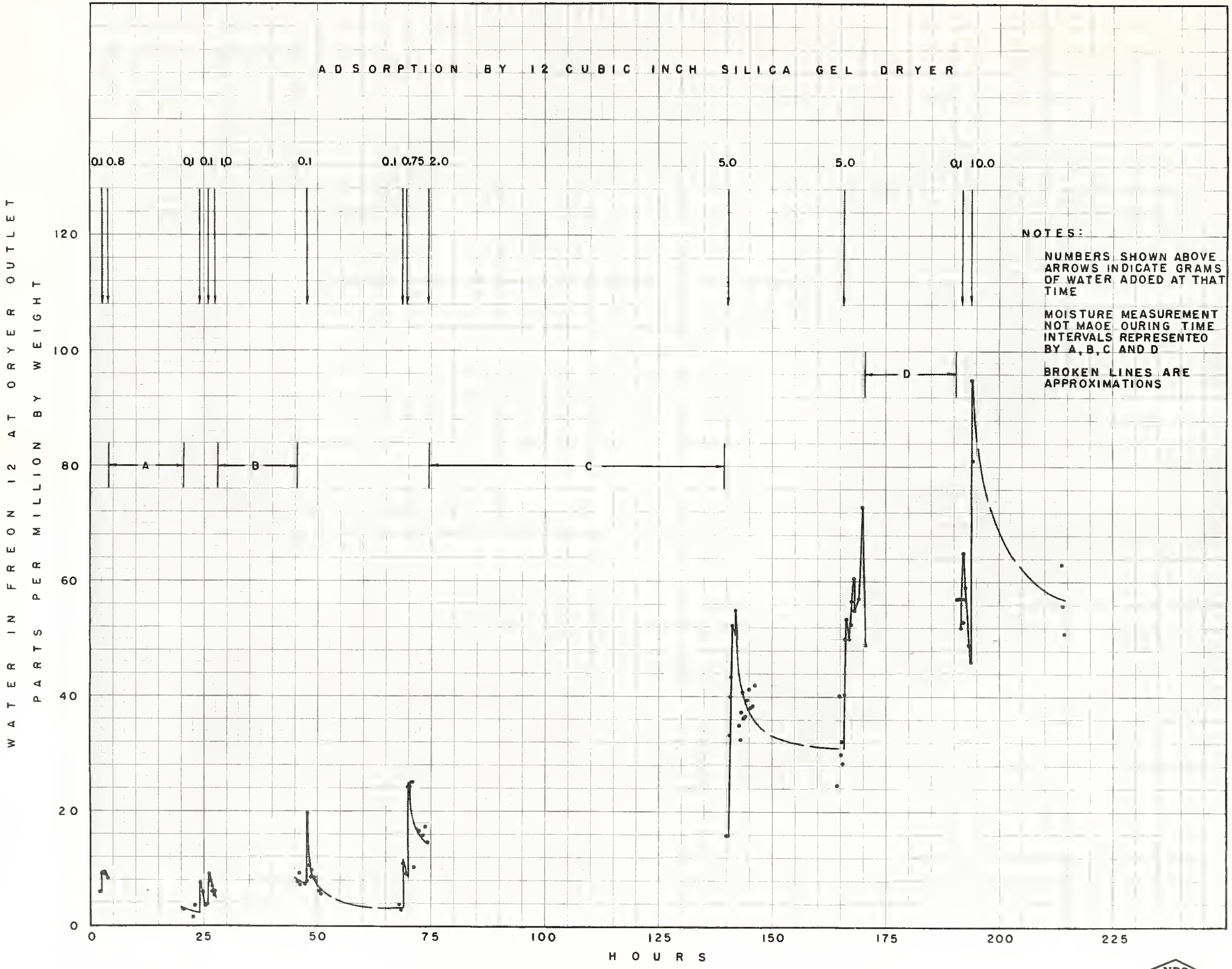

ADSORPTION BY 12 CUBIC INCH SILICA GEL DRYER
0.1 0.8
0.1 0.1 1.0
0.1
0.1 0.75 2.0
5.0
5.0
0.1 10.0
A
B
C
D
NOTES:
NUMBERS SHOWN ABOVE ARROWS INDICATE GRAMS OF WATER ADDED AT THAT TIME
MOISTURE MEASUREMENT NOT MADE DURING TIME INTERVALS REPRESENTED BY A, B, C AND D
BROKEN LINES ARE APPROXIMATIONS
WATER IN FREON 12 AT DRYER OUTLET
PARTS PER MILLION BY WEIGHT
120
100
80
60
40
20
0
0
25
50
75
100
125
150
175
200
225
HOURS

FIG.10

ABSORPTION BY CALCIUM CARBIDE DRYER

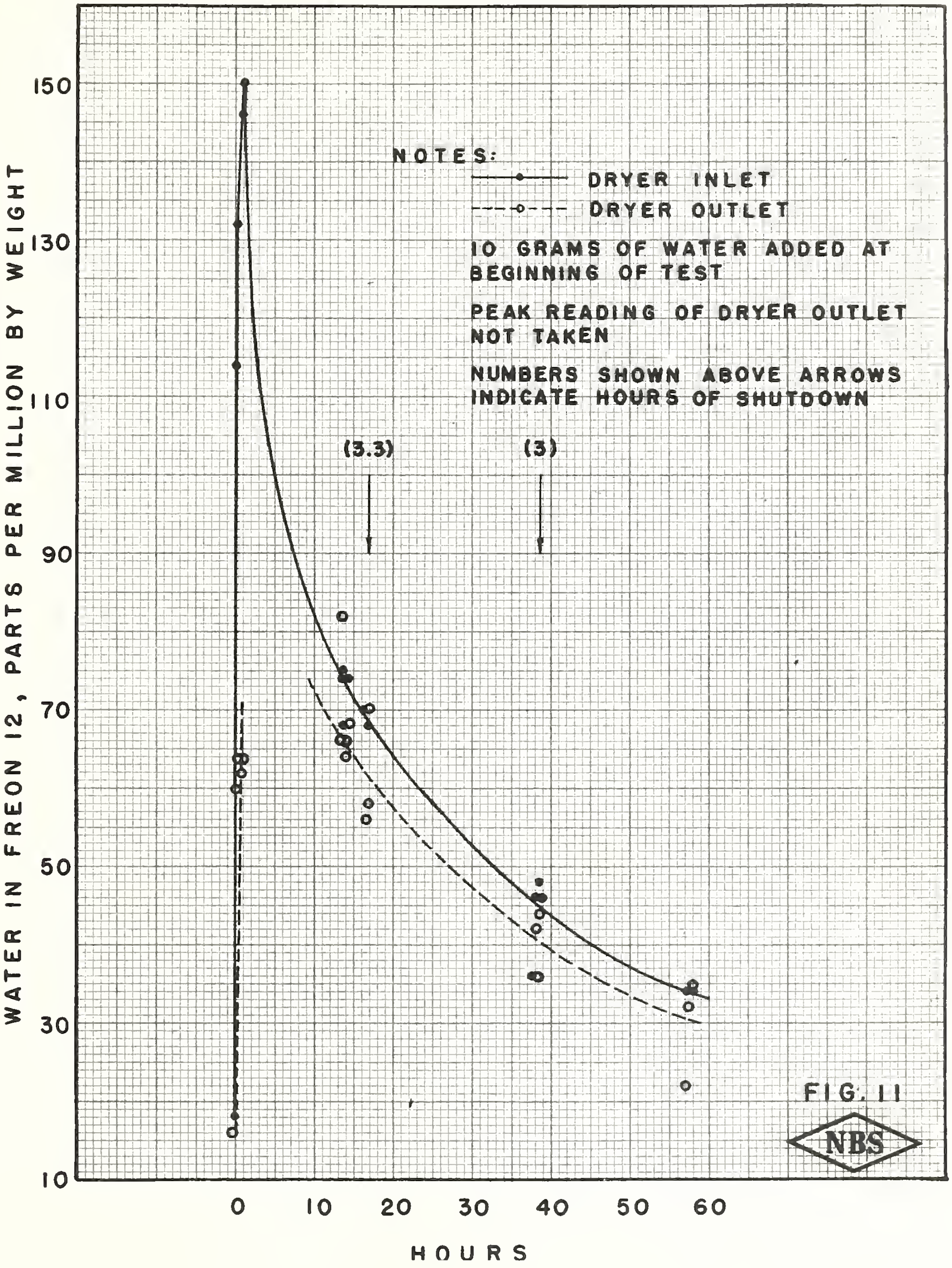


FIG. 11

Fig. 10 shows that the system was dried to approximately the original dryness in 1 to 2 hours after injection of 0.1 gram of water. However, the moisture content at the outlet of the drier increased appreciably for a short time when this small amount of water was added at one time showing that the desiccant did not remove all the moisture during its first passage through the drier.

The end system wetness at the drier outlet gradually increased as the amount of water adsorbed increased. This result is expected with an adsorption-type drier. After 5.05 grams of water had already been adsorbed, the addition of 5 more grams of water at one time caused the moisture content at the drier outlet to rise to 55 ppm for a brief time. Fig. 10 indicates that after 26 hours operation the moisture content was reduced to an average value of 34 ppm. During this 26-hour period, the expansion valve would be expected to freeze up at evaporator temperatures lower than 32° F.

Published data by Veltman and Waring[1] on the water-holding capacity of silica gel in equilibrium with liquid Freon-12 show that the residual water in Freon-12 would be about 33 ppm after adsorbing an amount of water equivalent in percentage to that adsorbed by the test specimen at this stage of the test. These results indicate that the capacity of this model silica gel drier was less than 10 grams of water when used in a Freon-12 system operating at an evaporator temperature a little below freezing.

A comparison of Figs. 9 and 10 reveals that the peak value of moisture content at the silica gel drier outlet was significantly lower than the peak value at the drier inlet following every addition of water to the system. This relation indicates more rapid removal of water by the silica gel drier than was observed with the Drifreez drier, and suggests that silica gel would be superior to calcium carbide for applications in which relatively large quantities of water were suddenly added to the stream of circulating refrigerant.

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[1] Desirable Desiccant Properties for Refrigerant Water Removal, by P. L. Veltman and C. E. Waring, Refrigerating Engineering, December 1947.

2. Miscellaneous Observations

In addition to the moisture absorption characteristics of the Drifreez driers certain other features were observed.

A Drifreez cartridge was completely filled with granular calcium carbide without steel wool filters or pads included and water was passed through the cartridge so that it could react with the calcium carbide. The calcium hydroxide resulting from the reaction became so densely compacted in the cartridge that the water flow through the cartridge could not be maintained. When the cartridge was cut open it was found that the carbide had not been completely consumed and the calcium hydroxide had to be removed with a hammer and chisel. This result indicates that the products from the reaction of calcium carbide and water occupy more space than the original carbide granules and reveals the importance of providing some room for expansion in the drier cartridges as they are manufactured.

A Drifreez cartridge was subjected to an internal hydrostatic pressure of 1700 psig for one hour without rupturing the cartridge.

The effect of temperature on the capacity of the Drifreez driers was not investigated because the desiccant was of the chemical absorption type and, therefore, not likely to be significantly affected by the usual range of refrigerant liquid line temperature.

The calcium hydroxide formed by the reaction of calcium carbide with water has a secondary dehydrating effect, but this effect is not likely to be of important magnitude in the presence of calcium carbide that has not reacted with water.

The filtering ability of the several Drifreez driers tested was examined by inspection of the expansion valve strainer and the system receiver at the conclusion of testing. The strainer at the inlet of the expansion valve contained very little foreign material resembling $Ca(OH)_2$. The receiver was cut in two and the interior inspected. There was no dirt nor deliquescent material found in the receiver. The liquid refrigerant in the receiver contained very little impurity.

No tests were made of the Drifreez drier with refrigerants other than Freon-12.

3. Comparison of Electrolytic and Gravimetric Methods of Moisture Determination

Comparison was made of the electrolytic method of moisture measurement with the phosphoric pentoxide (P_2O_5) gravimetric method. The electrolytic method, developed by Mr. E. R. Weaver of the National Bureau of Standards, was used for the Drifreez tests because it permitted rapid readings of more than one point or continuous readings of one point whereas the P_2O_5 gravimetric method required comparatively large samples for batch observation and provided an average indication of the moisture content of the gas extracted from the system over an extended period.

Several methods of comparing the two types of measurement were tried.

Method I involved a simultaneous removal of two separate vapor samples from a cylinder containing commercial liquid dichlorodifluoromethane (Freon-12). One sample was passed through a phosphorus pentoxide absorption train (P_2O_5 method) whereas the other sample was passed through a detector block (electrolytic method) by means of which electrical determinations were made at frequent intervals during the run. (The phosphorous pentoxide absorption train is explained later.) The valves obtained were plotted against the volume of vapor that had passed through the absorption train. A typical result is shown in Graph 1, Fig. 12, and in Table 1. The area under the curve obtained is proportional to the weight of water in the entire sample of refrigerant. The variation in moisture content revealed by the electrolytic measurement was believed to be caused by the evaporation of liquid refrigerant in the supply cylinder necessary to replace the vapor drawn as a sample. The evaporation of liquid refrigerant both chills the liquid at the surface and changes the moisture content of the vapor in contact with the liquid. Table 1 shows good agreement between the average moisture content valves observed by the two measuring methods.

TABLE 1

Comparison of Gravimetric and Electrolytic Methods of Moisture Determination

Method (or Test Procedure)	Moisture Content of Freon, ppm by Weight	
	Electrolytic Method	Gravimetric Method
I	4	3
"	7	8
"	26	23
II	13	14
"	24	26
"	26	27
III	7, 7	9
"	7, 7	9
"	11,11	12

Method II involved placing the detector-block directly in the line from the cylinder to the absorption train so both apparatuses would be making determinations on identically the same sample of gas. The sketch of the apparatus employed is shown in Fig. 13. (A) is the absorption train which was flushed thoroughly with dry air before the analysis. The absorption bulbs were allowed to reach temperature and pressure equilibrium and then weighed. A measured volume of Freon-12 gas was then passed through the train after which the bulbs were again flushed with dry air to remove all traces of refrigerant. The bulbs were again left until temperature pressure equilibrium was attained and then weighed. The gain in weight was the amount of water absorbed by P_2O_5. Referring to Fig. 13, (B) shows the apparatus used to provide dry air at point "a" in the absorption train and (C) is air enlarged sketch of one of the absorption bulbs.

Results obtained from Method II are shown in Graph 2, Fig. 12, and in Table 1. The resulting curve was

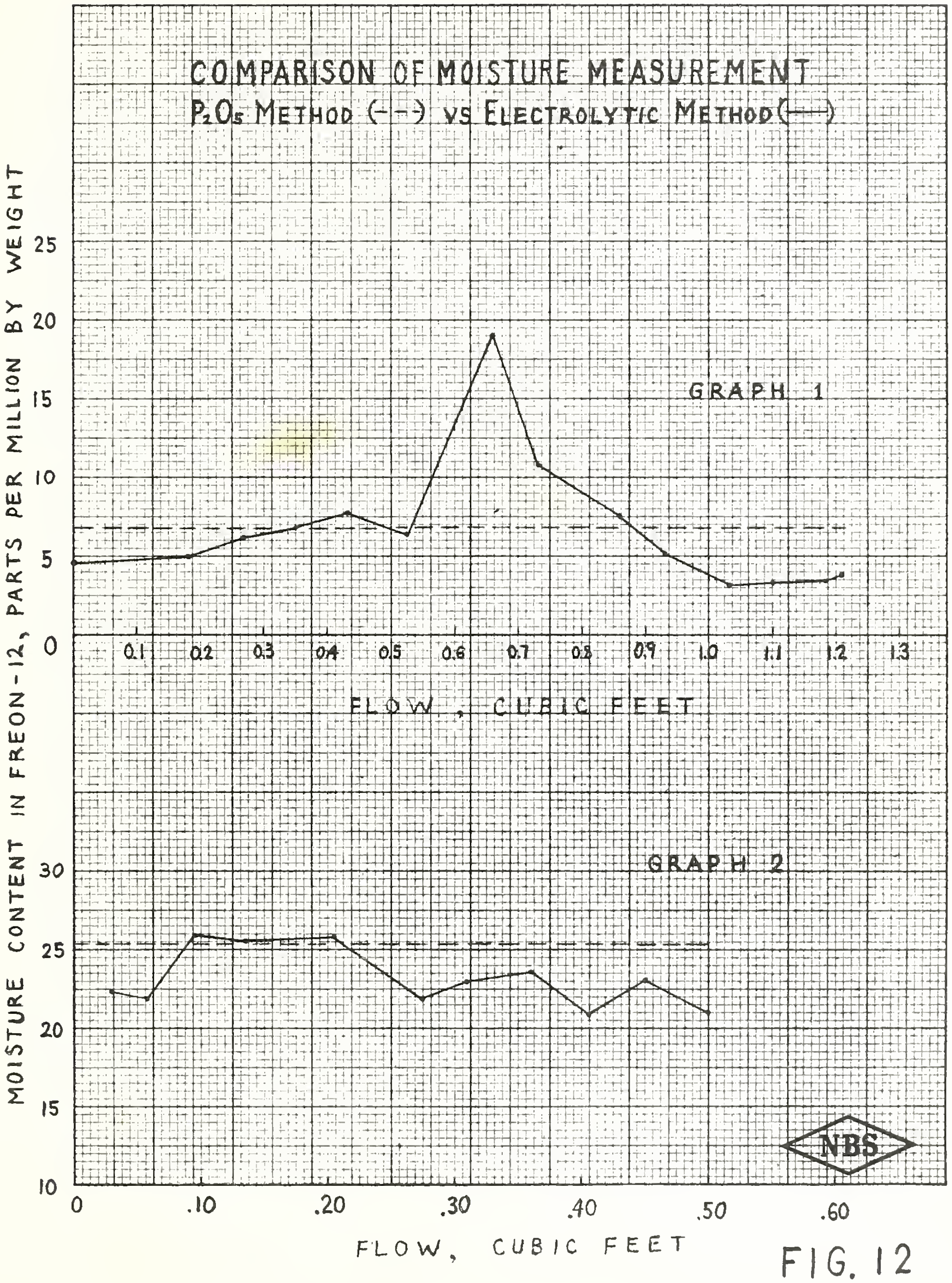
COMPARISON OF MOISTURE MEASUREMENT
P_2O_5 METHOD (- -) vs ELECTROLYTIC METHOD (—)
MOISTURE CONTENT IN FREON-12, PARTS PER MILLION BY WEIGHT
GRAPH 1
0
5
10
15
20
25
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
FLOW, CUBIC FEET
GRAPH 2
10
15
20
25
30
0
.10
.20
.30
.40
.50
.60
FLOW, CUBIC FEET
NBS

FIG. 12

PHOSPHORUS PENTOXIDE ABSORPTION METHOD

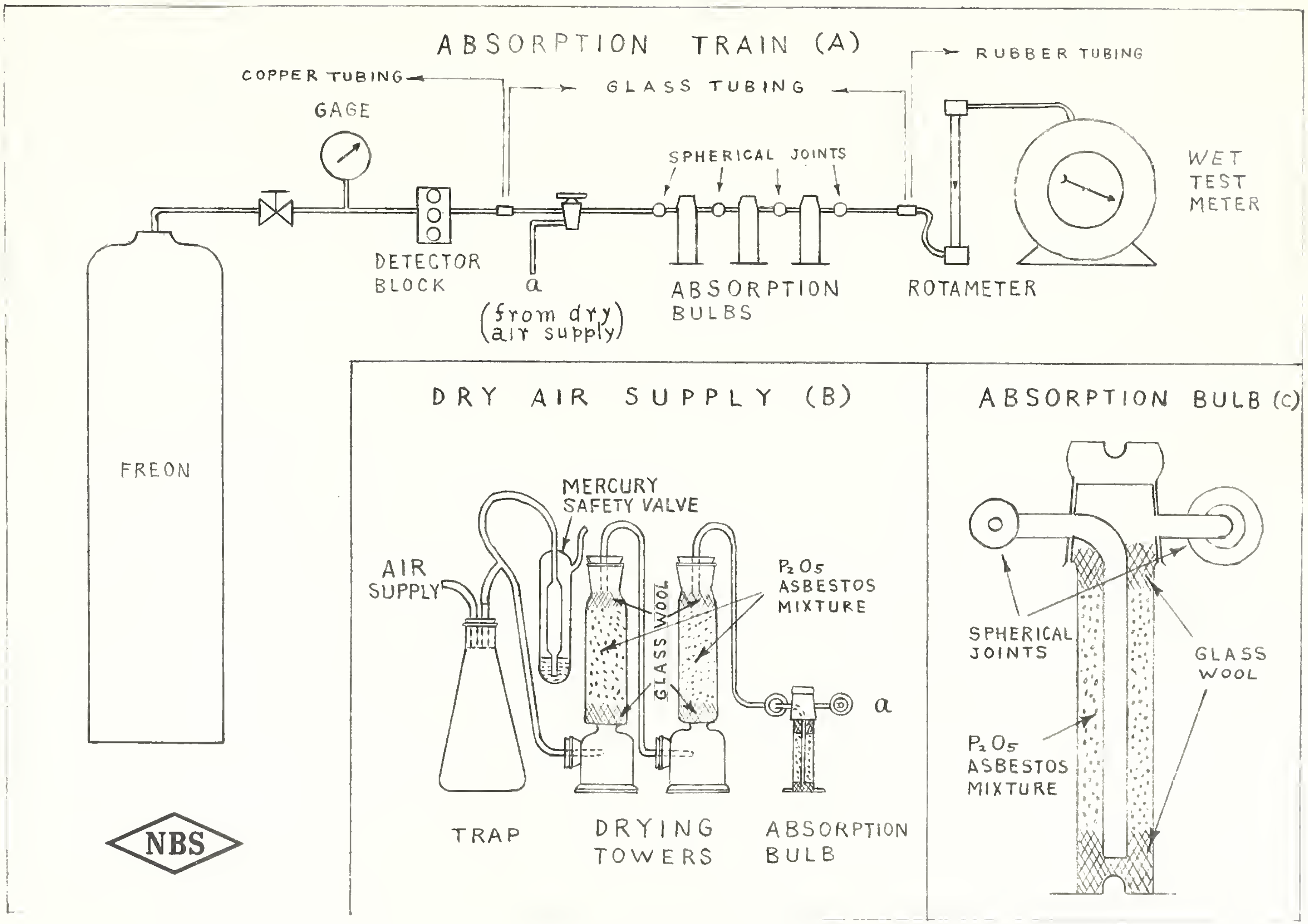

FIG. 13

not as regular as was expected and the slow flow of Freon gas past the detector prevented taking rapid and numerous electrical determinations. Method II still involved the disadvantage of evaporating liquid refrigerant in the supply tank.

Method III made use of a 1-1/2 cubic foot commercial refrigerant cylinder which was charged with moist Freon-12 vapor to a pressure just below the saturation pressure of Freon-12 at room temperature (70 psig). With this source of moisture-laden gas and the same apparatus as shown in Fig. 13, moisture determinations were made electrically before and after each gravimetric determination, and the results were compared. The size of the cylinder made it possible to run duplicate and triplicate analyses before having to recharge the cylinder. Results are shown in Table 1.

Tests were not made for all the ranges of moisture level. However, the results of these comparison tests indicate that the agreement between the two methods is close enough to validate the conclusions reached in the tests of the Drifreez drier.

VI. Discussion

The test results showed that the Drifreez drier removed moisture from liquid Freon-12 in the test system to an end dryness of less than 5 ppm. This permits operation of a Freon-12 refrigerating system without release of free water at the expansion valve for refrigerant temperatures down to approximately minus 15°F, as indicated by the saturation curve for Freon-12 in the A.S.R.E. Data Book, 7th Edition, page 329.

To compare the Drifreez drier with another drier, a silica gel drier of known trade acceptance was selected. Test results showed that this drier, when first installed, dried the test system to below 5 ppm. The selection of size of the silica gel drier for comparison was based on the respective manufacturers' rated maximum horsepower capacity and on the size of flare connection. The length of the silica gel drier was about 1-1/4" longer and the diameter was 5/8" larger than that of the Drifreez drier. Those differences made the total internal volume of the silica gel drier approximately twice that of the Drifreez drier. The Drifreez drier used a steel wool cushion for the desiccant and a filter which occupied a relatively large space in the cylinder of the drier whereas the entire space in the cylinder was occupied by drying agent in the silica gel drier. Thus, the drying ability of approximately 43 grams of calcium carbide, which removes water chemically, was compared with approximately 12 cu. in. or 116 grams of silica gel which removes water by adsorption. Based on price quotations obtained December 18, 1953 from an established refrigeration wholesaler in Washington, D. C., normally stocking the two driers involved in these tests, in lots of 25 or more, the wholesale price of the Drifreez drier was $3.58 each, whereas that of the silica gel drier was $3.60 each.

Except for the drying rates observed at conditions of peak wetness, the instantaneous drying rate of both driers was small enough that the relative drying rates could best be compared by observing the number of hours required for each drier to reduce the system wetness after comparable amounts of moisture have been removed by each drier.

Beginning with a residual moisture content of 3 ppm after absorbing 3.1 grams of water during the first 127 hours of the test, the first specimen of the third model Drifreez drier reduced the system dryness to about 74 ppm in approximately 26 hours after another 5 grams of water were added as shown in Fig. 8. In the same length of time, the silica gel drier reduced the system moisture content to about 34 ppm after 5 grams of water were added when it had already adsorbed 5.05 grams of water during the first 141 hours of the test and the residual moisture content was 16 ppm after that time as shown in Fig. 10. This comparison indicates more rapid moisture removal by the silica gel drier during the period cited. However, the Drifreez drier continued to absorb moisture and, in 96 hours after adding the 5 grams of water, had reduced the moisture content of the system to approximately 13 ppm at the drier outlet. The relatively rapid drying of the silica gel dryer is further shown in Fig. 10 by the drop in system wetness to about 37 ppm in 2-1/2 to 3 hours after the 5.0 grams were added at 141 hours.

Fig. 10 shows that after the test had been in progress for 74 hours, but prior to adding 2.0 grams to the system with the silica gel drier, the system wetness was approximately 16 ppm, and 67 hours after adding the 2.0 grams, making a total of 5.05 grams, the system wetness was again 16 ppm as indicated at an elapsed time of 141 hours in both Figs. 9 and 10. Data by Veltman and Waring[1] show that 16 ppm was an equilibrium value of water in liquid Freon-12 for the percentage of water adsorbed by the silica gel at this stage of the test. By comparison, the Drifreez drier was able to reduce the system wetness to an average of 13 ppm after absorbing 8.1 grams of water as shown on Fig. 8.

The test results showed that the third specimen of the third model Drifreez drier, after absorbing 15 grams was able to reduce the system wetness to 17 ppm whereas tests of the second specimen of the third model Drifreez drier showed that when about 20 grams of water was absorbed by the drier the system wetness was reduced to approximately 40 ppm. Veltman and Waring[1] show that the silica gel drier could be expected to adsorb only 5 grams of water without exceeding an end dryness of 17 ppm, and about 12 grams of water without exceeding an end dryness of 40 ppm.

The silica gel drier was able to reduce the system wetness to approximately 60 ppm after adsorbing 25.15 grams compared to 40 ppm for a Drifreeze drier after absorbing 20 grams. Since freezing problems occur at or below 20 to 30 ppm in Freon-12, the ability of the driers to reduce system wetness below these levels was of primary interest in this investigation. However, the ability to dry to a system wetness in the range above 20 to 30 ppm might be useful in service or maintenance work as an initial step in drying a very wet system. It would be expected that the Drifreez drier would lose its ability to remove water from the refrigerant when all of the calcium carbide had been consumed whereas the silica gel could continue to adsorb some water but with an ever-increasing end wetness of the system.

VII. Conclusion

The drying tests of various models of the test specimen Drifreez (calcium carbide) drier, compared with a 12 cu in. silica gel drier, lead to the following conclusions:

1. For a given end dryness below 30 ppm, the Drifreez drier removed and held more water than the silica gel drier. Moisture levels below 30 ppm are of particular interest in Freon-12 systems operating at 32° F or lower because freezing at the expansion valve is probable at higher moisture levels.

2. The instantaneous drying rate of the silica gel drier was higher than that of the Drifreez drier.

3. For equal moisture removal between 5 grams and 20 grams in each of the two types of driers, the Drifreez drier reduced the system wetness to a lower end point than the silica gel drier.

4. The capacity of the third model Drifreez drier, containing 43 grams of commercial grade calcium carbide, for absorbing water was between 15 and 20 grams of water when used in Freon-12 systems operating at evaporator temperatures no lower than 20° F.

PART B. HAZARD TESTS

I. Introduction

As requested by the Office of The Quartermaster General, tests were made to determine whether or not hazard resulted from the use of Drifreez driers (with calcium carbide as the desiccant) in a refrigerating system employing dichlorodifluoromethane (Freon-12) as the refrigerant.

Moisture removal by calcium carbide driers is achieved by chemical reaction (absorption) which results in the formation of acetylene and calcium hydroxide. The main objective of this investigation was to evaluate the degree of hazard due to the presence of acetylene in the refrigerating system and to determine whether or not a secondary product, copper acetylide, was formed in the system from the reaction of the acetylene with the copper in the piping circuit.

First, the products formed by chemical reaction as a result of using Drifreez driers for the removal of moisture in Freon-12 refrigeration unit were determined. The primary products of the reaction of calcium carbide and water were found to be acetylene and calcium hydroxide. As will be shown later, there was strong evidence that the acetylene reacted with the copper in the system to produce copper acetylide.

It was assumed for the purpose of this investigation that acetylene had no effect on lubricating oil, refrigerant, motor windings, or internal parts of the system other than the copper tubing. The next step was to study possible hazards that might arise from these products and the degree of danger under certain conditions.

II. Study of the Products of Reaction

1. Acetylene

Acetylene, formed by the reaction of calcium carbide and water, circulated in the system with the Freon-12. Any excess of acetylene over that which could be dissolved in Freon-12 would be expected to be trapped in the receiver and condenser. A one-third-ton air-cooled condensing unit with a specially built evaporater was used for the tests. Gas samples were extracted for analysis and the acetylene content in the Freon-12 was determined by the mass spectrometer from time to time both during the drying tests and during other special tests made for the purpose of evaluating acetylene production in the refrigerating system.

One gas sample was drawn from the vapor space in the top of the receiver after about 89 grams of water had been injected into the system. At this time a total of seven Drifreez driers had been used in the system. (35.15 grams of water adsorbed by three silica gel driers were not included in the 89 grams mentioned above.) The analysis of the gas showed the acetylene content in the sample to be 12.95 percent by volume.

Three gas samples were drawn from the discharge line between the oil separator and the condenser when the refrigeration unit was in operation. After about 26 grams of water had been absorbed by five Drifreez driers, the acetylene content of the gas was 0.82 percent, by volume. The second gas sample indicated 2.04 percent acetylene, by volume, after 89 grams of water had been absorbed by seven Drifreez driers. The third sample indicated 7.6 percent acetylene, by volume, after 121 grams of water had been absorbed by nine Drifreez driers.

Table 2 shows, in chronological order, the amount of water added, type and purpose of driers used, leakages in the system, and acetylene content. The table was prepared from the drying test data. It can be seen that silica gel driers and Drifreez driers were used not only for observations on the drier performance, but also for drying out the system either after a test specimen had ceased to dehydrate the system, or preliminary to beginning a new test. At the beginning of the test, 4.5 pounds of Freon-12 were charged into the system. Additional refrigerant had to be added to the system later because of leaks which developed during the test, and the amount added was not measured. Other mechanical difficulties interrupted the tests and made it necessary to replace the specimen driers twice during the course of the tests. Because several of the tests were not made to determine the total absorbing capacity of the driers, precise relationships between the acetylene content, amount of water injected, and amount of desiccant consumed were not established.

No literature was found on solubility of acetylene in Freon-12 and no tests were made to determine it.

Table 2 shows that 52 grams of water were added to the system after the last leak occurred in the system on November 7 necessitating the addition of some Freon. The equation for the reaction of calcium carbide and water shows that the absorption of 36 grams of water produces approximately 26 grams of acetylene. Thus, the absorption of 52 grams of water after November 7 would produce approximately 37.6 grams of acetylene or 0.083 lb. If the system were completely empty on November 7 when the leak was discovered and a full charge of 4.5 lb of Freon-12 were added at that time, the system would contain a little over 1.8 percent, by weight, of acetylene on February 3 after 52 grams of water had been absorbed. A concentration of 1.8 percent, by weight, of acetylene in Freon-12 would correspond to a concentration of about 6.5 percent acetylene by volume at atmospheric pressure with both materials in gaseous state.

The measured concentration of acetylene by volume in the discharge line was 7.6 percent on February 3 after 52 grams of water had been absorbed subsequent to the last addition of Freon-12 to the system. The composition of the mixture of Freon-12 and acetylene vapors in the discharge line should be about the same as that of the liquid in the receiver when the refrigerating unit is in steady operation. The difference between the observed volumetric concentration of 7.6 percent acetylene in the discharge line on February 3 and the value of 6.5 percent computed from the anticipated amount of acetylene formed in the system is not considered significant, but may indicate that the system was not completely empty on November 7 when the last leak occurred. The samples of the Freon-12-acetylene mixture analyzed on November 14 and 17 showed a concentration of 2.04 percent acetylene in the discharge line and 12.95 percent in the vapor space in the receiver. This comparison suggests that all of the acetylene produced was not readily absorbed in the liquid Freon-12 in the receiver. As mentioned previously in this report, no measurement of the solubility of acetylene in liquid Freon-12 was made.

Table 2. Tabulation of Water Addition and Driers Used on 1/3-ton Refrigerating Unit

Date	Water added	Type of new drier installed	Purpose of drier	Location of refrigerant leak	Acetylene, by volume
	Grams				Percent
Sept.					
16	---	Drifreez	Test	---	---
17	1.0			---	---
19	1.0			---	---
24	---	Drifreez	Test	Valve	---
24	0.1			---	---
26	0.1			---	---
Oct.					
1	0.1			---	---
6	---	Drifreez	Test	---	---
14	---	Do	Do	---	---
15	0.1			---	---
15	0.1			---	---
15	0.6			---	---
16	0.1			---	---
16	0.1			---	---
17	0.1			---	---
17	2.0			---	---
20	5.0			---	---
24	0.1			---	---
24	5.1			Line	---
27	8.1			---	---
27	---	Drifreez	To dry system	---	---
28	---	Silica Gel	Test	---	---
28	0.1			---	---
28	0.8			---	---
29	0.1			---	---
29	0.1			---	---
29	1.0			---	---
30	0.1			---	---
31	0.1			---	0.82
31	0.75			---	(sampled from
31	2.0				discharge line)
Nov.					
3	5.0			---	---
4	5.0			---	---
5	0.1			---	---
5	10.0			---	---
6	---	Silica Gel	To dry system	---	---

Table 2 (Continued)

Date	Water added	Type of new drier installed	Purpose of drier	Location of refrigerant leak	Acetylene, by volume
Nov.	Grams				Percent
6	20.0	Drifreez	Test	---	---
7	---			Detector block	---
7	---	Silica Gel	To dry system	---	---
7	---	Drifreez	Test	---	---
7	20.0			---	---
14	---			---	2.04 (sampled from discharge line)
17	---			---	12.95 (receiver)
19	5.0	Drifreez	Test	---	---
24	5.0			---	---
28	5.0				
Dec.				---	---
9	10.0	Drifreez	Test	---	---
12	5.0			---	---
19	2.0			---	---
Feb.					
3	---			---	7.6 (sampled from discharge line)

2. Calcium Hydroxide

Since the products formed by the reaction of calcium carbide and water are known to be calcium hydroxide and acetylene, no analyses were made to identify calcium hydroxide as one of these products.

Calcium hydroxide formed by the reaction of calcium carbide and water should be retained in the drier to avoid clogging of the system or damage to the compressor.

Observation made on the glass cylinder Drifreez drier (the demonstration model) indicated that the steel wool filter in the drier had retained large amounts of the calcium hydroxide in a pasty form. When the thermostatic expansion valve was replaced by an automatic expansion valve after eight Drifreez driers were used, the strainer at the inlet of the former was inspected. A very small amount of the paste-like substance which appeared to be calcium hydroxide was found. The amount was considered to be negligible.

The receiver was cut in half at the conclusion of the tests and its interior was inspected. Calcium hydroxide was not found.

3. Copper Acetylide

The tubing used in most Freon refrigeration systems is made of copper. It was not known whether or not the acetylene produced by a Drifreez drier would react with copper to form copper acetylide in the presence of Freon-12 in a refrigeration system.

The copper tubes used in the refrigeration unit employed for the drying tests were cut open at the end of the drying tests. The inside surface of the tubing throughout the system was found to be coated with a black material. This coating was thicker and darker in color immediately downstream from the drier.

The black material was identified by means of the following analyses:

(a) When pieces of tubing with the black coating were heated over a bunsen burner, small puffs of smoke were emitted from the open ends. Upon close investigation, after the tubing had been permitted to cool, it was found that the black coating had disappeared. Subsequent reheating of the same tubing did not cause any further puffing.

(b) While one of the pieces of tubing taken from the refrigeration system was being cut with a hacksaw, a mild explosion occurred which produced a dull yellow flash and some greyish-black fumes. A small spot of soot remained on the sawblade. It is unlikely that acetylene gas caused the explosion because the mass spectrometer analysis of the gases liberated upon heating the coated copper tubing showed only minute quantities of acetylene.

It has been established[1] that dry cuprous acetylide is exceedingly explosive and is sensitive to shock, friction, and heat.

(c) When pieces of the copper tubing were heated in vacua, much carbon dioxide, some carbon monoxide, and hydrogen were evolved as determined by a mass spectrometer. This indicated that the black material was probably an organic substance. A minute amount of acetylene was also indicated, but this may have been desorbed from the surface.

(d) Pieces of the coated copper tubing were treated with dilute hydrochloric acid in vacua and the gaseous product was examined in a mass spectrometer. The record from the analysis showed large ion currents at masses 24, 25, and 26 in the correct abundance ratio for acetylene. The ion current at mass 26 was 2200 divisions or over two-thirds full scale and acetylene was by far the most abundant component observed. In contrast, only a small amount of acetylene was found when the coated copper tubing was heated without the acid treatment .

It is well known[2] that the addition of dilute acids to copper acetylide releases acetylene according to the equation

$$Cu_2C_2 + 2HCl \longrightarrow C_2H_2 \uparrow + Cu_2Cl_2$$

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[1] Handbook of Dangerous Materials by N. Irving Sax.

[2] The Chemistry of Organic Compounds by James B. Conant.

(e) Some of the strips of the coated copper tubing were treated with dilute hydrochloric acid and the gas evolved was bubbled through an ammoniacal solution of cuprous chloride which was kept in a reduced state by hydroxyl amine hydrochloride. A red precipitate was observed.

It is known[2] that when acetylene is shaken with ammoniacal cuprous or silver solutions, precipitates of metallic acetylide are found as indicated by the following equation:

$$C_2H_2 + Cu_2Cl_2 + 2NH_4OH \rightarrow Cu_2C_2 + 2NH_4Cl + 2H_2O$$

Thus, the gas liberated upon treatment of the coated copper tubing with dilute hydrochloric acid was confirmed by an independent chemical method as being acetylene.

The conclusion drawn from the above observations and experiments was that the black material covering the inner surface of the copper tubing contained copper acetylide which was formed by reaction of the copper with acetylene liberated by the several Drifreez dehydrators.

Referring to Fig. 1, both tubes numbered "1" were taken from the liquid line upstream of the drier and those numbered "2" were taken from the liquid line downstream of the drier and were cut longitudinally. A piece of new unused copper tube is numbered "3" and is shown for comparison purpose. The hacksaw blade used to cut the tubes is numbered "4". The arrow pointing at the black soot on the hacksaw indicates the location at which explosion occurred while cutting one of the tubes numbered "1". The arrow pointing at the lower picture of tube numbered "1" indicates the part of tube that was being cut when the explosion occurred.

III. Results of Hazard Tests

Among the three products (calcium hydroxide, acetylene, and copper acetylide) formed by chemical reaction of calcium carbide, water, and copper in a refrigeration system, calcium hydroxide was not found to have escaped from the Drifreez drier in sufficient quantity to cause clogging of the lines or damage to the compressor, nor was it considered to be hazardous chemically in the refrigeration system. However, further investigations were made to determine the

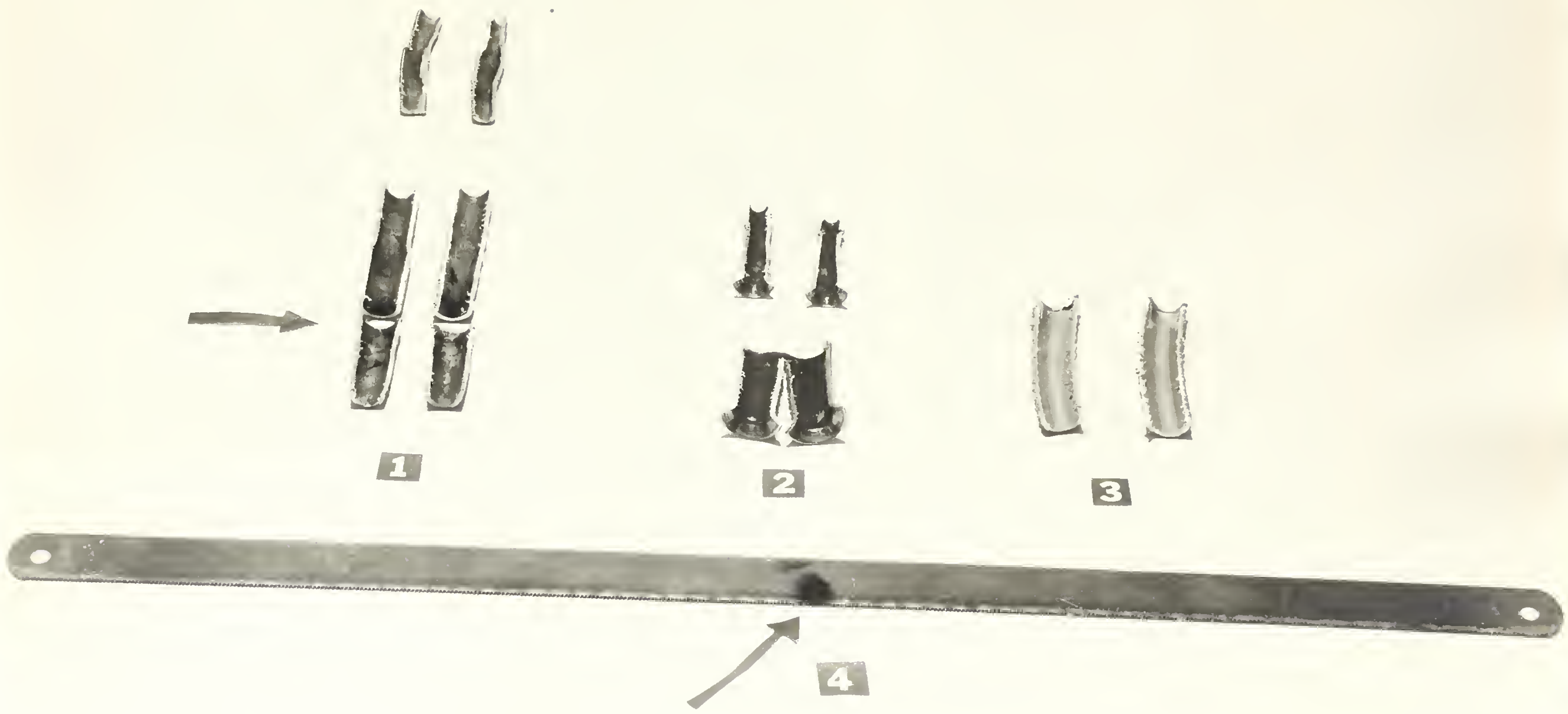

FIG. 1

conditions that might be hazardous and to study the possible extent of damage by acetylene and copper acetylide. Possible hazards could be explosion of copper acetylide, dissociation of acetylene, and explosion of air-acetylene mixtures.

1. Dissociation of Acetylene in Presence of Freon-12

Tests were made to find the amount of Freon-12 necessary to prevent dissociation of acetylene under 300 pounds per square inch gage pressure. According to the past experience of the acetylene manufacturing industry, the causes and conditions for the spontaneous dissociation of acetylene were not precisely known. A comprehensive study of the conditions of heat pressure, friction, or impact that would initiate dissociation of acetylene would be hazardous so it was decided to detonate a sample with a spark plug, if possible. Although it happens infrequently, a spark may be produced in the refrigerant vapor in a hermetically-sealed motor-compressor unit by failure of the windings of the motor.

The apparatus employed is shown in Fig. 2. All of the tubes of the system shown in the figure were filled with water by means of vacuum pump C. Acetylene was produced in the generator A by dropping water from funnel B. The acetylene gas thus produced and Freon-12 from tank J were charged into the 100 ml burette F to obtain the desired mixture. By manipulation of valves, the acetylene-Freon mixture was charged into bomb H. This was accomplished by means of vacuum created in the system by the vacuum pump C. The gas mixture was compressed using air from tank I through reservoir E to bomb H by manipulating suitable valves. The mixture in bomb H was ignited by a marine spark plug K installed on top of the bomb C. The spark plug was fastened by a ball sleeve fitting so that if an explosion took place the spark plug would serve as a safety valve.

Under 300 pounds per square inch gage pressure, the gas mixture did not explode when its composition was 8 percent Freon-12 and 92 percent acetylene (by volume) measured at atmospheric pressure. Under the same pressure, it exploded most of the time when the composition was 7 percent Freon-12 and 93 percent acetylene (by volume) measured at atmospheric pressure. Inconsistency in explosiveness at the latter concentration was believed to be due to differences in the time lag between charging the gases and igniting the mixture under pressure during the several tests. Appreciable change in composition of the mixture was expected after the pressure was applied because of the difference in solubilities of acetylene and Freon-12 in water and the change in the relative partial pressures. In order to find the true composition under pressure, a gas mixture of 8 percent Freon-12 and 92 percent acetylene (by volume) was charged in the bomb and pressure was applied by exactly the same proceedure. At the time when it would normally be ignited, the mixture was extracted from the bomb into a glass tube sampler for analysis. The mass spectrometer showed that the real composition under pressure was 9.2 percent Freon-12 and 90.8 percent acetylene (by volume).

2. Explosiveness of Ideal Mixture of Acetylene and Air in Presence of Freon-12

The amount of Freon-12 necessary to prevent explosion of ideal mixtures of acetylene and air under one and two atmospheres of pressure was determined.

The apparatus employed was simpler than the one used for dissociation of acetylene under pressure. The desired composition of a mixture of Freon-12, air, and acetylene was obtained in a 100 ml burette. It was then transferred to a spherical explosion pipette by means of a levelling bottle. One or two atmospheres of pressure was applied to the gas mixture by the levelling bottle and it was ignited by a spark produced between electrodes in the pipette. A rubber cap placed on the charging inlet of the pipette served as a safety valve when explosion occurred. Mercury instead of water was used in the pipette levelling bottle and the lines.

It was found that under one atmosphere pressure, a concentration above 12 percent Freon-12 (by volume) prevented explosion of ideal mixtures of air and acetylene (7 to 13 percent acetylene by volume). Ideal mixtures of air and acetylene exploded in mixture with 12 percent Freon-12 (by volume).

Under two atmospheres of pressure, mixtures containing more than 16 percent Freon-12, by volume, did not explode with ideal mixtures of air and acetylene.

FIG. 2

FIG. 3

3. Explosion of Copper Acetylide

Attempts were made to explode the deposit found on the inside surface of the copper tubing taken from the refrigeration system. Heating, scratching, and tapping did not cause it to explode.

However, a mild localized explosion was observed while sawing one of the pieces as described earlier in this report.

Copper acetylide oxidizes rather rapidly when exposed to the air which may account for the inability to deliberately produce an explosion by heating, tapping, or scratching the deposit.

4. Explosion of Compressor and Copper Tubing

A hermetically sealed 1/5-horsepower compressor was subjected to an explosion of an ideal mixture of air and acetylene to determine its ability to withstand such an explosion or to examine the extent of its damage.

Fig. 3 shows the apparatus employed. Acetylene was generated in the cartridge C, filled with calcium carbide, by feeding water from cylinder E. A separator D was used to separate water and calcium hydroxide from acetylene. After acetylene was charged into the compressor in the explosion test chamber A, air was charged from compressed-air tank, F, which can be seen behind the gage board G. The initial pressure to which the compressor was charged with acetylene and the final pressure to which it was charged by adding air were selected so that the mixture would fall in the ideal mixture range (from 7 to 13 percent acetylene, by volume). No Freon-12 was present in the compressor during these tests. The compressor, charged with the mixture, was heated by heat lamps to a temperature higher than the ambient temperature, which was about 40° F. The mixture was ignited by an ordinary automobile spark plug.

Under 160 pounds per square inch gage pressure, the mixture of air and acetylene (7.2 percent by volume) exploded on ignition. The explosion caused the compressor to fail at the welded joint of the steel housing. Fig. 4 shows the interior of the test chamber after the explosion. Fig. 5 shows the close-up of the damaged compressor. A and B are the upper and lower half of the housing, respectively. C is the motor and compressor. D is the spark plug, shown in Fig. 5 only.

Prior to the above test during which explosion of the compressor took place, explosion or rupture of 1/4-in. copper tubing occurred while acetylene was being generated. The line immediately after the generator was clogged up by calcium hydroxide which was pushed into the line by rapid generation of acetylene. This created high pressure in the line and probably caused the explosion. Pieces of copper tubing which failed are shown in Fig. 6. The arrows indicate the direction of gas flow. It was not known whether the explosion was caused by dissociation of acetylene or by detonation of copper acetylide. The localized areas of rupture indicate very sudden rises in pressure because the tube was not noticeably stretched even a short distance from the ruptured areas.

IV. Discussion and Conclusions

The hazard tests developed the following information regarding the effects of using Drifreez driers (calcium carbide) to absorb water in a Freon-12 refrigerating system:

(1) The normal products of the reaction of calcium carbide and water; namely, acetylene and calcium hydroxide, were produced in the system.

(2) Nearly all of the calcium hydroxide was retained in the drier cartridge. That which escaped from the drier did not present any problem of clogging in the strainers or refrigerant lines.

(3) As much as 13 percent, by volume, of acetylene was found in the vapor space of the receiver after 89 grams of water had been absorbed in seven Drifreez driers.

(4) At 300 psig pressure, 9 percent or more of Freon-12, by volume, prevented the ignition of acetylene gas by means of an electrical spark.

(5) At atmospheric pressure concentrations of Freon-12 above 12 percent, by volume, prevented explosions of ideal mixtures of air and acetylene when a spark discharge was used for ignition. At two atmospheres pressure, concentrations of Freon-12 above 16 percent were required to prevent similar explosions.

FIG. 4

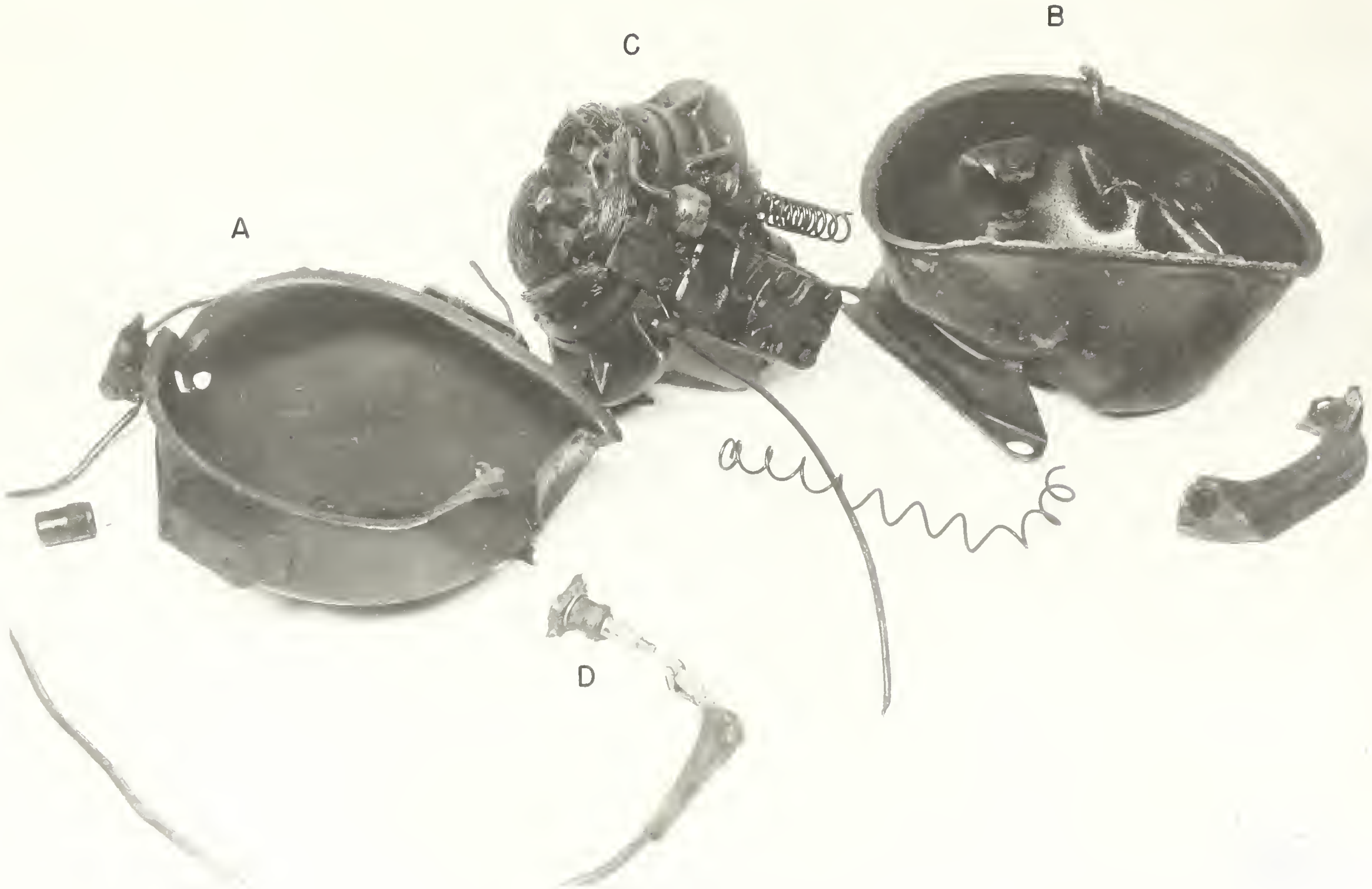

FIG. 5

FIG. 6

(6) The explosion of a mixture of 7 percent acetylene and 93 percent air reptured a typical hermetic compressor-motor housing. Copper tubing was also ruptured either by the dissociation of acetylene gas or copper acetylide.

(7) Copper acetylide was formed as a coating on the inside of the copper tubes in a Freon-12 refrigerating system in which about 121 grams of water had been absorbed by 9 Drifreez driers. The presence of copper acetylide was established by:

(a) The sudden disappearance of the black coating accompanied by mild puffs or explosions upon being heated.

(b) A small explosion during the process of cutting the coated copper tubing with a hacksaw at the conclusion of the test.

(c) The production of acetylene in appreciable quantities when the coated tubing was treated in vacuum with dilute hydrochloric acid as compared with only minute quantities of acetylene released on heating pieces of the copper tubing in vacuum without acid treatment.

A principal hazard arising from the use of calcium carbide as a drier is related to the highly explosive nature of copper acetylide which was shown to have been deposited in the refrigerating system. While it was not shown that the copper acetylide would explode in a normally-operating Freon-12 refrigerating system, and no information has come to our attention to indicate that any of the thousands of systems in use that contain Drifreez driers as reported by the manufacturer has experienced an explosion, it was shown that cutting of a copper refrigerant line internally coated with copper acetylide did produce a mild explosion. Such an explosion might occur during the repair of any similar system in the field to which heat, friction, or sharp blows were applied to copper tubing from which the refrigerant had been removed.

The absorption of 121 grams of water in a 1/3-hp refrigerating system, as in the case of these tests, probably represents an exaggerated example of drying refrigerating units although such an occurrence in practice is not impossible.

With one possible exception, it is considered very unlikely that a combination of circumstances would ever exist in the use of a refrigerating system that would produce an explosive mixture of air and acetylene; Freon-12 and acetylene; or air, Freon-12, and acetylene inside the system even though spark discharges or local heating might occasionally occur in a hermetic motor-compressor housing that could act as an ignition source. In view of the relatively low precentages of Freon-12 required to inhibit explosions of acetylene or acetylene-air mixtures, it is probable that difficulties with high discharge pressure would occur in a refrigerating system long before enough acetylene was present to explode in mixture with Freon-12 or before enough air could be drawn into a system to approach explosive mixtures with acetylene and Freon-12.

A calcium carbide drier should never be used to dry air by itself in a refrigerating system because, without the Freon-12 being present, an explosive mixture might readily be produced. In new installations or in service work on repaired systems, drying is often done by circulating air throughout the system with driers in the circuit prior to charging with refrigerant. The use of calcium carbide driers in such a manner, because of the wide range of explosive mixtures of acetylene and air, could create a serious hazard, either from possible internal explosion or from external ignition of the gas being purged from the system.

It is recognized that several conditions would have to be favorable for explosion hazards, resulting from use of calcium carbide in a refrigerating system using Freon-12, to actually culminate in an explosion. A conclusion drawn from these tests is that it is possible for these conditions to be produced or to occur simultaneously in a normal refrigerating system.

The Drifreez driers examined in these tests were constructed in such a manner that expansion and heating of the calcium carbide particles was adequately distributed so as to prevent abnormal pressures or hot spots in the drier. The use of calcium carbide as a filler for drier cartridges without regard for the expansion and extreme heating that occurs as water is absorbed would present a serious hazard and should be avoided.

PART C. VIBRATION TEST

I. Introduction

The Office of The Quartermaster General requested that vibration tests be made to determine whether or not the Drifreez cartridges were able to withstand the kind of vibration encountered in field refrigeration units driven by four-cycle gasoline engines without excessive breakage and pulverization of the desiccant.

Representative vibration of dryers installed in field refrigeration units operated by four-cycle gasoline engines was difficult to determine because of the many variables involved. Probable factors affecting the frequency and amplitude of the vibration which in turn would affect the acceleration were considered to include the following:

1. Speed of rotation of 4 cycle-gasoline engine.
2. Mounting of refrigeration unit.
3. Mounting of other components of refrigeration unit.
4. Location, position (vertical or horizontal) and mounting of dryer.
5. Size, shape, and length of tube connecting the various components.

II. Description of Test Specimen

The specimen Drifreez dryer was identified as follows:

Drifreez Cartridge
Berna Corporation
3/8" flare connections
6 cubic inch

An exterior view of the specimen on the vibration table is shown in Fig. 1. New cartridges which were sealed to prevent deterioration of the dehydrating material were obtained from the manufacturer. The specimen used for this test was of the type originally submitted for this investigation. The desiccant used in the brass cartridge was raw calcium carbide particles ranging in size from 0.4 in. to 8 mesh.

Approximately 43 grams of the desiccant were dispersed on a layer of fine steel wool (See Fig. 2). The size of particles and total weight of the desiccant varied among the units and it was not uniformly distributed on the steel wool. The steel wool containing the desiccant was rolled (See Fig. 3) and inserted in a brass cartridge which had 64 x 88 mesh brass wire screens soft-soldered into both ends. At the outlet end of the cartridge a steel wool pad was sandwiched between the screen and steel wool roll. The ends were soft-soldered to the cylinder. Baffles were inserted between the caps and screens at the two ends to support the screens.

The physical dimensions of the drier cartridge were as follows:

Length......... 6-3/4" (total)
Diameter....... 1-5/16" (O.D.)
Weight, about - 254 grams (total with caps)
Volume, about - 6 cu. in. (screen to screen)

III. Test Method and Procedure

Since it was desirable to make an accelerated test and because the vibration in actual use with a gasoline engine is subject to so many variables, an arbitrary selection of the most severe vibration that could be obtained with an available vibrator was used. This was a simple harmonic motion with a frequency of 55 cycles per second and a total amplitude of 0.075 in which corresponded to a maximum acceleration of 373.5 ft/sec^2 or 11.6 g. A 2-cylinder, 4-cycle gasoline engine running at 3300 rpm would have 55 power strokes per second and could produce a vibration similar to that selected. The vibrator used was identified as All-American Vibration Fatigue Testing Machine, Model 25 HA, manufactured by the All-American Tool and Manufacturing Company. The vibration machine is shown in Fig. 1. A vibration test at resonant frequency was not made because such a frequency would usually be avoided, if possible, in an actual installation.

Two driers were installed horizontally in parallel liquid lines connected to the receiver outlet of a 3/4 hp refrigerating unit. One of the driers was subject to vibration by the vibrator and the other was subject to the normal vibration of the test 3/4 H.P. refrigerating unit only, which was negligible. Freon 12 was used as the refrigerant and the flow in the parallel liquid lines was alternated every 30 seconds from one drier to the other by means of solenoid valves shown in the background

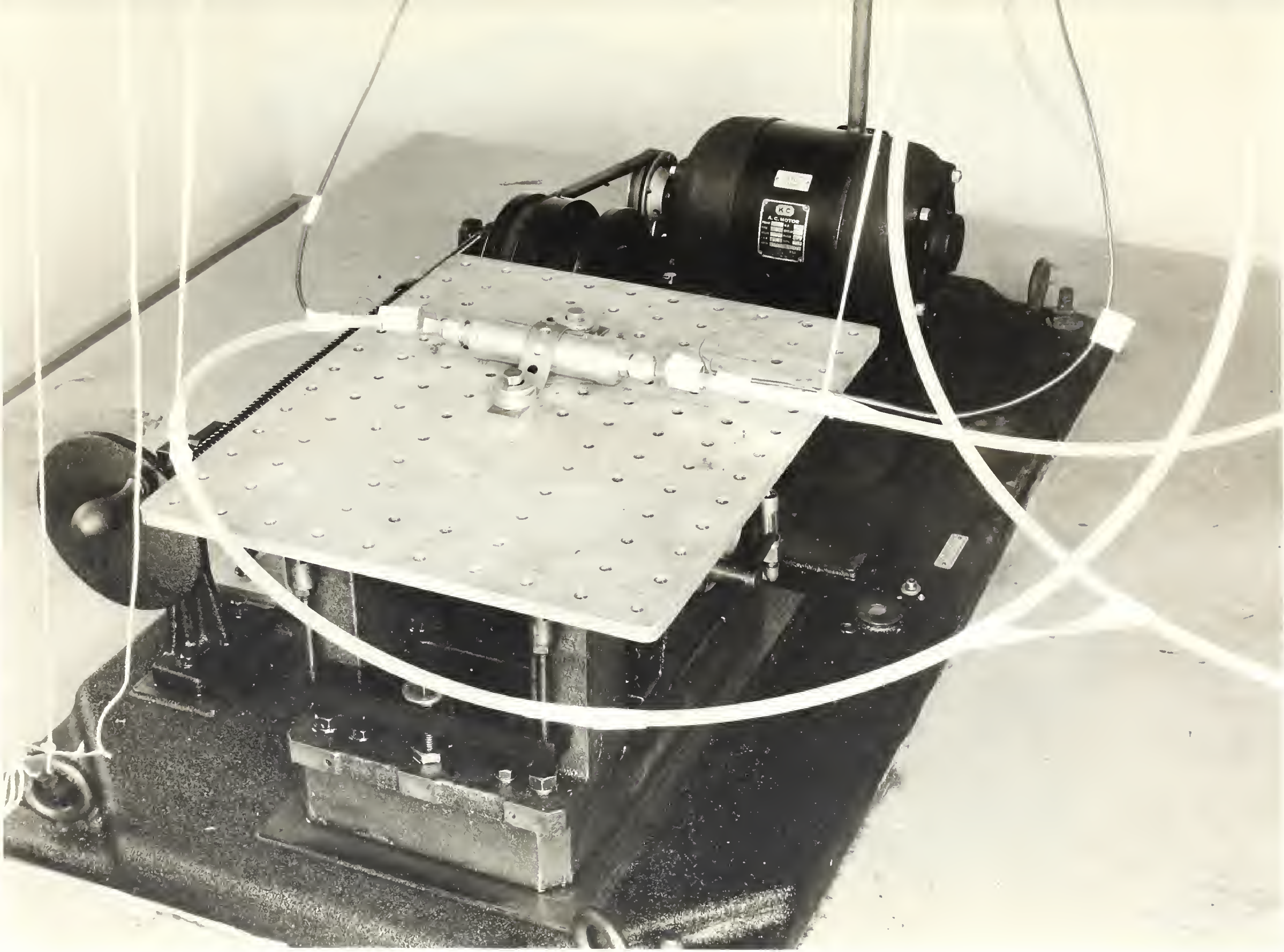

FIG. 1

Fig. 2

VIBRATION

Fig. 3

of Fig. 4 and a timing switch not shown. Alternating the liquid flow between driers caused a sudden application of the liquid pressure to the interior of the driers or pulsing action similar to that occurring in a refrigerating unit when it operated intermittently. The refrigerating unit was operated continuously with a suction pressure of about 40 psig during the vibration tests.

In order to detect and compare the pulverization of desiccant resulting from vibration, a filter containing two layers of fine nylon cloth was placed downstream of each drier. These filters were made from the same piece of nylon cloth. The filters are shown in the foreground of Fig. 4. The nylon cloth, cut open, is shown in Fig. 5.

After assembling the refrigerating unit, the system was thoroughly dried out using a vacuum pump. Although several breaks in tube connections occurred during the test as a result of the vibration. the system probably remained fairly dry because it was operated at a positive pressure throughout the refrigerant circuit.

The drier to be vibrated was securely fastened at the middle of the cartridge to the table of the vibrator. (See Fig. 1). The simple harmonic motion was horizontal and the center line of the drier was perpendicular to the table movement.

The total amplitude was set at 0.075" at the start of the test and there was no need of further adjustment. A General Radio Strobotac was used to set the frequency at 55 cycles per second by illuminating the shaft of the vibrating mechanism under the table. The specimen drier was subjected to vibration for a total of 100 hours.

IV. Test Results

Fig. 2 shows the desiccant on the steel wool as it appeared at the conclusion of the test. The specimen on the left was not subject to vibration and the one on the right was subject to vibration for 100 hours. No difference was observed between the portions of desiccant in the two specimen driers.

Fig. 5 shows the two nylon cloth filters cut open; the one on the right was used on the liquid line downstream of the drier attached to the vibrator table, and the one on the left was installed on the other leg of the parallel circuit downstream of the drier not subject to vibration. Following the test the nylon filter installed after the vibrated drier was found to have been discolored slightly more than the other. Microscopic examination showed that the discoloration was caused primarily by oil and fine particles of the desiccant. The powdered desiccant was so fine and in such small quantity, it was impossible to identify the powder by naked eye. Also it was impractical to separate the particles from the nylon cloth for any quantitative or qualitative analysis because of the glutenous effect of the oil deposit on the nylon.

Under microscopic observation, the size of holes in the nylon cloth of the filters was measured to be about 3.3 microns (0.00012 in.) in length and 1.7 microns (0.00007 in.) in width. The size of the particles found on the filter downstream from the vibrated drier ranged from 8 to 32 microns (0.00032 to 0.00125 in.) in diameter. On the other filter, size of the particles was about 2 microns (0.00008 in.) in diameter.

Fig. 3 shows the two steel wool filters in which the calcium carbide was wrapped as they appeared at the end of the test. No difference between the two was observed.

No change in pressure drop across either drier developed during the 100-hr vibration test. This indicates that any particles larger than 32 microns that might have been separated from the original calcium carbide granules and retained within the Drifreez cartridge had no measurable effect on its overall pressure drop.

V. Discussion and Conclusion

The severity of the vibration with an acceleration of 11.6 g. can be gauged to some extent by the 16 failures of the system during the 100-hour test that were attributable to vibration. The failures could be summarized as follows; one broken thermocouple, one loosened Allen screw on hub of vibration shaft, two worn out V-belts between electric motor and adjustable-speed couplings, 12 refrigerant leaks at flare joints and soldered joints.

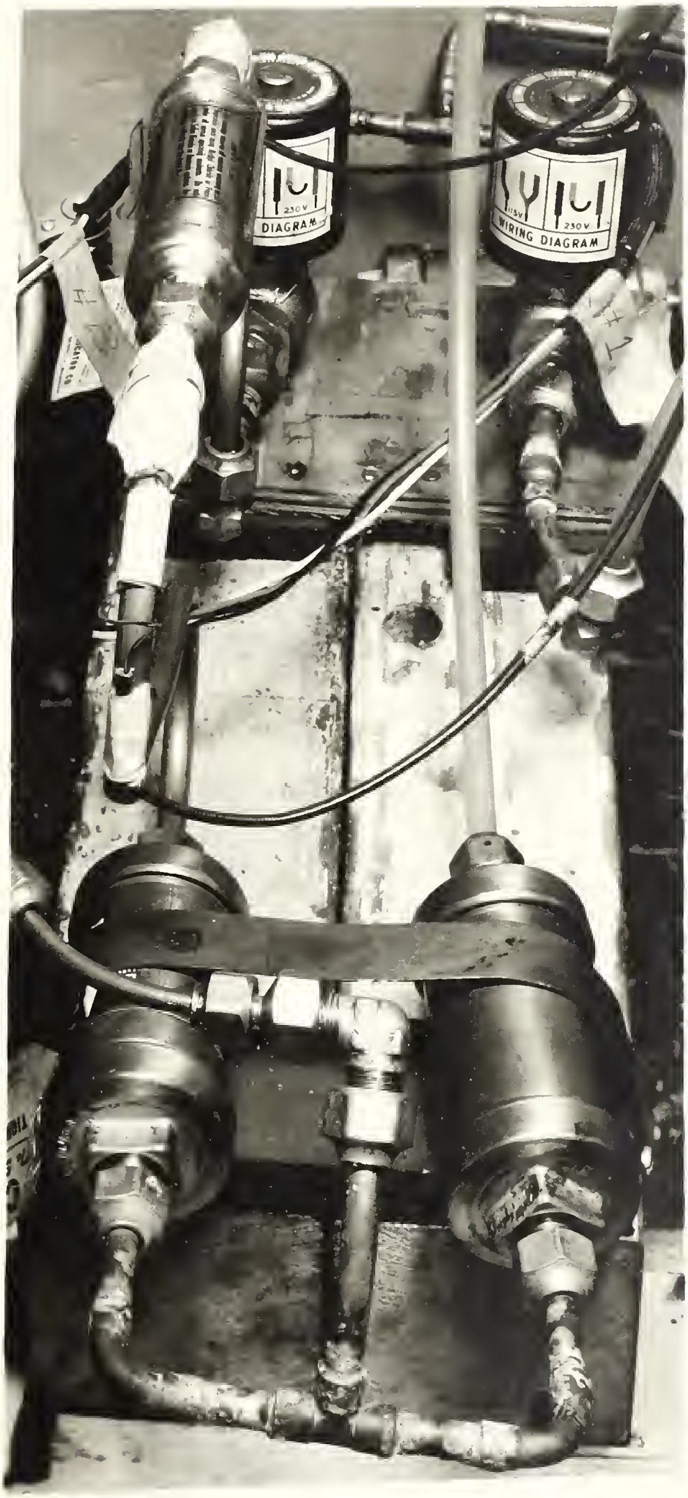

FIG. 4

VIBRATION

FIG. 5

The usual tubing loops used for absorbing vibration in a refrigeration-unit failed to prevent breakages during the test. Plastic tubing was finally substituted for copper tubing to connect the dryer on the vibrator table into the refrigerant circuit. The plastic tubing was successful in preventing joint failures.

The test results showed that the pulverization of the desiccant was increased by the severe vibration of the vibrating table as compared to that observed for the normal vibration of the small refrigerating unit used for the test. However, the particles of material collected downstream from the driers ranged in diameter from 0.00008 in. to 0.00125 in. and would probably pass through any screen or strainer likely to be used in the refrigerating circuit. It is also probable that particles in this size range would pass between the pistons and cylinder walls of a compressor without significant cutting action. If the vibration caused particles larger than 0.00125 in. to be dislodged from the calcium carbide granules they were retained by the filter in the outlet of the driers. The pulverization of the calcium carbide was undoubtedly decreased by the fact that the pieces were distributed rather sparsely on a steel wool pad which acted as a cushion.

It was not possible from the data taken to express the effect of the 100-hour accelerated vibration test in terms of equivalent days, months, or years of normal vibration in a refrigerating system with respect to the pulverization of the desiccant.

Vibration tests of the drier in a wet refrigerating system were not made. When the desiccant, calcium carbide, reacts with water, it forms calcium hydroxide and acetylene. No tests were made to determine the ability of the filter in the drier to retain the fine powder of calcium hydroxide under vibration. However, in mixture with liquid Freon the fine powder of calcium hydroxide was observed to become very pasty and thus not likely to flow through the filters. The evidence that calcium hydroxide in liquid Freon became pasty and was not likely to flow through the filters was obtained by observation of the glass cylinder drier used during the drying tests described in Part A. The glass cylinder was partially filled with calcium carbide without a wrapping of steel wool, and a steel wool pad was inserted at either end of the glass cylinder. As the desiccant reacted with moisture in the system, calcium hydroxide accumulated upstream of the filter pad at the outlet of the container. A distinct boundary between the steel wool and calcium hydroxide was observed and the pressure drop across the drier increased to 110 pounds per square inch gage indicating that the drier was clogged up.

It was concluded from these tests that granular calcium carbide, embedded in steel wool, would pulverize to some extent during normal operation in a dry refrigerating system because of vibration, but the particles that left the drier would be too small to clog strainers and would probably not score compressor cylinder walls.

VI. Evaluation of the Drifreez Drier

The investigation of the Drifreez drier indicated the following conclusions with respect to its drying characteristics, the hazards associated with its use, and its pulverization characteristics.

1. For values of end dryness in the important range below 30 ppm, the model of the Drifreez drier used for the investigation removed and held more water than a silica gel drier of about twice the internal volume and selling currently for equal price. On the other hand, the instantaneous drying rate of the silica gel drier was higher than that of the Drifreez drier. After having removed equal amounts of moisture in the range between 5 and 20 grams, the Drifreez drier produced a lower end dryness than the silica gel drier of equal cost.

2. Two sources of hazard were revealed from the introduction of acetylene gas into a refrigerating system as a result of the reaction between calcium carbide and water. These hazards are (a) the production of copper acetylide, by reaction with copper tubing, which is sensitive to explosion by heat, friction, or impact, and (b) the production of an explosive mixture of air and acetylene if a calcium carbide drier were used to dry a system while air only was being circulated in the system. Although it is believed that the simultaneous development of all the circumstances necessary for an explosion would not occur very often, either hazard is possible in normal operation or servicing of a refrigerating system.

3. Vibration pulverized the granular calcium carbide to some extent even when embedded in steel wool as it was in the Drifreez drier, but the particles that left the drier were too small to clog strainers normally used for liquid refrigerant and would probably not score compressor cylinder walls.

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