EXPLOSIVE CHARACTERISTICS OF TITANIUM, ZIRCONIUM, THORIUM, URANIUM AND THEIR HYDRIDES

BY IRVING HARTMANN, JOHN NAGY, AND MURRAY JACOBSON

* * * * * * * * * **Report of Investigations 4835**

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by

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ILLUSTRATIONS

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ILLUSTRATIONS (Cont.)

INTRODUCTION

The results of the first experimental study by the Bureau of Mines on the explosive properties of metal powders were published in 1943.[4] Since that time the explosibility of numerous other industrial dusts and powders has been investigated. Part of this information has been published,[5] to [15] but most of the data have not been released to date.

This paper summarizes the results of experiments on 22 samples of titanium, zirconium, thorium, uranium, and hydrides of these metals. The major part of the investigation was made under a cooperative agreement with the Atomic Energy Commission.

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SUMMARY

The investigation disclosed that dust clouds of the powders in air constitute severe potential explosion hazards. Some of the samples were pyrophoric; these were stored and prepared for testing in a helium atmosphere in a special cabinet.

Layers of uranium, uranium hydride, and thorium hydride ignited spontaneously at room temperature within a few minutes after exposure in air. Layers of the other powders ignited in air at temperatures of 100° to 540° C. Layers of several dusts ignited at elevated temperatures in carbon dioxide and in nitrogen.

Dust clouds of ~~uranium~~, ~~uranium~~ hydride, and ~~zirconium~~ ignited at room temperature immediately upon dispersion. Clouds of the other powders ignited in air at 260° to 590° C. Some dust clouds also ignited at elevated temperatures in carbon dioxide. All dust clouds could be ignited in air by weak electrical sparks. In the presence of a high-voltage electric spark, dust clouds of several powders ignited in ~~carbon dioxide~~, but none ignited in ~~nitrogen~~, argon, or ~~helium~~.

The energy required to ignite thin layers of the powders in air by electrical-condenser discharge sparks ranged from less than 1 microjoule to 3 millijoules, and the igniting energy for dust clouds ranged from 3 to 200 millijoules.

The lower explosive limits of dust clouds in air ranged from 45 to 300 ~~milligrams per~~ liter (approximately 0.045 to 0.300 ounce per cubic foot). Explosions of dust clouds in a laboratory test bomb produced pressures as high as 127 ~~pounds per square~~ inch (the abbreviation p.s.i. will be used for this unit); average rates of pressure rise up to 5,100 p.s.i. ~~per second~~ and maximum rates to over 10,000 p.s.i. ~~per second~~.

A thin surface coating of ~~copper~~ on ~~titanium~~ and ~~zirconium~~ powders reduced the ignition sensitivity somewhat; but, upon ignition, dust clouds of the ~~copper~~-coated powders produced explosions that were nearly as strong as those of the untreated powders.

The study indicates the advisability of processing and handling several of these powders when in the dry state under ~~helium~~ or ~~argon~~ gas. /end

ACKNOWLEDGMENTS

The cooperative agreement with the Atomic Energy Commission was arranged by Edward J. Kehoe, chief, Fire and Accident Branch, Health and Safety Division, of the New York office of the A.E.C., and Dr. Bernard Lewis, chief, Explosives and Physical Sciences Division, Bureau of Mines. Nine of the powders used in the study were prepared for the A.E.C. by Sylvania Electric Products Co., Bayside, Long Island. E. J. Kehoe, F. L. Brannigan, and Paul Klevin of the New York office of A.E.C. and Dr. Bernard Kopelman of Sylvania cooperated most helpfully with the Bureau of Mines throughout this phase of the work.

A few samples of titanium and zirconium and one hydride of each were obtained through the courtesy of Metal Hydrides, Inc., Beverly, Mass.

Much of the laboratory test work was done by Austin R. Cooper, physical science aide, and Roger P. Williams, laboratory mechanic, Dust Explosions Section, Bureau of Mines.

DESCRIPTION OF SAMPLES

The test samples were numbered in the order of their receipt at the laboratory. The samples will be designated by these numbers in this report.

Most of the powders were received in 1-pound lots; this quantity is usually enough to conduct all of the tests. Some samples that arrived in the dry state were shipped in air, others were shipped dry under argon gas or in an evacuated container, and a few came as a sludge under a liquid.

A description of the appearance, analysis, and particle-size distribution of the samples follows. Unless otherwise noted, the samples were tested in the fineness in which they were received.

Titanium. - Seven titanium powders, including two copper-coated samples, were tested.

No. 740. - Received in dry state; dark-gray angular particles. Spectrographic analysis indicated 2 to 3 percent metallic impurities. Ninety-nine percent of the particles were finer than 100-mesh (Tyler-sieve scale), 68 percent finer than 200-mesh, and 62 percent finer than 270-mesh. Explosibility tests were made on the powder in the fineness in which it was received, and additional tests were made on the fraction through 200-mesh. This is the titanium sample reported in Report of Investigations 3722. For the sake of completeness, the information is included in this report.

No. 864. - Received in dry state. All particles were finer than 200-mesh, and 50 percent were reported to be finer than 325-mesh (43 microns). Analysis was given as 68.67 percent Ti, 8-9 percent Al, 2.4-2.8 percent Si, 0.05 percent C, 3-4 percent Fe, 1-1.25 percent Cu and the balance alumina (Al_2O_3).

No. 1555. - Received in moistened condition. A portion of the sample was dried at 75° C. for 24 hours, giving off 22.7 percent moisture. The tests were made on the dried powder after it had been passed through a 200-mesh sieve to break up agglomeration. The particle-size distribution is given in table 1, together with data for 10 other samples. Chemical analysis was reported to show 96.3 percent Ti.

No. 1556. - Received in dry state. This is a specially prepared sample (supposedly from the same batch as 1555) with a thin copper coating on the surface of the powder particles. Application of the coating and heat treatment of the powder are in an experimental stage. Analysis was reported to show 88.2 percent Ti, 7.0 percent Cu. Assuming spherical particles of 10 microns diameter, a copper content of 2 percent was considered to represent a thickness of copper coating of 1.6 millimicrons.

No. 1605. - This is an untreated titanium powder similar to 1555. The sample was received in dry state under argon gas. It was used only for a few tests.

No. 1606. - This powder was taken from the same lot as 1605, but the particles contained a surface coating of copper. (See also 1556). It was reported to contain 85.6 percent Ti and 12.7 percent Cu. The sample was received dry under argon.

No. 1648. - Received in dry state under argon gas. The metal was reported to contain 0.08 percent hydrogen, 0.82 percent oxygen, and 0.062 percent nitrogen. The average particle diameter determined by the subsieve sizer was given as 10.5 microns. The particle-size distribution by the photelometer method was reported to be as follows: 24.0 percent, by weight, 0-10 microns; 40.3 percent, 10-20 microns; 35.7 percent, 20-40 microns; average, 17.8 microns.

Titanium Hydride (TiH_2). - The following two samples were tested:

No. 1428. - Gray powder, received in dry condition. Reportedly, over 98 percent of the particles were finer than 325-mesh, with the greater portion in the 10- to 25-micron range. The composition was reported as 95.0 percent Ti, 3.78 percent H_2, 0.1 percent Ca, and 0.1 percent C.

No. 1649. - Received dry under argon gas. Analysis was reported to show 2.83 percent H_2, 0.24 percent O_2, 0.071 percent N_2. Although this hydride contained only 70 percent of the theoretical hydrogen for TiH_2, it was said to behave in many ways as a fully hydrided material. The average particle diameter by subsieve-sizer analysis was given as 4.9 microns. Photelometer measurements were reported to give 88.1 percent particles between 0-10 microns; 10.0 percent, 10-20 microns; 1.9 percent, 20-40 microns; average, 5.2 microns.

Zirconium. - Seven zirconium powders, including one copper-coated sample, were tested.

No. 745. - Gray powder; received in a moistened state as a sludge. The metal contained 2 to 3 percent metallic impurities. The particles were reported to be finer than 325-mesh. The test data for this sample were reported in Report of Investigations 3722.

No. 1028. - Received as a sludge. Apparently finer than 325-mesh; particle-size distribution not known. This sample was reportedly taken from a wooden keg in which zirconium is stored under water before it is used for spraying plates and other parts of vacuum tubes.

No. 1029. - Received as a sludge from same source as 1028. This powder represents the fine particles that are carried away in the air stream of the spraying room.

No. 1557. - Received in dry state. Reportedly contains 98.7 percent Zr.

No. 1558. - Received in dry state. This sample was from same batch as 1557 but had a thin surface coating of copper (see remarks for 1556). Reported to contain 90.5 percent Zr and 4.4 percent Cu.

No. 1632. - Received under water. Reported to contain 3.0 percent O_2. The average particle diameter by photelometer measurements was given as 3.3 microns.

No. 1633. - Received dry under argon. The material was said to contain 0.29 percent O_2 and 0.025 percent N_2. Average diameter by photelometer measurements was given as 17.9 microns. This zirconium was prepared from its hydride (1627).

Zirconium Hydride (ZrH_2). - The following two samples of hydride were tested:

No. 1429. - Received in dry state. Over 98 percent of the powder reported to be finer than 325-mesh, with the major portion of the particles between 10-25 microns. The composition was reported as 93.6 percent Zr, 2.08 percent H_2, 0.18 percent Ca, 0.07 percent Fe, 0.01 percent C, 1.0 percent Hf, 0.70 percent SiO_2.

No. 1627. - Received under argon. Analysis reportedly gave 0.19 percent O_2 and 0.022 percent N_2. Average particle diameter by photelometer measurement was 4.7 microns.

Thorium.

No. 1652. - Dark-gray powder, received in an evacuated pyrex bulb. Reported to contain 0.032 percent H_2, 1.20 percent O_2, and 0.19 percent N_2. Average particle diameter by subsieve sizer given as 7.2 microns and by photelometer as 7.4 microns.

Thorium Hydride (ThH_2).

No. 1653. - Greenish-gray powder received in an evacuated pyrex bottle. Analysis reported to show 0.94 percent H_2, 1.07 percent O_2, and 0.16 percent N_2. Theoretical hydrogen percentage of ThH_2 is 0.86. Average particle diameter by subsieve sizer was given as 3.8 microns and by photelometer measurement as 2.9 microns.

Uranium.

No. 1625. - Silver-gray powder, received under argon. When the sample arrived, the upper portion of the powder had been considerably darkened. No important difference was observed between the explosibility of the light and the darkened portion. Analysis was reported to give 0.07 percent O_2, and 0.008 percent N_2. Average particle diameter by photelometer measurement 10.8 microns.

Uranium Hydride (UH_3).

No. 1626. - Dark-gray powder, received under argon. No chemical analysis was reported. Average particle diameter by subsieve sizer was 3.6 microns and by photelometer, 3.3 microns.

More detailed information of the particle-size distribution of 11 of the above powders is given in table 1.

TEST EQUIPMENT AND PROCEDURE

The equipment and test procedure were, for the most part, similar to those described in Report of Investigations 3722 (see reference 4/). Modifications and improvements made since the original construction will be pointed out. The dry powders were tested in the fineness and form as received. To prepare test samples from the powders received as sludge, small quantities were washed with alcohol, and the excess liquid was drained off; the resulting powder was dried by slow heating. As some of the powders were pyrophoric, great care was taken to prevent fires during storage and handling of the dry samples. They were kept either in evacuated containers or under inert gas.

TABLE 1. - Particle-size distribution of powders

Fineness, microns	Percent by weight[1]				Percent by weight[2]						
	No. 1555	1556	1557	1558	1625	1626	1627	1632	1633	1652	1653
0-1	27	28	15	23	4.0	10.6	10.6	5.9	2.1	2.8	3.5
1-2	29	20	24	31	-	27.7	20.1	19.2	-	6.5	10.0
2-3	22	15	23	23	2.0	17.5	14.2	27.3	1.5	13.9	28.2
3-4	10	12	13	12	3.1	11.9	23.5	18.7	1.2	11.6	19.3
4-5	5	11	10	6	5.0	8.5	6.3	14.3	1.5	10.9	14.3
5-6	2	4	4	1	4.8	10.7	7.7	8.5	2.8	8.3	9.6
6-8	2	5	7	-	14.1	10.3	2.4	3.3	5.0	14.0	8.7
8-10	1	2	2	3	16.3	2.2	1.8	.9	7.0	7.4	4.4
10-12	1	-	-	-	15.6	.6	3.8	1.7	7.6	5.6	2.0
12-14	-	2	-	-	13.0	-	2.6	-	7.8	6.2	-
14-16	Trace	-	-	-	9.8	-	2.2	-	8.5	4.2	-
16-20	-	-	1	-	6.0	-	3.7	-	18.3	4.5	-
20-30	-	-	-	-	4.9	-	1.3	-	26.8	4.1	-
30-40	-	-	-	-	1.3	-	-	-	10.0	-	-

[1] By microscopic analysis.

[2] By photolometer analysis.

Inert Gas Cabinet

During the recent investigation of the last nine powders, a special cabinet was constructed for handling and storing. The cabinet consists of a main chamber (approximately 24 x 24 x 30 inches) and an airlock or transfer chamber (6 x 6 x 8 inches). The construction is of 1/4-inch steel welded at all seams. Figure 1 is a general view of the cabinet. The main chamber has a glass viewing window, 3/4-inch thick and 12 inches square, in the front wall. In the back wall is a 20-inch square vent sealed with a reinforced, plastic-impregnated, cloth diaphragm. The purpose of this vent is to relieve pressure in case of an accidental explosion in the cabinet. The airlock is welded to the left side of the chamber; the doors of the airlock close on rubber gaskets, forming airtight seals. Equipment in the main chamber includes an analytical balance, a fluorescent light, and tools and jars for working with the powders. All manipulations in the cabinet are made by an operator wearing special gloves, which are sealed to portals welded to the main section.

In designing the equipment, provisions were made for evacuating the main chamber and airlock and filling them with highly purified helium gas obtained from the U. S. Helium Production Co., Amarillo, Tex. Gas and mass spectrograph analyses showed that, initially, the system had to be evacuated and flushed with helium three times to attain the desired inert atmosphere. The helium pressure in the cabinet at all times was maintained at between 1-1/2 and 3-1/2 ounces. per square inch gage by means of a sensitive pressure switch and a solenoid valve. A mercury check valve was placed in the system to prevent excess pressure.

Following receipt of a sample, the original container was placed in the inert-gas cabinet, and a small quantity of powder was transferred in the inert atmosphere to a 2-ounce screw-top jar. The original container was resealed carefully and removed from the cabinet for storage until it was needed again. The test samples were weighed in the cabinet and removed only a few minutes before actual testing.

Test Procedure

Several tests were performed on the dusts to determine the ease of ignition and the various factors that influence the explosion hazard. A brief outline of these tests follows:

The ignition temperature of the dust clouds was determined in a vertical, electrically heated cylindrical-tube furnace, the top of which is connected to a small brass chamber, or dust boat, into which a weighed amount of dust can be placed. The dust was projected by compressed air downward through the furnace, and ignition was indicated by the appearance of a flame at the open furnace mouth at the bottom. The electric heating circuit of the furnace includes an automatic thermostatic control. The lowest furnace temperature at which ignition occurs was considered to be the ignition temperature of the dust cloud. The furnace is shown on the left in figure 2.

The furnace was used in a modified form to determine the ignition temperature of dust layers. In these tests the top was open, and a small amount of dust was placed on an aluminum oxide disc at the center of the furnace. A slow stream of air flowed upward through the furnace and around the heated dust layer. The lowest temperature at which the dust ignites or glows strongly, or at which its temperature shows a sudden rapid rise, was considered as the ignition temperature.

The procedures for determining the ignition temperatures of dusts in gases other than air were similar, but before the dust sample was placed in the boat or on the aluminum oxide disk the entire system was flushed thoroughly with the gas to be investigated, and the dust was protected from air throughout the test.

The relative flammability of the powder denotes the amount of inert dust, expressed as the percentage of the total mixture, required in admixture with the powder to prevent ignition when the mixture is blown through the cylindrical furnace under a standard set of conditions. This system of rating was originally developed for coal dusts and is significant because it gives a measure of the amount of rock dust required to prevent the propagation of coal dust explosions in mines. The inert dust used in the laboratory tests was calcined fuller's earth. The relative flammability of several powders was determined also in a second test in which a high-voltage, low-energy, continuous-induction spark was substituted for the heated furnace as an ignition source. The pyrex spark tube, with a gooseneck-shaped top can be seen on the right near the center of figure 2.

To measure the minimum energy required for ignition of dust clouds experiments were conducted with electrical-condenser discharge sparks. A condenser was charged to a definite potential, and the formation of the dust cloud in a cylindrical lucite tube was synchronized with the discharge of the condenser through the primary winding of a luminous-tube step-up transformer. The e.m.f., induced in the secondary circuit of the transformer, produced a spark between the electrodes in the dust cloud within the lucite tube. Condensers of different capacities were tried to find the weakest spark that would ignite the sample. Figure 3 shows the apparatus used in these tests. The cylindrical lucite tube (I.D. 2.75 inches, length 12 inches) is shown on a stand near the center of the figure. To the right of the tube are a small compressed-air tank and a magnetic valve, through which the air flows to the bottom of the lucite tube and disperses the dust upward. To the left and slightly in back of the tube is the luminous-tube transformer. On the left of the figure is a box containing the electronic timing and control circuits. A variable condenser can be seen on top of this box.

In the experiments on the ignition of dust layers, the condenser was discharged, without step-up in voltage, directly through the spark gap between a point electrode and a grounded metal disk on which the dust was placed.

The minimum explosive concentration or lower explosive limit of the dust clouds was found by determining the lowest average dust concentration in the lucite-tube apparatus in which a dust ignited and propagated flame throughout the cloud, as indicated by the development of enough pressure to break the weak filter-paper diaphragm at the top of the tube. The igniting source used in these experiments is a high-voltage continuous electrical-induction spark having an average power of 24 watts.

The maximum pressure and the rates of pressure rise developed during a dust explosion indicate the structural damage that might result. They also furnish some information on the vent requirements in buildings or in equipment where explosions may occur. The apparatus used for measuring pressures and rates is shown in figure 4. It consists essentially of a chromium-plated cylindrical steel test bomb (1.23 liters) in which the dust cloud is formed and ignited and a recording pressure manometer mounted above the bomb. The manometer is of the diaphragm type; the deflection of the diaphragm is magnified by an optical system. A pressure-time record of the explosion is obtained on a photographic film mounted on a rotating drum.

A weighed amount of the dust to be tested was placed into a specially designed brass cup at the bottom of the bomb. This dust was dispersed upward by the sudden release of a small volume of compressed air. Originally the compressed air was placed in a 1.3-liter container at 8-12 p.s.i. pressure. Recent experiments with many dusts, including the comparatively heavy metal powders, have shown that better dust clouds are formed and stronger explosions produced if the air used for dispersion is released from a 50-cc. cylinder at a pressure of 100 p.s.i. This arrangement was used in most tests in this investigation.

Figure 5 is an enlargement of an actual pressure-time record. It illustrates the manner in which the pressure and the rates of pressure rise are computed from the film record. The distance between successive dots on the horizontal time axis represents an interval of 1/120 second. As can be seen on the figure, following ignition of the dust (at point A) the pressure rises slowly at first, then very rapidly for a time (D to F), and again less rapidly, reaching a maximum value at point C, after which it starts to decrease.

The use of inert gas to reduce or eliminate the hazard of dust explosions is fairly common in some industrial processes where highly explosive dusts or powders are handled. In this investigation, the ignition temperatures of dust clouds and of dust layers were determined in commercially pure carbon dioxide and in nitrogen; the ignitibility of dust layers was studied at 850° C. in a 50-50 mixture of air and helium. In addition, a series of mixtures of air-carbon dioxide, air-nitrogen, air-argon, and air-helium, was prepared and tests were made in the induction-spark apparatus to determine the limiting mixtures that would prevent ignitions and explosions of the dust clouds. A schematic diagram of the apparatus is shown in figure 6.

Before each test the entire system was flushed thoroughly with the gas mixture, and the spherical glass bulb was filled with the gas for dispersing the dust from the dust boat through the spark tube. A water manometer indicated the rate of flow of gas that was bled slowly through the spark tube during the entire test.

Those engaged in handling the powders and in the actual experimental work wore protective gloves; all operations were performed in such a manner as to protect personnel against dust and fumes. All ignition and explosion tests were made under closed, well-ventilated hoods, and other necessary safeguards were taken to insure satisfactory health conditions for the experimenters.

RESULTS OF EXPERIMENTS

The data obtained in the explosibility tests are recorded below in tables and figures, which are largely self-explanatory. Unusual effects noted in the work and the results of special tests will be discussed briefly.

Ignition Temperature

The ignition temperature of dust clouds and of undispersed dust layers, determined in air, carbon dioxide, and nitrogen, is shown in table 2. In tests with dust clouds, the dust (usually 1 gram) was projected rapidly through the furnace, passing through the hot zone in less than 1 second. In the tests with undispersed layers, the dust was kept at the center of the hot furnace for several minutes (up to 15 minutes if no ignition occured).

When samples of uranium, uranium hydride, and several zirconium powders were dispersed through the furnace at room temperature, (approximately 20° C.) strong ignitions resulted. In this respect zirconium sample 1633 did not behave like other untreated zirconiums, and the dust cloud in air did not ignite below 350° C. Copper-coated zirconium 1558 had a minimum ignition temperature of 480° C., compared with 20° C. for untreated sample 1557 from the same batch. Dust clouds of copper-coated titanium 1556 ignited at approximately the same temperature as untreated sample 1555 from the same batch, but copper-coated titanium 1606 ignited at a temperature about 100° C. higher than untreated sample 1605 from the same batch.

Dust clouds of four of the nine powders tested in an atmosphere of carbon dioxide ignited, but none of the dust clouds tested in nitrogen ignited.

No ignitions resulted with 1 to 3 grams of uranium hydride exposed in layers in air at room temperature; 1 gram of the powder ignited at minimum temperature of 110° C. When 5 grams of uranium hydride was placed on a watch glass at room temperature, the surface darkened immediately and a few bright spots appeared; within a few minutes a slight popping noise was heard, a yellow flame was seen over the surface, and the entire mass assumed a dull-red glow; the residue was black. Three grams of thorium hydride exposed in air at room temperature ignited within a few minutes; the ignition was characterized by an intense yellow glow; the residue was a powdery white dust. It is quite possible that other metals or hydrides might ignite spontaneously if large quantitites of the powders were exposed to air. In fact, uranium powder did ignite when a pile of about 300 grams was prepared for disposal.

0723-019

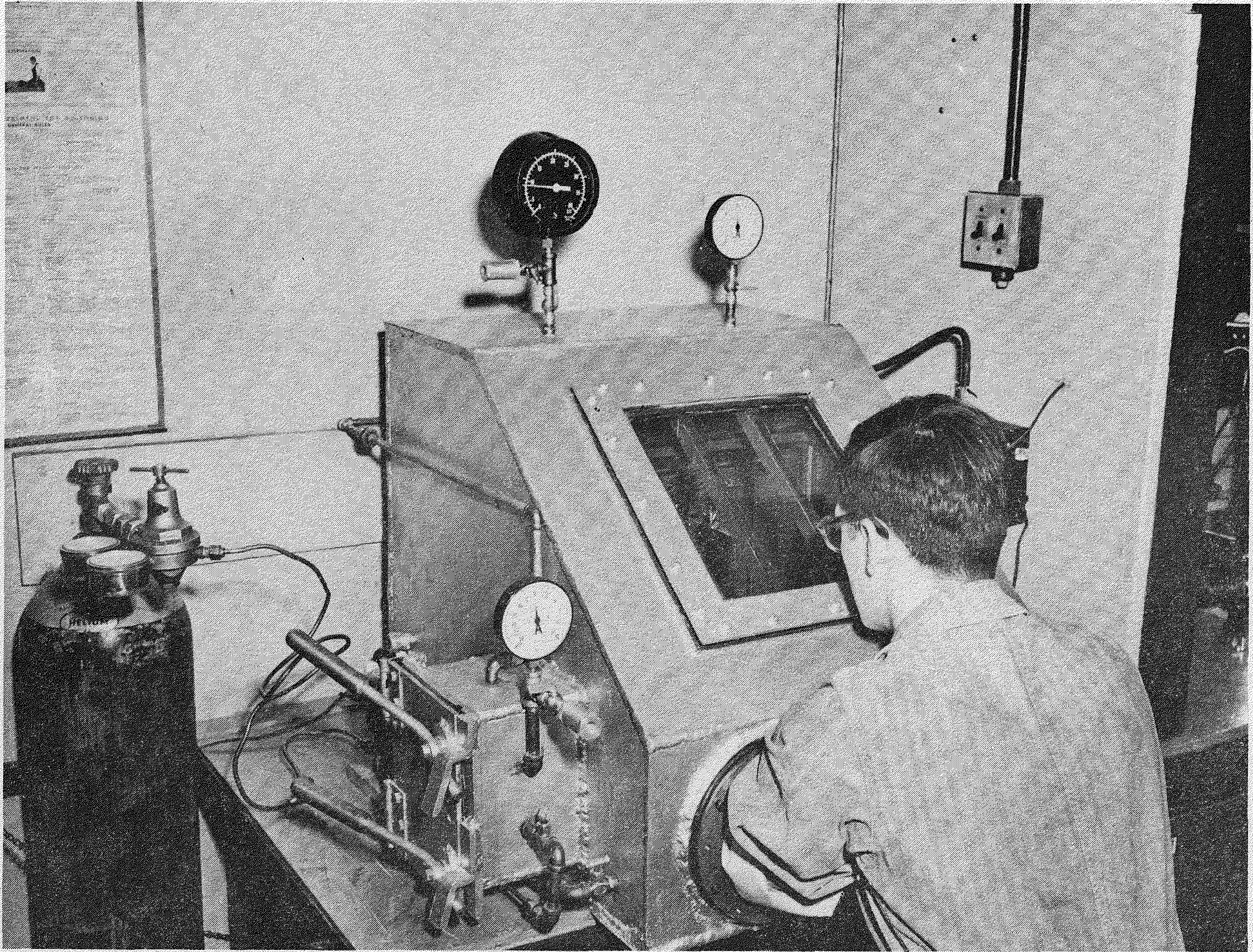

Figure I. - Inert-gas cabinet.

0723 010

TABLE 2. - Ignition temperature and relative flammability of powders

Sample	Ignition temperature of dust clouds, °C.			Ignition temperature of dust layers, °C.			Relative flammability, percent inert	
	Air	CO_2	N_2	Air	CO_2	N_2	In furnace at 700° C.	Spark apparatus
Ti-740	480	-	-	460	680	-	55	77.5
864	530	-	-	470	-	-	25	37.5
1555	470	-	-	480	-	-	90	85
1556	460	-	-	430	-	-	90	85
1605	480	-	-	460	-	-	-	-
1606	590	-	-	380	-	-	-	-
1648	330	n.i.[1]	n.i.	510	550	760	-	-
TiH_2-1428	480	-	-	540	-	-	80	70
1649	440	n.i.	n.i.	500	710	750	-	-
Zr-745	20[2]	-	-	210	560	530	90+	90+
1028	20	-	-	260	-	-	90+	90+
1029	20	-	-	290	-	-	90+	90+
1557	20	-	-	220	-	-	90+	90+
1558	480	-	-	320	-	-	90	90
1632	20	650	n.i.	190	620	790	-	-
1633	350	n.i.	n.i.	300	710	n.i.	-	-
ZrH_2-1429	350	-	-	270	-	-	85	80
1627	430	n.i.	n.i.	340	650	n.i.	-	-
Th-1652	270	740	n.i.	280	450	500	-	-
ThH_2-1653	260	n.i.	n.i.	20	340	330	-	-
U-1625	20	560	n.i.	100	350	410	-	-
UH_3-1626	20	720	n.i.	20	360	210	-	-

[1] n.i. denotes no ignition at 850° C., the highest temperature used in these tests.

[2] "20" in this table denotes ignition at room temperature, approximately 20° C. It is probable that in dust clouds this ignition was caused by an electrostatic discharge within the cloud, although frictional heat developed during the movement of the powder may have been a contributing factor. Ignition of dust layers of ThH_2 and UH_3 at room temperature indicates their highly pyrophoric character.

The ignition temperature of an undispersed layer of copper-coated zirconium (1558) was 100° C. higher than for an untreated zirconium sample (1557) from the same batch. In contrast to this, both copper-coated titanium samples (1556 and 1606) had lower ignition temperatures than the corresponding untreated titanium powders (1555 and 1605).

At elevated temperatures, dust layers of all samples tested in carbon dioxide and of all except two of the samples in nitrogen ignited.

Small layers of the nine metal powders most recently tested were exposed at 850° C. in an atmosphere of 50 percent air and 50 percent helium, by volume. All dusts ignited within a few minutes. The test was not made at other temperatures.

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Relative Flammability

The results of the relative flammability tests conducted on many of the powders are recorded in the last two columns of table 2. The lowest values were obtained for dust clouds of the relatively impure titanium powder, 864, followed by the comparatively coarse titanium, No. 740. All other powders tested required a mixture of at least 70 percent, and at most 80-90 percent, inert dust to prevent ignition and suppress flame propagation. A value of 90+ percent indicates that more than 90 percent inert dust was required for this purpose.

Minimum Energy Required for Ignition

Table 3 contains the data from the ignition tests with condenser discharge sparks. The energy value for dust clouds ranges from 3 to 200 millijoules; that for dust layers ranges from less than 1 microjoule to 3 millijoules. In tests with dust clouds, considerable preliminary work was required to find the optimum conditions for ignition. The minimum igniting energy depends, among other factors, on the particle size of the dust, the concentration of the dust cloud, the characteristics of the igniting circuit, and the timing of the igniting spark relative to the formation of the cloud.

TABLE 3. - Minimum electrical igniting energy and lower explosive limit of powders

Sample	Minimum energy required for ignition: Dust cloud, millijoules[1]	Minimum energy required for ignition: Dust layer, microjoules	Lower explosive limit, oz. per cu. ft.[2]
Ti-740-1[3]	-	-	0.070
740-2	200	-	.045
864	120	3000	.300
1555	15	8	.045
1556	10	200	.050
1605	25	40	.050
1606	30	80	.065
1648	25	24	.045
TiH_2-1428	60	-	.070
1649	60	1600	.080
Zr-745	40	-	.190
1028	15	0.4	.040
1029	25	0.8	.070
1557	5	1	.045
1558	15	30	.060
1632	15	6.4	.045
1633	12	240	.045
ZrH_2-1429	60	320	.085
1627	100	64	.120
Th-1652	5	4	.075
ThH_2-1653	3	6.4[4]	.080
U-1625	45	4[4]	.060
UH_3-1626	5	32[4]	.060

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[1] 1 joule = 1,000 millijoules = 10^6 microjoules = 0.00095 B.t.u. = 0.24 gram-calorie.

[2] 1 oz. per cu.ft. is approximately equivalent to 1 gram per liter.

[3] Ti-740-1 is titanium sample No. 740 tested in the fineness as received; Ti-740-2 is the through 200-mesh fraction of the above.

[4] In this test less than 1 gram of powder was used. Larger quantities ignite spontaneously without a spark, as has been mentioned.

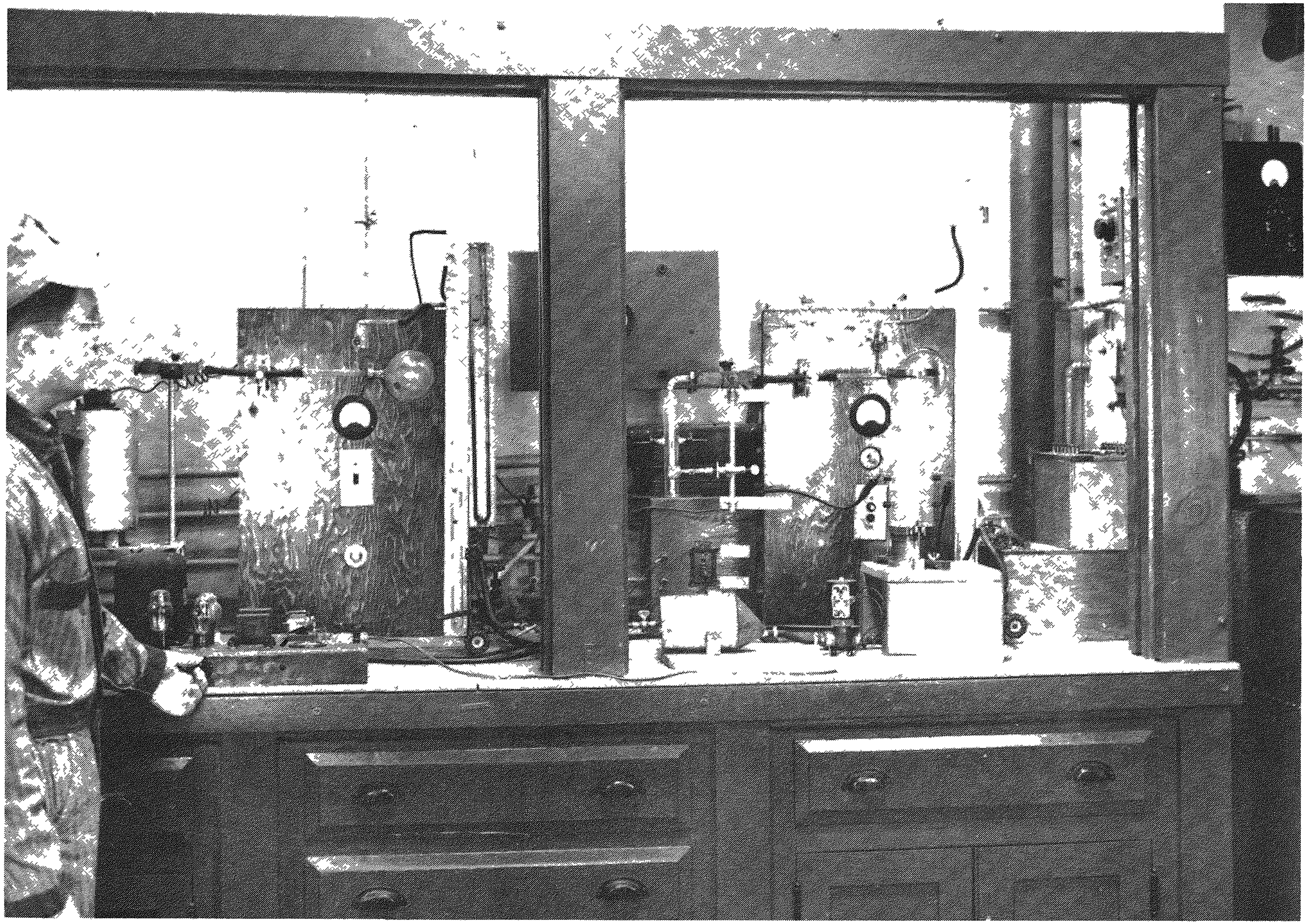

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Figure 2. - Laboratory furnace and spark ignition apparatus.

Figure 7 shows the effect of dust concentration on the minimum igniting energy of dust clouds of titanium powder 1648.

The minimum energy value for samples 1555, 1556, 1557, and 1558, shown in table 3, was determined immediately after removal of the powders from the original containers (Ti-1555 was dried first). At the same time portions of these powders were exposed in the laboratory air for 6 weeks, out of direct sunlight, to determine the effect of oxidation or other surface changes. After this exposure, the samples again were subjected to minimum-energy tests. Table 4 shows a comparison of the data.

TABLE 4. - Effect of exposure in air on igniting energy of powders

Sample	Minimum energy required for ignition, joules			
	Dust cloud		Dust layer	
	Before exposure	After 6 weeks exposure	Before exposure	After 6 weeks exposure
Ti-1555...........	0.015	0.025	$8x10^{-6}$	$8x10^{-6}$
1556...........	.010	.015	$2x10^{-4}$	$8x10^{-5}$
Zr-1557...........	.005	.015	$1x10^{-6}$	$1x10^{-6}$
1558...........	.015	1/	$3x10^{-5}$	$1x10^{-5}$

1/ No ignitions were obtained at 0.025 joule; exact limit not determined.

The above values show that copper-coated zirconium (1558) required more energy for ignition than untreated zirconium (1557), whether dispersed in a dust cloud or as a layer. Dust layers of copper-coated titanium powder (1556) also were more difficult to ignite than untreated titanium (1555); but, when dispersed in the air, the untreated powder required a slightly higher energy for ignition, possibly owing to its somewhat agglomerated character. On the other hand, a second copper-coated titanium powder (1606, table 3) was less sensitive to ignition by sparks in undispersed form, as well as in a dust cloud, than the corresponding untreated titanium (No. 1605).

Exposure of the four titanium powders in air for several weeks resulted in an increase in the energy required for ignition of the dust clouds. The energy needed for ignition of dust layers remained the same for the untreated titanium and zirconium powders, but the copper-coated powders were ignited by somewhat weaker sparks after exposure.

Minimum Explosive Concentration

The minimum explosive concentration or lower explosive limit of the powders in air is given in the last column of table 3. The experimental values of this limit are influenced greatly by the fineness of the dust, the uniformity of the dust cloud, the nature of the igniting source, and other test conditions. For this reason, data determined by different investigators are rarely in complete agreement.

Pressures and Rates of Pressure Rise

The pressure measurements in the 1.23-liter steel test bomb (fig. 4) were made at concentrations ranging from 0.1 to 4.0 ounces per cubic foot. The test data for 11 samples are given in table 5, and the values for 9 samples are plotted individually on figures 8 to 16. Comparison of the data in the last four columns of table 5, which give the test results by the old method of dust dispersion in the bomb with the results of tests by the new dispersion technique, shows that the latter explosions consistently developed higher pressures and higher rates of pressure rise.

For most of the samples plotted on figures 8 to 16 the pressures and the rates developed by the explosions attained maximum values within the concentration range investigated. In general, there was no sharply defined optimum limit at which definite peak values were reached. As a matter of interest, the stoichiometric concentrations for the oxides are indicated near the bottom of several figures, although it is not known definitely which oxides are formed (when more than one oxide exists) in the experimental explosions, or whether nitrides also are formed.

In the experiments, the highest pressures were produced by explosions of titanium hydride and the next-highest by zirconium hydride. The highest average rates of pressure rise were produced by zirconium, zirconium hydride, titanium hydride, and uranium hydride. Explosions of several powders developed maximum rates of pressure rise over 10,000 p.s.i. per second.

Ignition by Electric Sparks in Inert Atmospheres

As mentioned above, in the manufacture of highly explosive powders, operations, such as grinding, sieving, and conveying, occasionally are performed in atmospheres having a reduced oxygen content. The data on the ignition temperatures of the samples used for these tests (see table 2) indicate that dust clouds of some of the metal powders can be ignited at elevated temperatures in carbon dioxide and that layers of nearly all the powders can be ignited at elevated temperatures in carbon dioxide and in nitrogen. Therefore those gases would offer little protection against ignition of the powders by hot surfaces or by flames. However, in many industrial processes, electric sparks of static or other origin constitute the principal igniting sources.

To study the prevention of ignition by electric sparks, experiments were made with dust clouds of nine powders in various mixtures of air with carbon dioxide, nitrogen, helium, and argon. The clouds were formed in the presence of a high-voltage electrical-induction spark in the spark tube shown schematically in figure 6. The results of the experiments are plotted in figure 17. As illustrated, ignitions by electric sparks of dust clouds of the metals and of uranium hydride could be prevented most effectively in atmospheres containing mixtures of air and helium. The limit mixtures in these atmospheres contained more oxygen than the others. Mixtures of air and nitrogen and air and argon were about equal in effectiveness, and carbon dioxide was not effective in preventing ignitions.

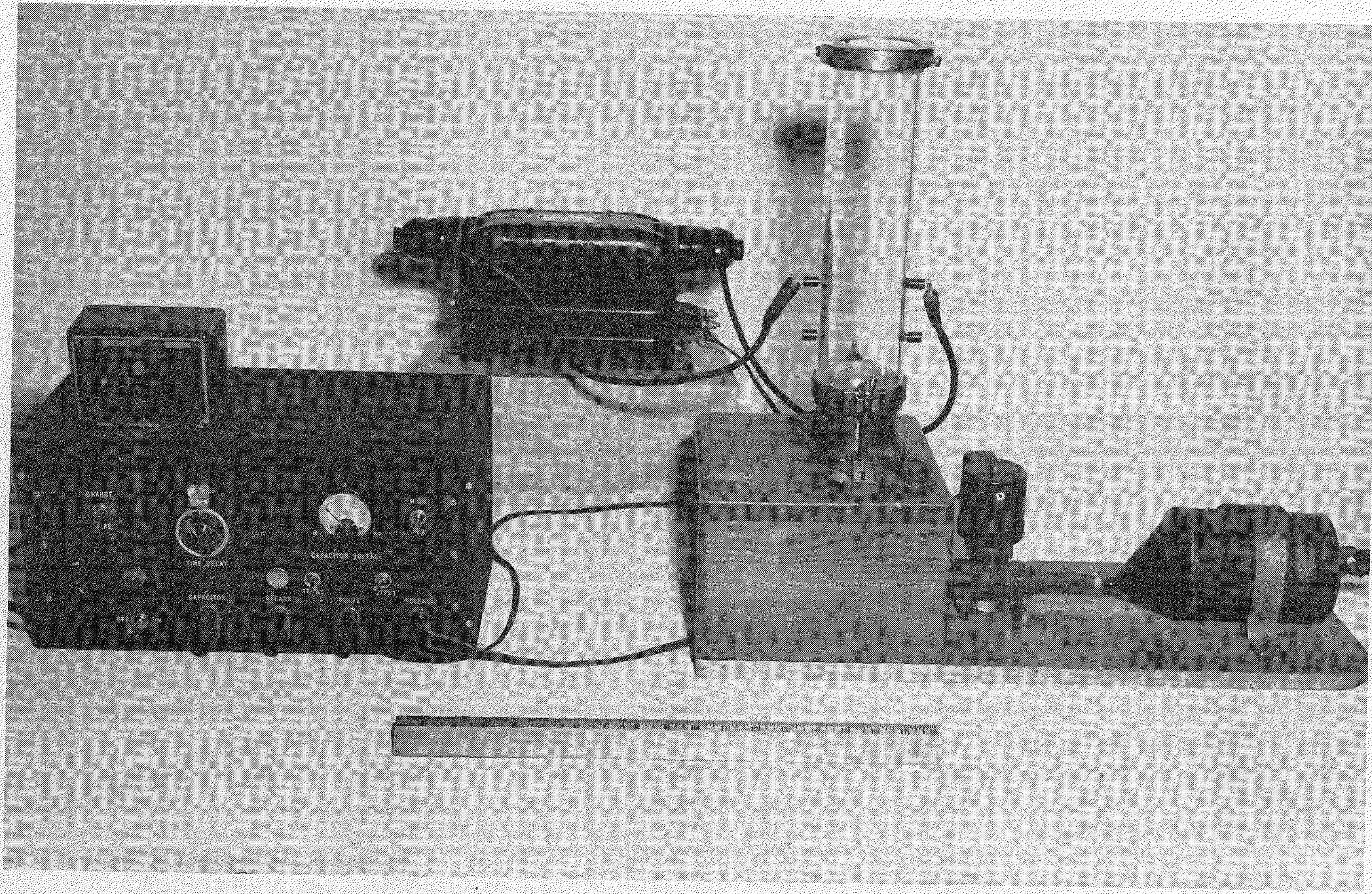

Figure 3. - Apparatus for determining minimum explosive concentrations and minimum igniting energies of dust clouds.

TABLE 5. - Maximum pressures and rates of pressure rise developed in explosions of several powders

	Data with new method of dispersion, concentration, oz./cu.ft.				Data with old method of dispersion, concentration, oz./cu.ft.			
Sample	0.1	0.2	0.5	1.0	0.1	0.2	0.5	1.0
			Part A: Maximum pressures, p.s.i.					
Ti-740-1	-	-	-	-	15	35	40	43
740-2	-	-	-	-	26	41	44	52
864	-	-	46	65	-	-	33	45
1555	43	56	81	86	-	-	-	-
1556	36	56	78	80	-	-	-	-
TiH_2-1428	30	62	96	121	18	44	66	71
Zr-745	-	-	-	-	-	14	31	42
1028	28	43	59	68	20	34	42	50
1029	22	42	57	62	16	32	41	49
1557	44	55	66	76	-	-	-	-
1558	33	49	60	78	-	-	-	-
ZrH_2-1429	29	46	69	90	19	40	57	65
			Part B: Average rates of pressure rise, p.s.i./sec.					
Ti-740-1	-	-	-	-	100	200	750	500
740-2	-	-	-	-	250	400	750	750
864	-	-	250	700	-	-	100	250
1555	1,700	2,800	3,400	3,300	-	-	-	-
1556	1,300	2,300	3,100	3,300	-	-	-	-
TiH_2-1428	400	1,850	3,850	2,800	250	1,050	2,100	1,250
Zr-745	-	-	-	-	-	100	350	600
1028	1,750	2,700	3,900	5,100	400	1,350	1,450	1,450
1029	750	2,050	3,150	4,300	150	750	1,000	1,250
1557	2,400	2,600	2,750	3,050	-	-	-	-
1558	1,400	2,350	2,350	3,050	-	-	-	-
ZrH_2-1429	800	2,150	4,000	4,000	250	1,100	2,700	3,800
			Part C: Maximum rates of pressure rise, p.s.i./sec.					
Ti-740-1	-	-	-	-	150	400	1,100	1,200
740-2	-	-	-	-	450	850	1,100	1,650
864	-	-	550	2,300	-	-	200	500
1555	4,150	7,600	over 10,000	over 10,000	-	-	-	-
1556	3,850	7,600	10,000	10,000	-	-	-	-
TiH_2-1428	600	4,300	over 10,000	9,000	400	2,150	over 5,000	4,050
Zr-745	-	-	-	-	-	150	1,600	2,600
1028	4,500	6,400	9,500	over 10,000	1,250	2,450	3,800	over 5,000
1029	1,350	5,100	7,100	9,500	400	1,300	3,150	4,400
1557	5,700	7,600	8,800	over 10,000	-	-	-	-
1558	2,750	6,300	8,800	over 10,000	-	-	-	-
ZrH_2-1429	1,600	5,200	8,800	9,500	450	2,250	over 5,000	over 5,000

The ineffectiveness of carbon dioxide is not surprising. Past work with other metals, including magnesium and magnesium-aluminum alloys, and the present experiments in the furnace have shown that dust clouds of highly reactive powders can ignite and explode in carbon dioxide. The greater effectiveness of helium evidently is due to its high thermal conductivity. Helium-air mixtures are definitely more effective in preventing explosions of these five metal powders and uranium hydride than are argon-air mixtures. Even with helium-air mixtures, however, the oxygen content of the atmosphere had to be 7 percent or less to prevent ignitions, and it is quite likely that in most applications it might be more practical to maintain an atmosphere of pure helium rather than attempt to prepare helium-air mixtures.

On the other hand, carbon dioxide-air mixtures were the most effective portection against ignitions of dust clouds of thorium, zirconium, and titanium hydrides. Tests also were made in carbon dioxide-air mixtures with titanium hydride 1428 and zirconium hydride 1429. The oxygen limits were determined to be 13.0 and 8.5 percent, respectively. Helium-air and nitrogen-air mixtures were nearly equal in effectiveness. These findings correspond closely to the experimental data for methane gas, as reported by Coward and Jones.16/ The greater effectiveness of carbon dioxide is probably due to its higher specific heat per unit volume. Helium has high thermal conductivity, but its specific heat is less than half that of carbon dioxide. The specific heat of argon is slightly higher than that of helium, but its thermal conductivity is very much smaller than that of helium.

REDUCTION OF FIRE AND EXPLOSION HAZARDS

The investigation has shown that the fire and explosion hazards incident to the manufacture and handling of large quantities of the subject powders can be considerable. The hazards are comparable to, or even exceed, those encountered in the manufacture of finely divided magnesium or flaked-aluminum powders. It is suggested that laboratories or plants contemplating production of these powders on an important scale should consult and follow, insofar as is possible and pertinent, the recommendations outlined in the Codes for the Prevention of Dust Explosions in the Manufacture of Aluminum Bronze Powder and of Maganesium Powder or Dust, published by the National Fire Protection Association, Boston, Mass. Important recommendations include eliminating all ignition sources near dusty processes, reducing the production of fine dust as much as possible, good housekeeping to prevent dissemination of dust in the plant, and the use of inert-gas atmospheres where practicable. Whenever possible at least some, if not all, of the manufacturing operations of the more hazardous powders should be performed in atmospheres of helium or argon.

An important safety measure against structural damage by explosions is the provision of pressure-relief vents in equipment and other affected structures. The function of these vents is to release gases during the initial stages of an explosion, thereby preventing the development of high pressures.

Recommendations on storing, shipping, extinguishing fires, and other control measures for zirconium powder were published in a Safety Digest by the National Safety Council, Chicago, Ill. Some of this information is also applicable to the preparation and handling of the other powders described in this report.

16/ Coward, H. F., and Jones, G. W., Limits of Inflammability of Gases and Vapors: Bureau of Mines Bull. 279, 1939, fig. 22, p. 54.

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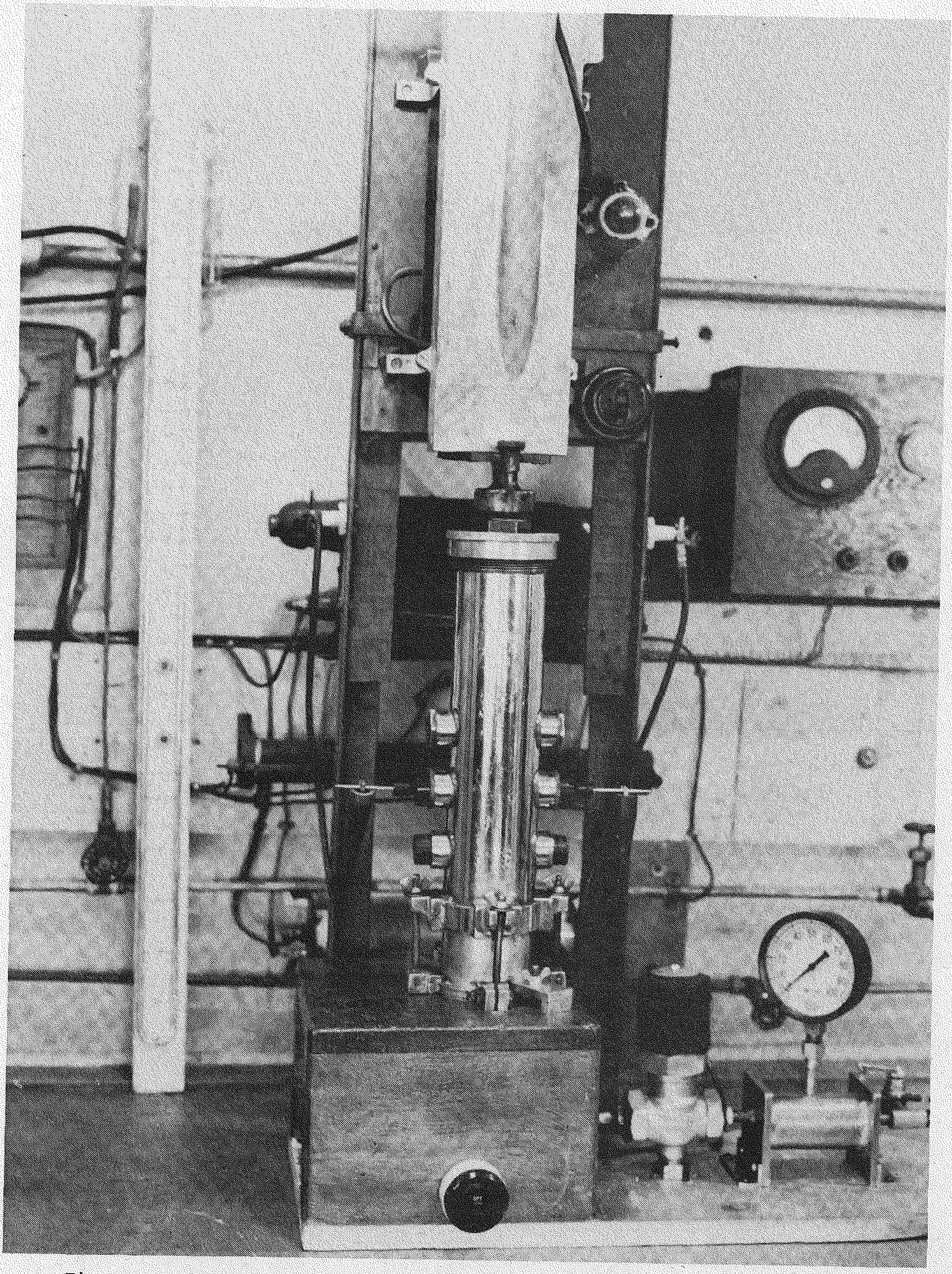

Figure 4. - Apparatus for determining pressures produced by dust explosions.

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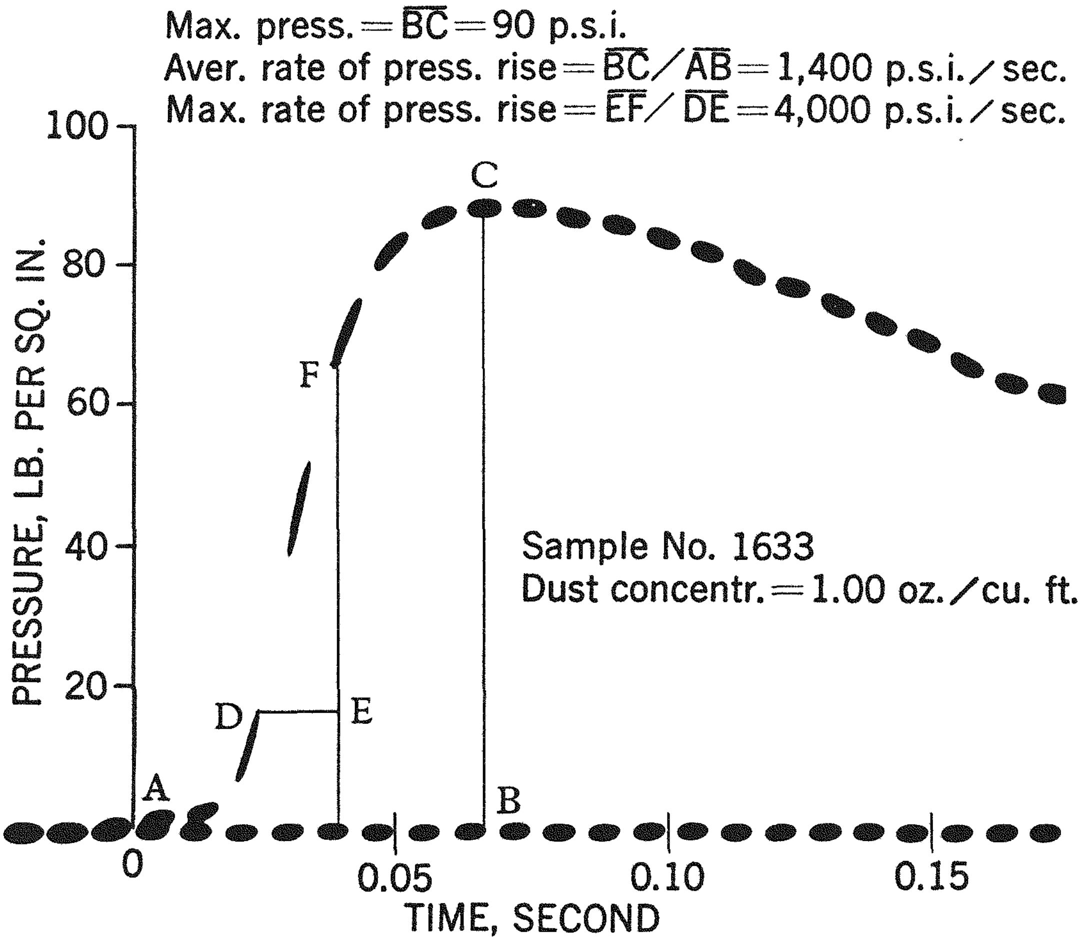

Figure 5. - Pressure-time record of zirconium powder explosion in laboratory test bomb.

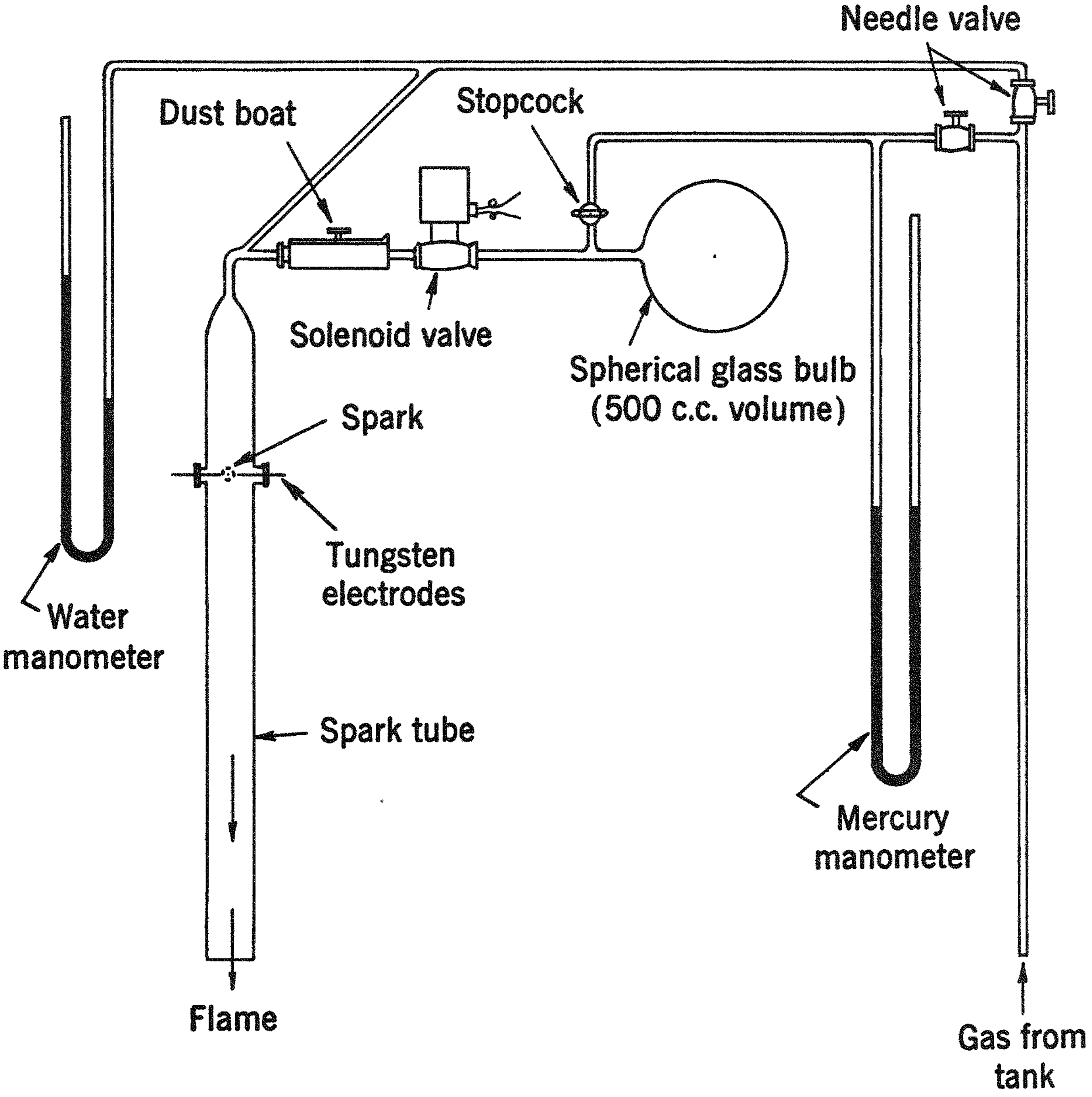

Figure 6. - Spark apparatus for testing dust flammability in various gases.

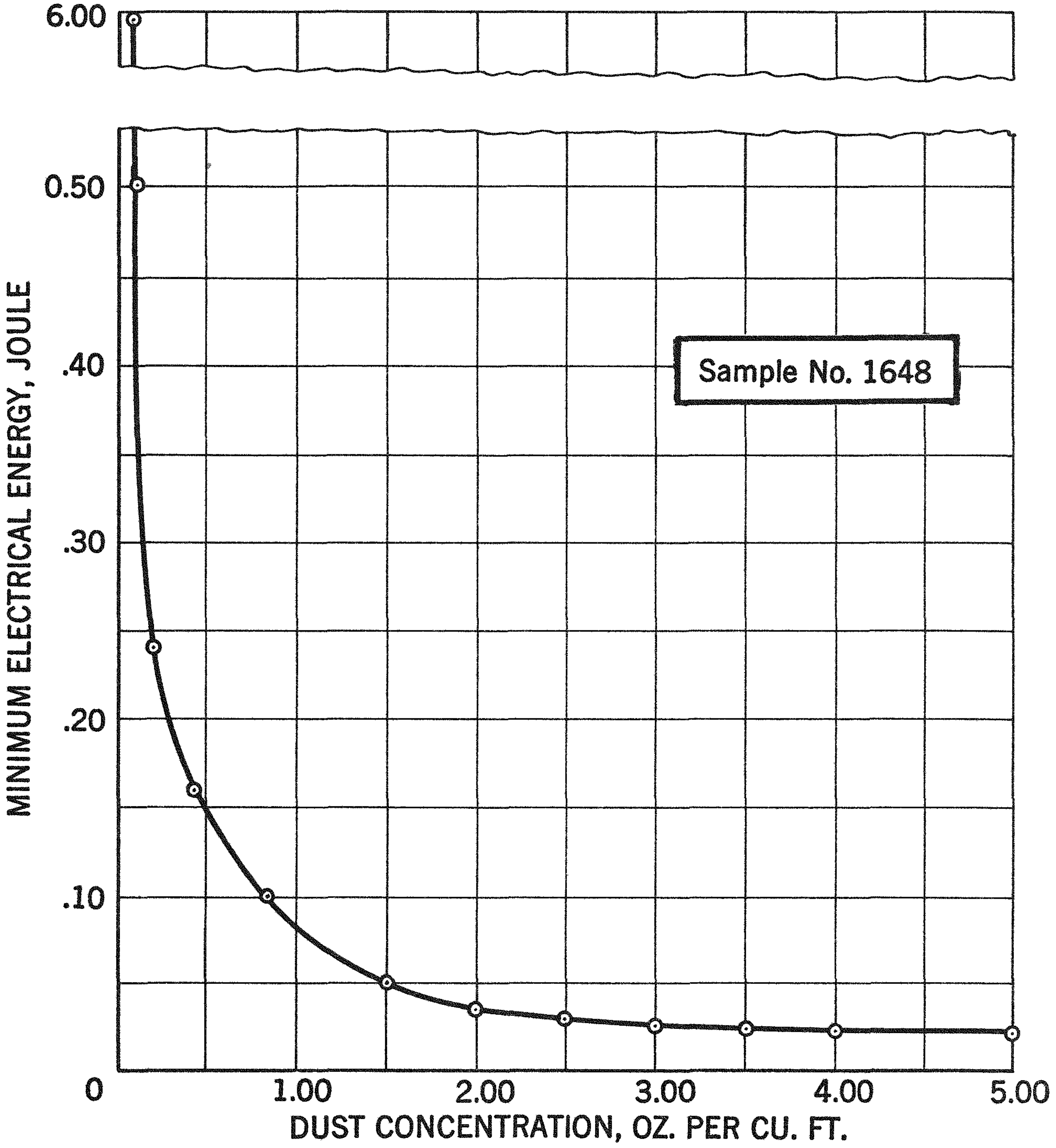

Figure 7. - Minimum electrical energy required to ignite dust clouds of titanium.

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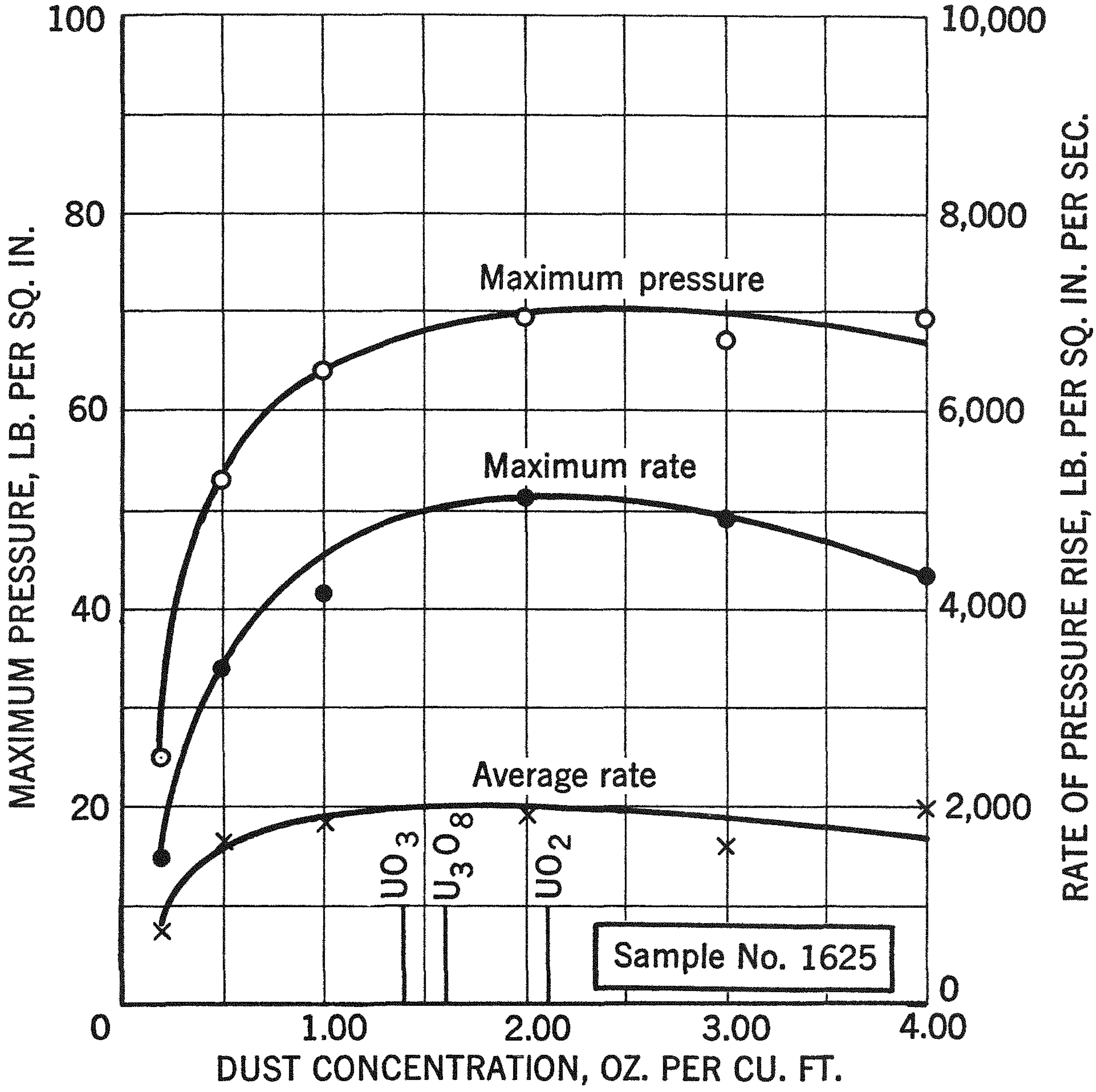

Figure 8. - Maximum pressure and rates of pressure rise developed by explosions of uranium.

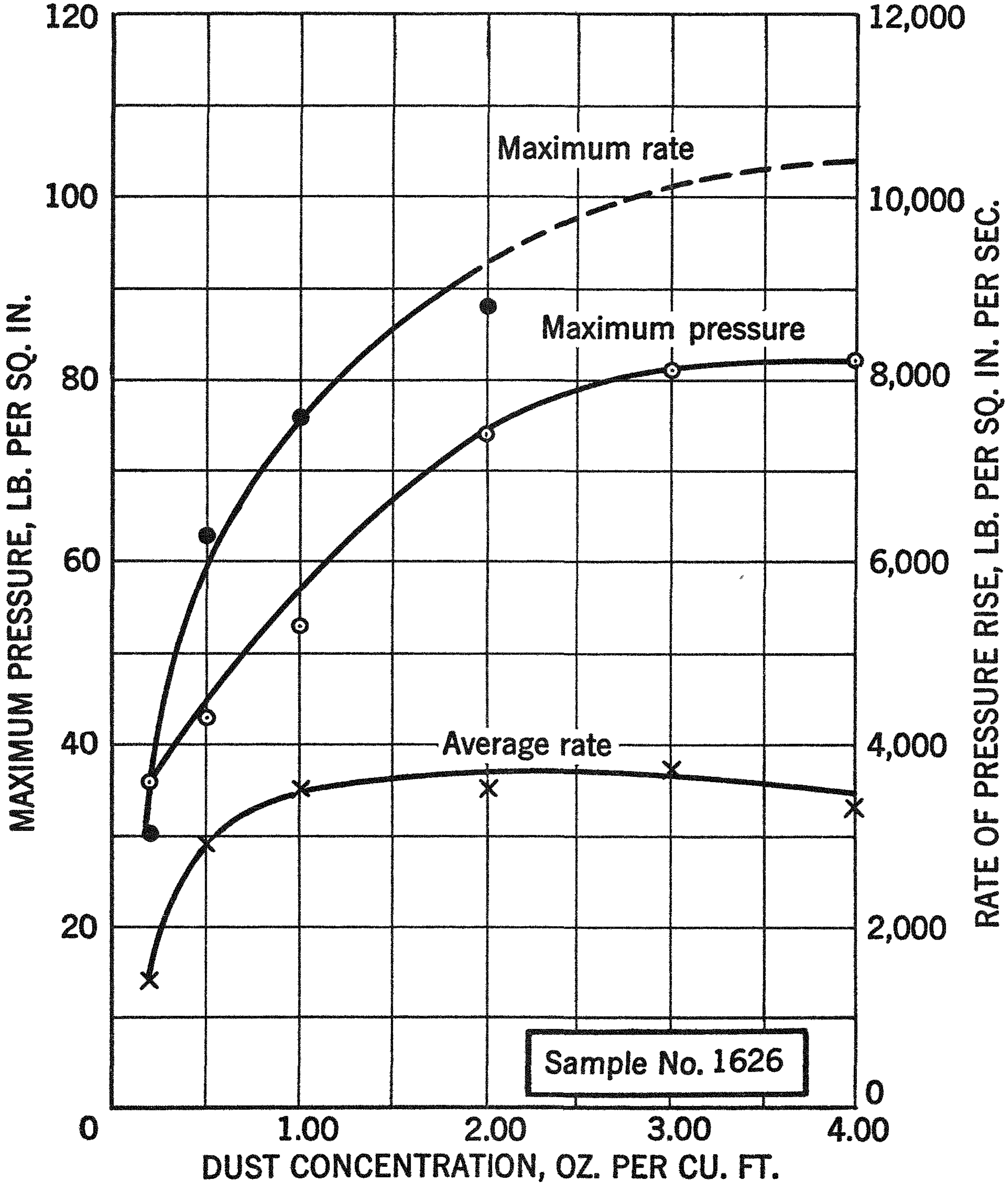

Figure 9. - Maximum pressure and rates of pressure rise developed by explosions of uranium hydride.

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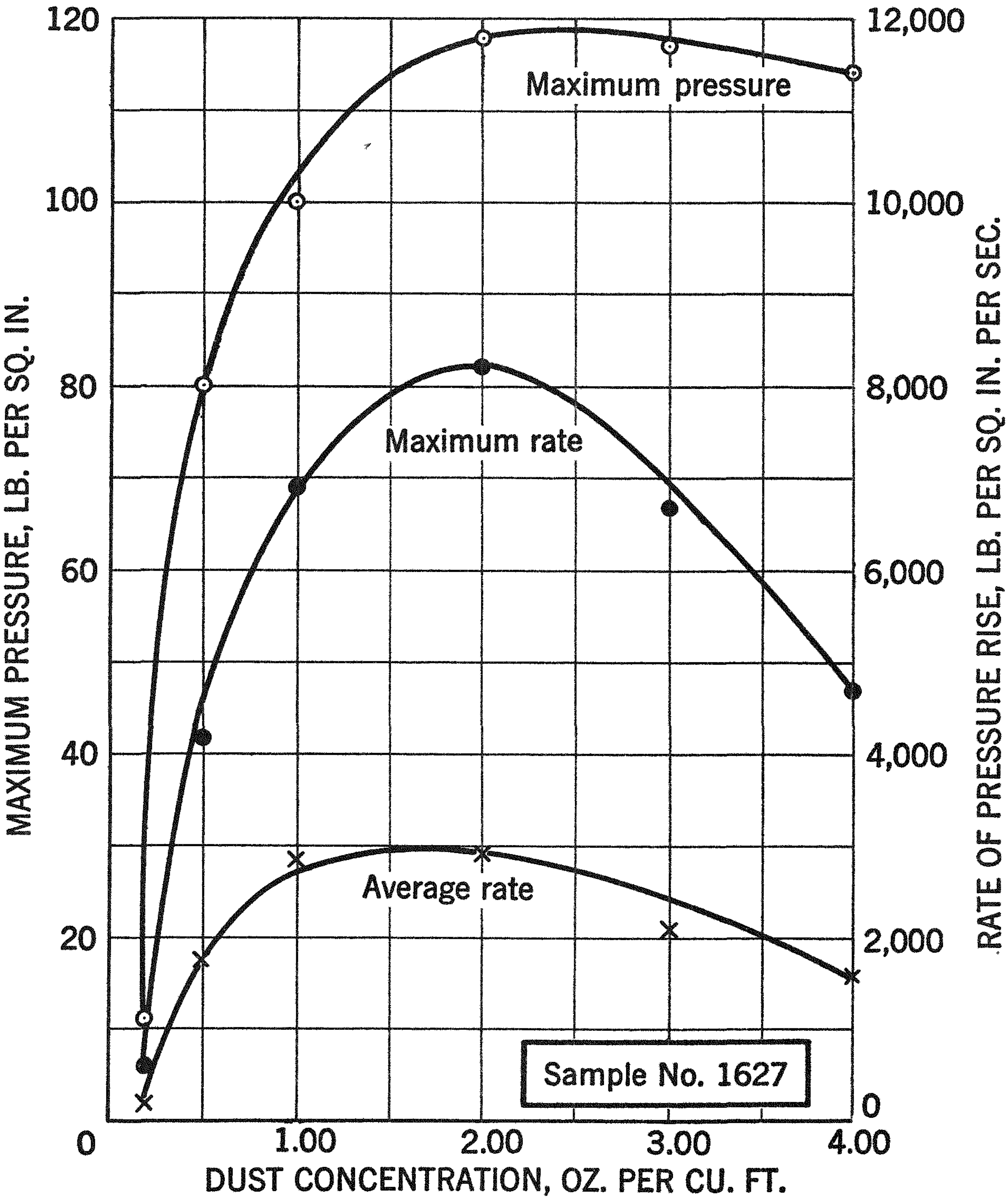

Figure 10. - Maximum pressure and rates of pressure rise developed by explosions of zirconium hydride.

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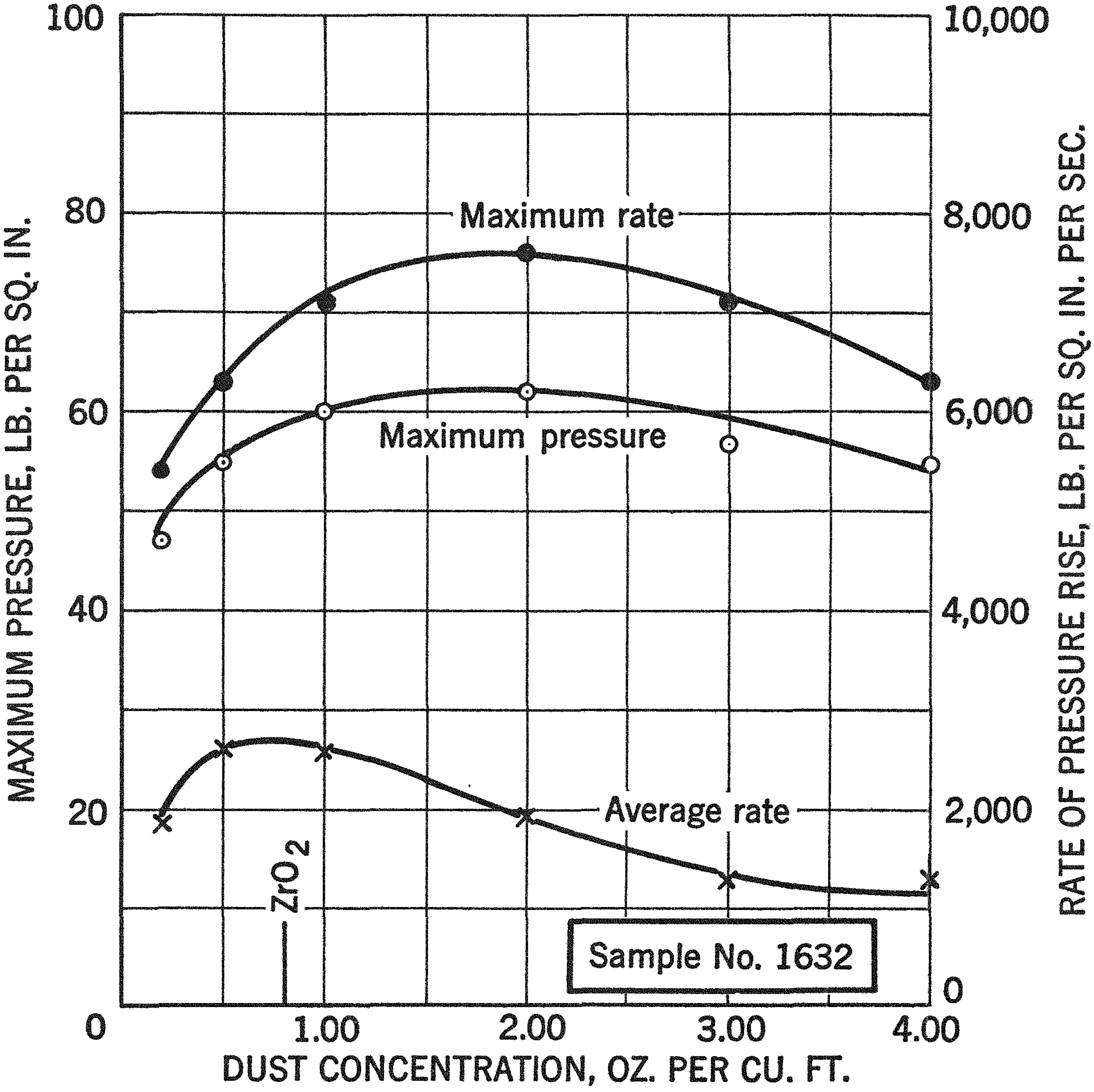

Figure 11. - Maximum pressure and rates of pressure rise developed by explosions of fine zirconium.

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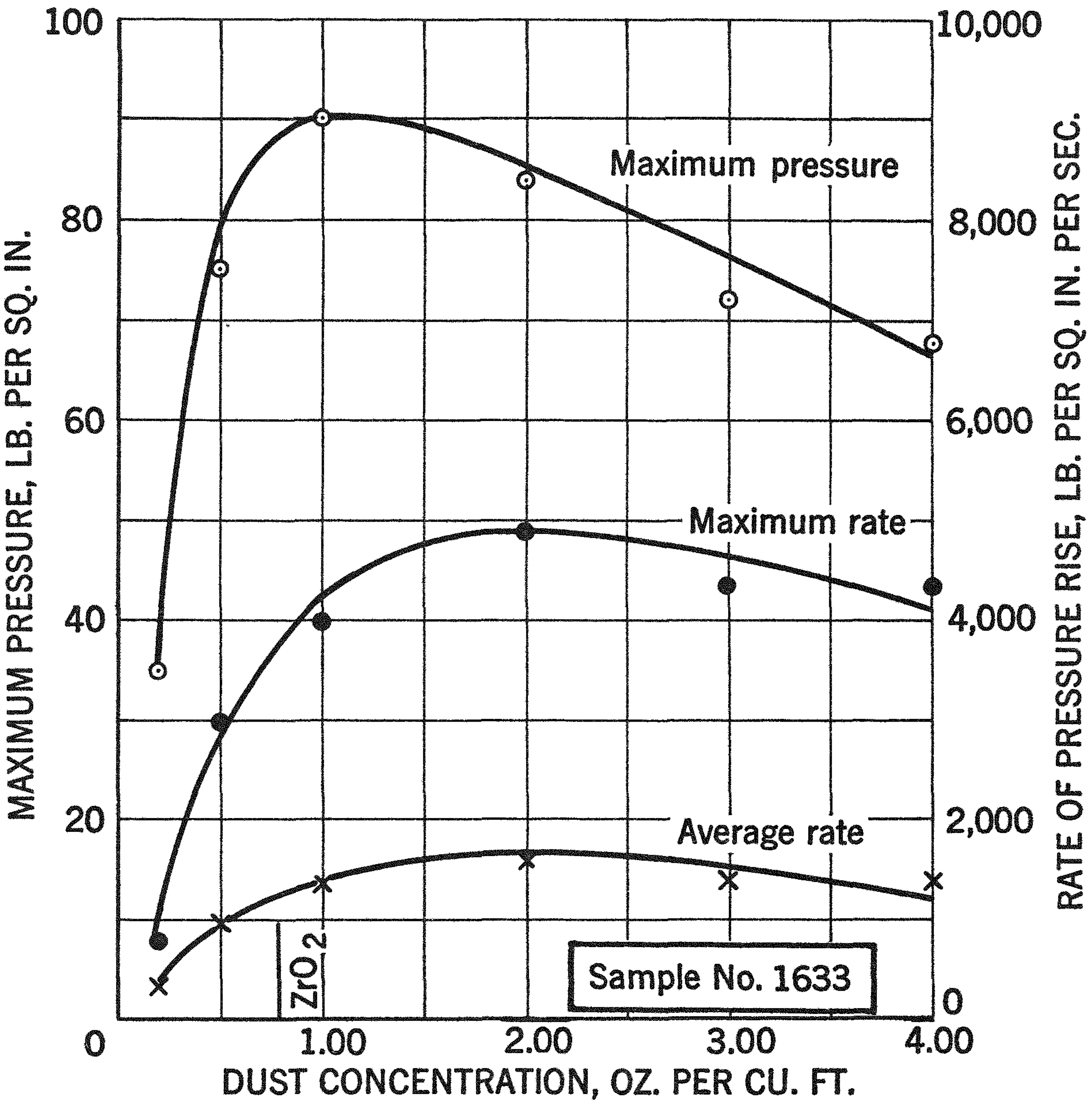

Figure 12. - Maximum pressure and rates of pressure rise developed by explosions of zirconium.

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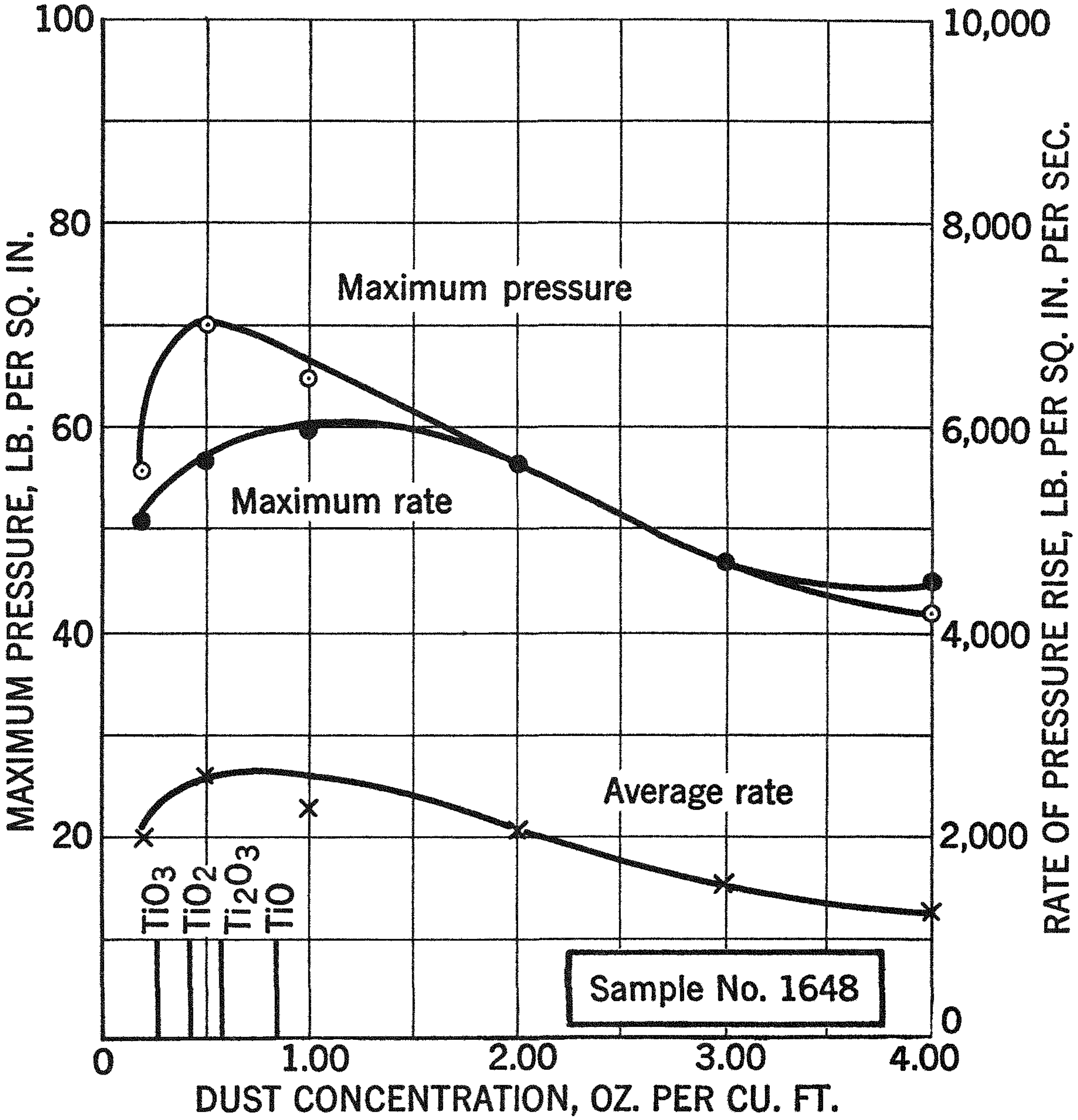

Figure 13. - Maximum pressure and rates of pressure rise developed by explosions of titanium.

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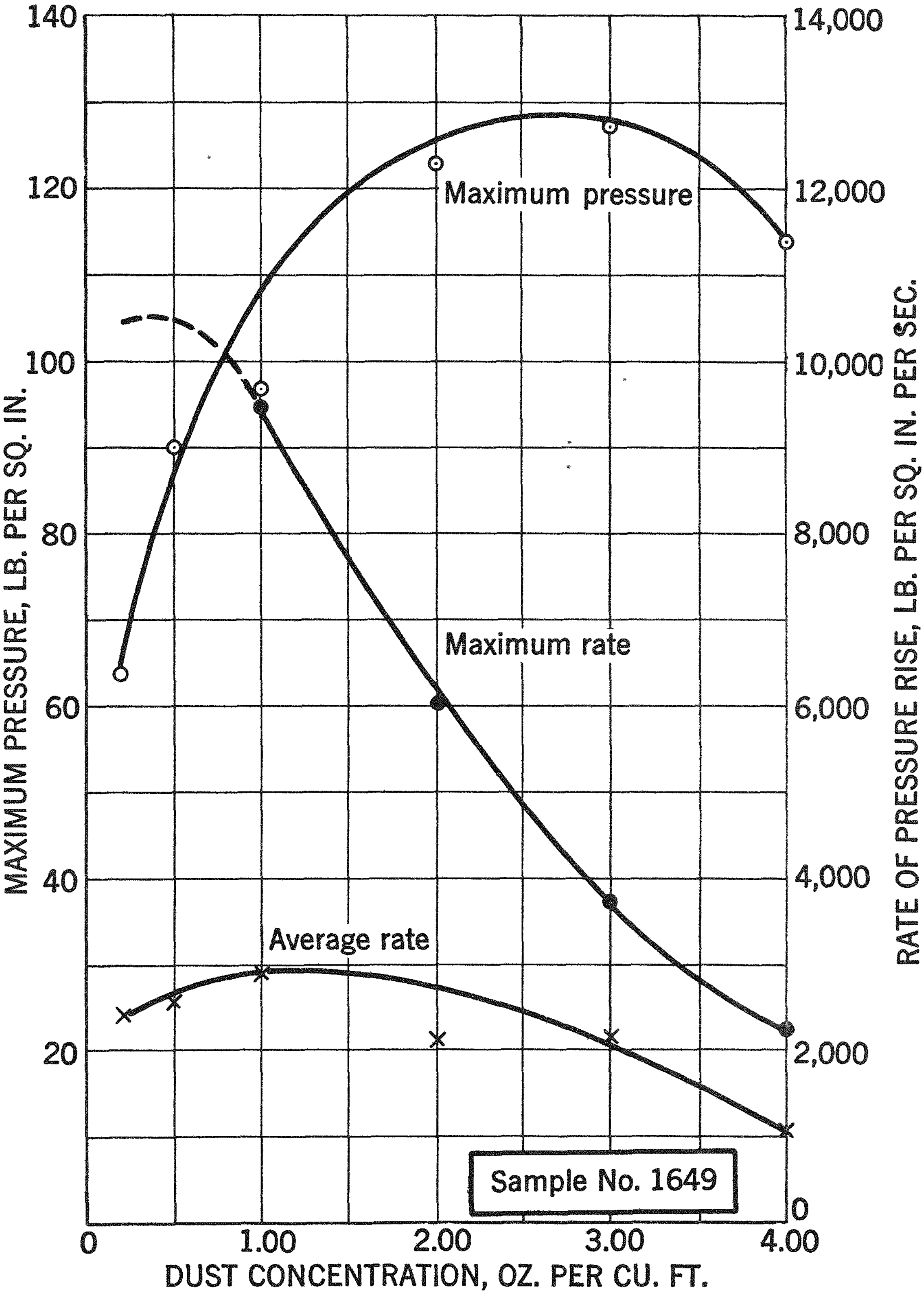

Figure 14. - Maximum pressure and rates of pressure rise developed by explosions of titanium hydride.

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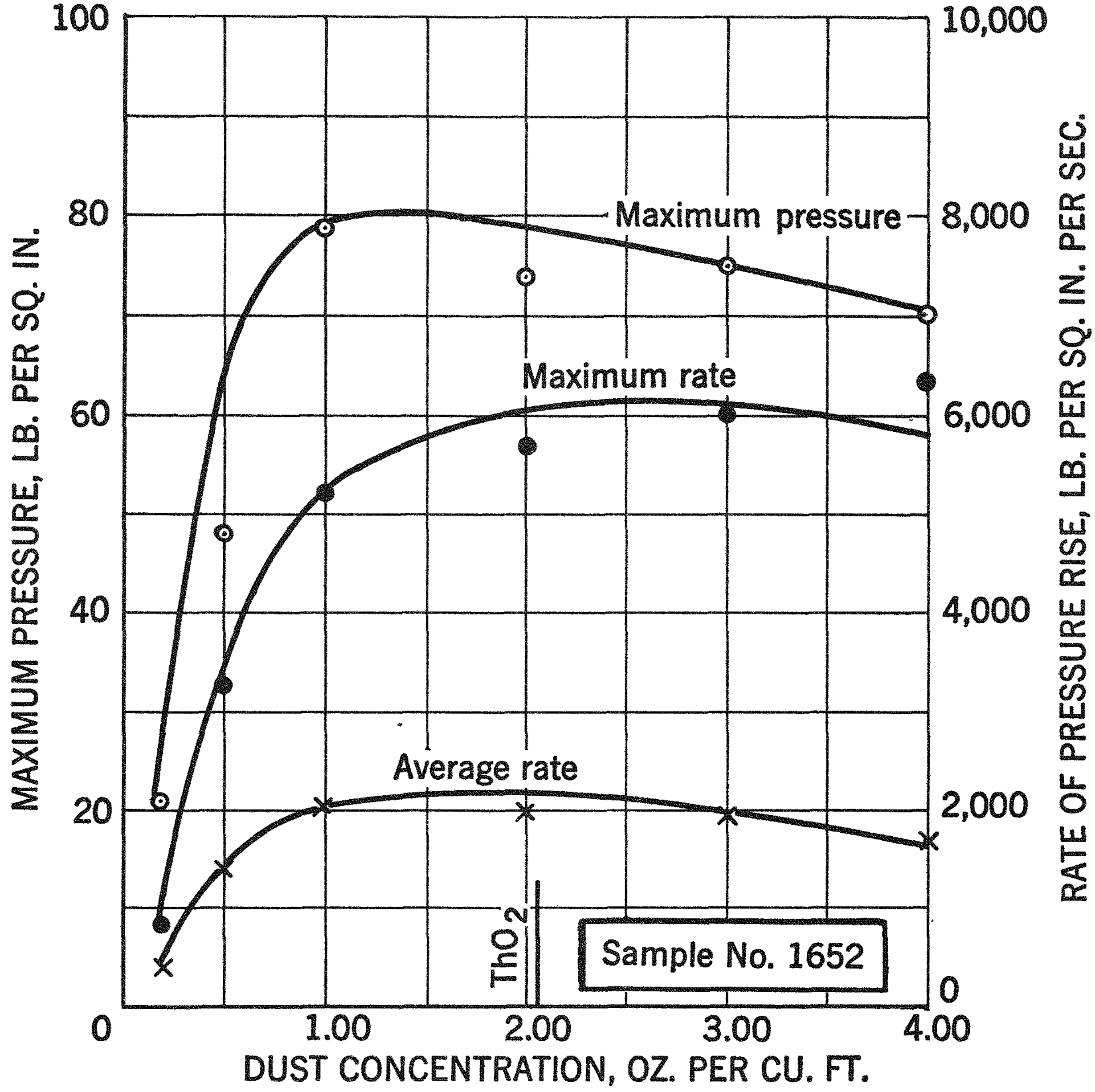

Figure 15. - Maximum pressure and rates of pressure rise developed by explosions of thorium.

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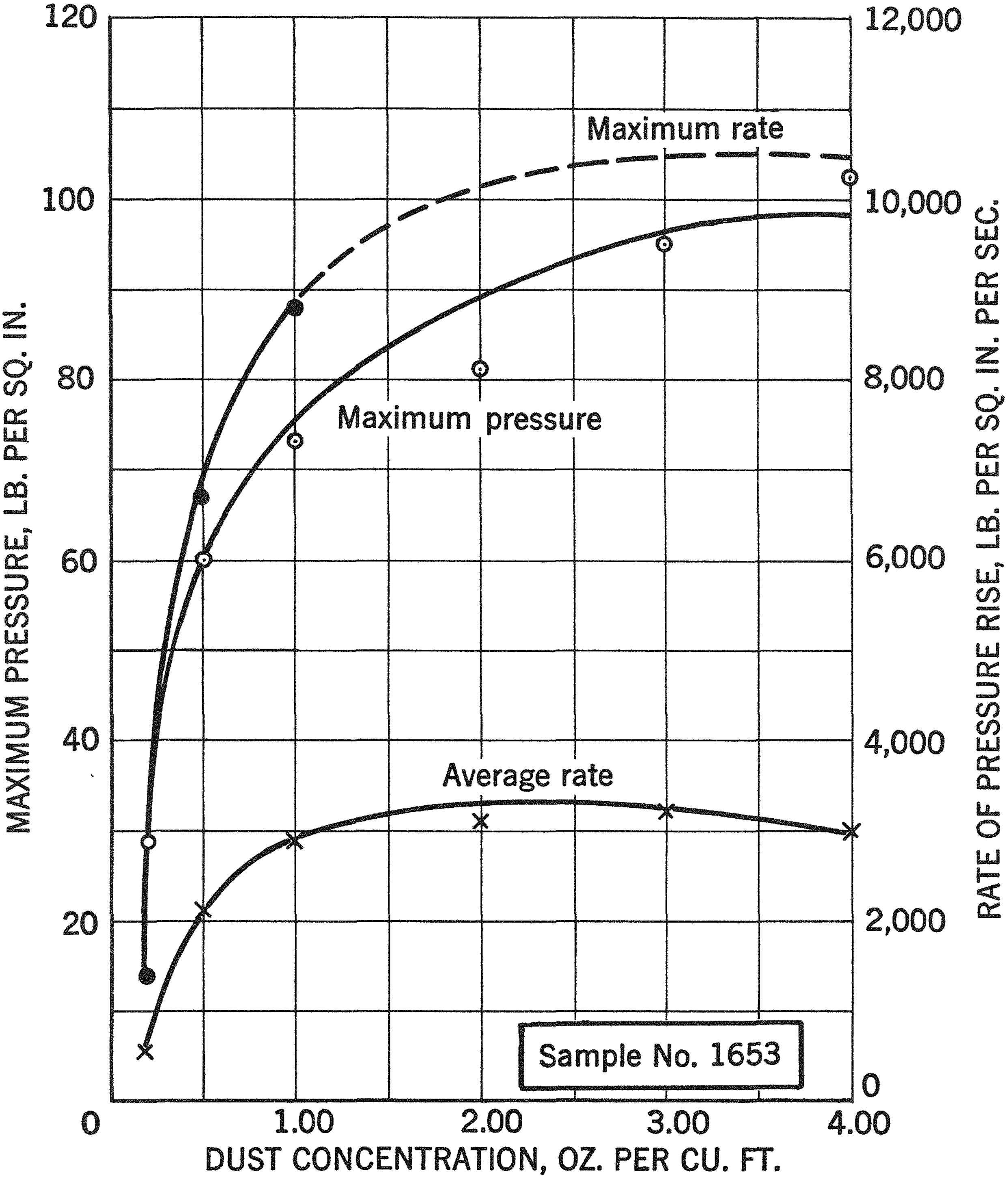

Figure 16. - Maximum pressure and rates of pressure rise developed by explosions of thorium hydride.

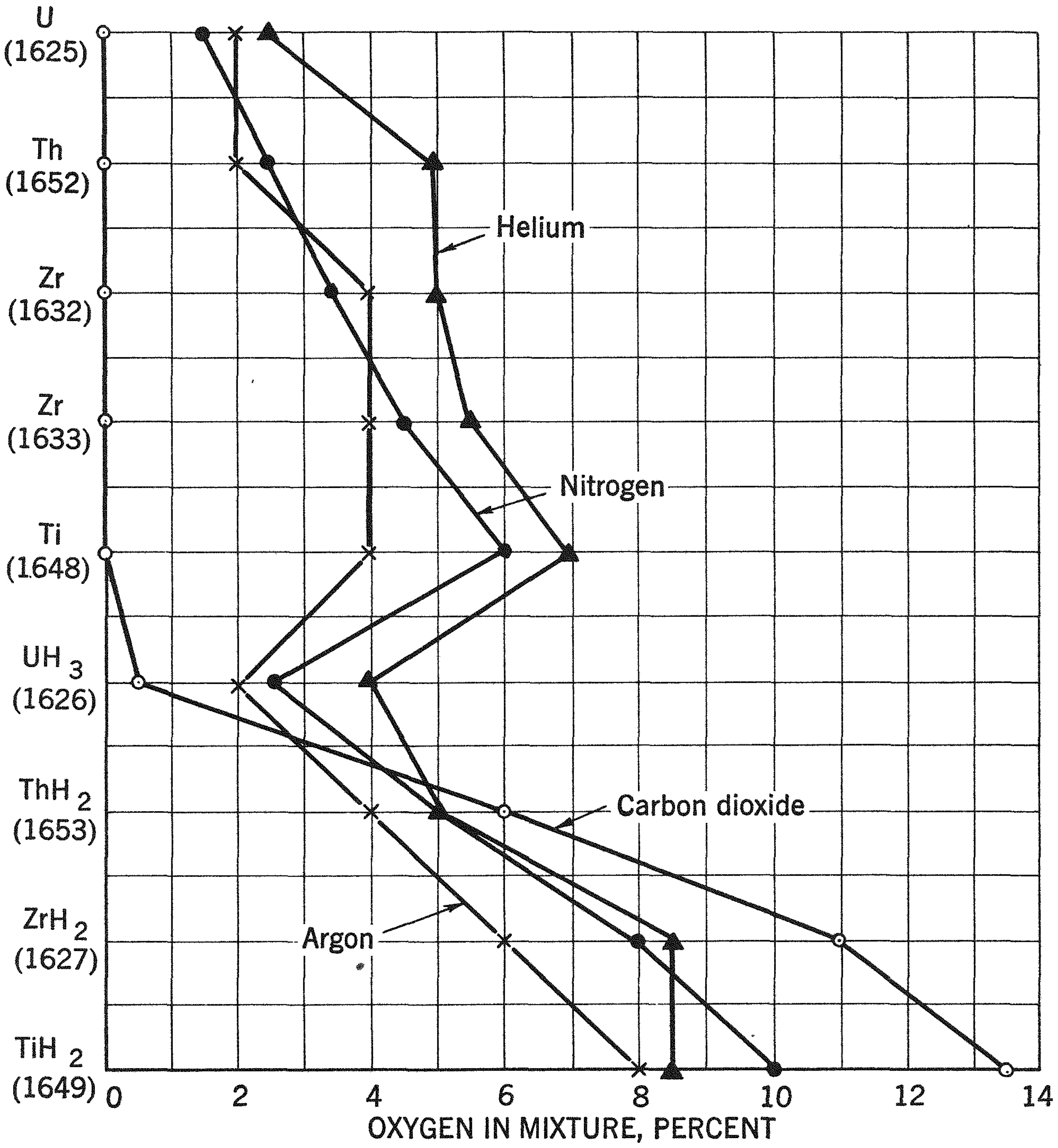

Figure 17. - Limiting oxygen contents in air-inert gas mixtures for preventing ignition of dust clouds by electric sparks.

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