AF/SSD-TR-61-40

R-3217

RESEARCH ON HAZARD CLASSIFICATION OF NEW LIQUID ROCKET PROPELLANTS

FINAL REPORT
VOLUME I

ROCKETDYNE
A DIVISION OF NORTH AMERICAN AVIATION, INC.
6633 CANOGA AVENUE, CANOGA PARK, CALIFORNIA

CONTRACT AF 33(616)-6939
PROJECT NO. 3148
TASK NO. 314801

OCTOBER 1961

ROCKET TEST ANNEX
SPACE SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

EDWARDS AIR FORCE BASE, CALIFORNIA

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FOREWORD

The final report on the hazard classification of new liquid rocket propellants is in fulfillment of basic Air Force Contract AF33(616)-6939, PN 3148, TN 314801. The report consists of two volumes: Volume I covers work performed on the basic contract and Supplemental Agreement 2; Volume II (AF/SSD-TR-61-40) covers Supplemental Agreement 3, Titan II Model Missile Tests.

The administration and technical direction was provided by Mr. F.S. Forbes of the Space System Division, Air Force Systems Command, Edwards AFB, California. Mr. D. J. Hatz of Rocketdyne, Project Engineer for the program, directed the work presented in volume I with the assistance of Mr. A. E. Chambers and Mr. E. Suarez-Alfonso.

Supplemental Agreement 1 to the basic contract was fulfilled in the following publications:

Motion Film	Handling and Storage of High-Energy Liquid Propellants
AF/SSD-TR-61-3	Mechanical System Design-Criteria Manual for Pentaborane
AF/SSD-TR-61-4	Mechanical System Design-Criteria Manual for Chlorine Trifluoride
AF/SSD-TR-61-5	Mechanical System Design-Criteria Manual for Nitrogen Tetroxide
AF/SSD-TR-61-6	Mechanical System Design-Criteria Manual for Hydrazine
AF/SSD-TR-61-7	Hydrazine Handling Manual
AF/SSD-TR-61-8	Nitrogen Tetroxide Handling Manual
AF/SSD-TR-61-9	Chlorine Trifluoride Handling Manual
AF/SSD-TR-61-10	Pentaborane Handling Manual

ABSTRACT

This report presents the test results of a program to develop safety and design criteria for the bulk storage and handling of nitrogen tetroxide, chlorine trifluoride, hydrazine, and pentaborane. A total of 92 small-scale tests were performed at the Propulsion Field Laboratory using propellant quantities not exceeding five pounds in weight. Propellant weights used on the nine large-scale tests at Haystack Butte, Edwards AFB, ranged from 135 to 1800 pounds of total propellant. Biological studies were performed on three of the large-scale tests of the hazard classification program. Techniques were also developed for the establishment of safe-distance values for the storage of the propellants.

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INTRODUCTION

The evaluation of the hazards of nitrogen tetroxide, chlorine trifluoride, hydrazine, and pentaborane was established under Air Force Contract AF33 (616)-6939, to provide needed information on handling, storage, and safety problems posed by the application of these highly reactive, storable propellants to advanced propulsion systems. Increased storage capacities that are required in maintaining an operational system as compared to research and development activity, have required that new safety and design criteria for propellant storage and handling be established.

The purpose of the basic hazard evaluation program was to determine the various hazards involved in the storage and handling of bulk quantities of high-energy propellants so that insight on procedures and techniques for both the normal and emergency operation of a storage facility containing up to 5,000,000 pounds of propellant could be gained.

The test programs for the basic hazards evaluation program consisted of (1) small-scale hazard classification tests, concerned primarily with the evaluation and interpretation of small propellant spills, simulating line leakage or failure, on various common materials of construction, and (2) large-scale hazard classification tests concerned with the evaluation of hazards of large spills, simulating major tank failure, in a tray or revetment. Included in these large-scale tests were biological studies for developing medical criteria on toxicology. An evaluation of meteorological aspects as they pertain to atmospheric contamination are included in a presentation of safe-distance calculations for both on-site and off-site considerations in locating and operating a storage facility.

The results of these test programs, coupled with our propellant storage and handling experience and a survey of the pertinent literature, were used to prepare design manuals, handling manuals, and a training film for the safe storage and handling of hydrazine, nitrogen tetroxide, chlorine trifluoride, and pentaborane. The manuals and the training film were published separately.

Discussed separately in volume II of this final report are the results of the test program designed to determine safety criteria and silo design criteria for the Titan II launch complex.

SUMMARY

SMALL-SCALE HAZARD DETERMINATION TESTS

The hazards resulting from leakage and/or line rupture of storable propellant systems were simulated with propellant spills by controlled operation of four small-scale propellant dump systems. Ninety-two small spills of chlorine trifluoride, nitrogen tetroxide, hydrazine, and pentaborane were made singly and in pairs, on various materials of construction under different ambient conditions. Results from all combination spills were recorded by direct observation and color motion pictures. Blast instrumentation was used in the latter portion of the program to record overpressures that occurred during the spills.

Equipment, safety practices, propellant handling, and test operations were evaluated. During the course of the test program, an incident occurred which involved an unplanned hazard in the test area. The events that occurred and the methods used to prevent reoccurrence of the hazard were described.

Single spills of nitrogen tetroxide and hydrazine on various surfaces failed to react. Hazards were present from the fumes and liquids until decontamination was complete; however, no incident resulted from these hazards during the course of the program. Chlorine trifluoride reacted with all surfaces, except concrete, to cause either ignition or very small explosions. Spills of pentaborane on various surfaces resulted in spontaneous ignition with air under some of the conditions tested. On all surfaces, except water, the propellant ignited above ambient temperatures of 70 F; on dirt and asphalt surfaces, reaction between the surface and fuel ignited the propellant below this temperature.

Combined spills of nitrogen tetroxide and chlorine trifluoride failed to show any indication of reactions under any of the conditions tested. Hydrazine ignited instantaneously with chlorine trifluoride under all test conditions. Some of the tests resulted in a series of very small

explosions. The maximum TNT equivalent obtained for this liquid combination was 0.0045 percent. From the motion pictures and the overpressure measurements taken during these tests, the explosions were traced to reactions between hydrazine vapors and air.

Spills of pentaborane and chlorine trifluoride resulted in hypergolic ignition and intense fireballs. Explosions of an insignificant magnitude were recorded on 6 of the 12 combination spills. Reactions that initiated the shock wave were thought to be reactions of free hydrogen, generated by the pyrolysis and oxidization of pentaborane, and air.

Spills of hydrazine and nitrogen tetroxide resulted in an immediate ignition of the propellants under all conditions tested. A series of explosions were recorded on the majority of these tests, with a maximum TNT equivalent yield of 0.75 percent. Explosions from spills on an absorbent or cooling surface, or with an oxidizer lead, were found to be less severe. The hydrazine vapor-air explosions originated from points a few feet above the spill surface.

The largest explosions that were recorded during the test program were caused by combined spills of hydrazine and pentaborane on concrete, dirt, and asphalt. The explosions occurred as a single shock wave with reflections, and were originated at times varying from slightly after ignition to the start of the post-test purge. A majority of the shock waves that resulted from these tests apparently had not "shocked up" by the time the wave had reached the overpressure transducers located at 10 feet. The largest explosion was recorded at a point 15 feet from the origin and was 3.15 percent equivalent yield of TNT. Initiation of the shock wave in each test appeared to be a result of a hydrogen-air explosion in which the hydrogen was generated by bipropellant reaction.

Nitrogen tetroxide-pentaborane spills were conducted without blast instrumentation; thus, no TNT equivalents were calculated. However, it was concluded that this combination was potentially the most hazardous of the combinations tested. Single, large explosions were noted on all tests; a simultaneous spill of the combination on water resulted in damage to the surrounding area with the explosion heard for several hundred yards. The source of the explosion appeared to be near the spill surface and was concluded to be a result of a "hard ignition" of the combination.

LARGE-SCALE HAZARD DETERMINATION TESTS

The magnitude of the hazards involved during leakage or rupture of propellant systems containing pentaborane, hydrazine, chlorine trifluoride, and nitrogen tetroxide was determined by performing controlled spills of large quantities of propellants. A total of nine tests was made which included five singular and three multiple spill tests, and one propellant heating test. The propellants were spilled into a 20 x 20 ft x 2-ft-deep steel tray from 150- or 165-gallon tanks. The propellants were expelled from the tanks in less than two seconds, with the exception of the first two tests which required 25 and 2 minutes, respectively. All the tests were monitored by air-sampling instruments, color motion pictures, and direct observation. Several of the multiple spills were additionally monitored by blast-recording instruments, and fireball temperature and size grids.

Standard operating and safety procedures for handling the propellants were followed during the test program, emphasizing the areas of safety applying to the hazards of the particular propellants tested.

Spills of nitrogen tetroxide, one with a water deluge and another on a dry tray, released highly concentrated dark red-brown vapors. The boiloff rate of the propellant was accelerated by the reaction between nitrogen tetroxide and water; whereas the propellant spilled on a dry tray self-refrigerated, reducing the boiloff rate.

Both nitrogen tetroxide and chlorine trifluoride ignited upon contact when spilled with hydrazine, resulting in large fireballs lasting several seconds, and hydrazine afterfires. The majority of the oxidizers were either burned or vaporized during the initial reactions, stacking 25 to 100 feet. The nitrogen tetroxide-hydrazine spill was accompanied by a series of small explosions. The blast instrumentation failed, but comparison with similar tests indicates that the maximum TNT equivalent yield would be less than 0.5 percent. The reaction between chlorine trifluoride and hydrazine was very rapid and erratic. No explosions occurred during the test.

Chlorine trifluoride behaved similarly to nitrogen tetroxide when spilled singularly. The vapors were initially yellow-green in color, changing to light brown after a few seconds. Chlorine trifluoride was much more reactive than nitrogen tetroxide, reacting violently with water and other contaminants, causing a rapid boiloff rate. Very small explosions occurred during the reaction between chlorine trifluoride and water.

The propellant vapors from the spills did not diffuse readily and appeared to travel downwind in channels or rivers at fairly high concentrations, gradually rising and diffusing.

The spilled pentaborane ignited upon contact with air, resulting in an intense fire lasting several minutes. No explosions occurred during the test. A gray-white cloud was given off, stacking to 1000 feet. Extensive heat damage was incurred to the test equipment during the test.

Several large explosions were recorded during the combined pentaborane-hydrazine spill test. The explosions occurred in less than one second after the propellants ignited. The largest explosion gave a TNT equivalent yield of 2.4 percent. A large fireball followed the series of explosions, changing to a gray-white, mushroom-shaped cloud, stacking to 1000 feet.

Hydrazine was heated inside a stainless-steel, 100-psig tank with 90-percent ullage for five minutes, resulting in a hydrazine explosion which fragmented the tank and scattered pieces over a radius of 1100 feet. The TNT equivalent yield of the explosion was about one percent. A 3/4-inch relief valve opening was sufficient to vent the gases generated without overpressurizing the tank, up to the time of the explosion.

MEDICAL STUDIES

Sixty-three hamsters were exposed to the nitrogen tetroxide vapors released during large-scale spill test No. 2. The animals were placed at 21 locations, ranging from 100 to 5000 feet downwind of the spill tray. The gross and microscopic pathology of the exposed and control hamsters did not reveal any effects that could be attributed to the nitrogen tetroxide.

Thirty-six hamsters were exposed to the chlorine trifluoride vapors released during large-scale spill test No. 5. The animals were placed at four locations; two at 100 feet, and two at 500 feet downwind of the spill tray. None of the animals died during the test. Six animals died in approximately one to nine days after the test. These animals were positioned at the 100-foot locations. The most consistent finding associated with the deaths was severe enteritis (inflamed intestinal tract). All the animals exposed showed some degree of hair loss, eye opacities and possibly an initial, but transient rhinitis (inflamed nasal mucous membrane), and kidney damage.

All of the 54 hamsters located downwind of the spill tray and at the upwind control position during large-scale spill test No. 8 (pentaborane-hydrazine), were found dead in their cages after the test. The temperature at the time of the test was 103 F. Gross and microscopic pathology of the exposed and control hamsters indicated that the animals died from circulatory collapse resulting from hyperthermia (fever). None of the deaths could be attributed to the spilled pentaborane or hydrazine.

SAFE-DISTANCE VALUES

Techniques were developed during this program for the establishment of safe-distance values for the storage of bulk quantities of hydrazine, pentaborane, nitrogen tetroxide and chlorine trifluoride. Consideration was given to the location of storage facilities for these propellants relative to on-site and off-site populated areas. The analysis was based on toxic, blast, and fire hazards.

Two sample problems were solved for the cases of propellants spilled at air temperatures both above and below the boiling point of the propellants. Nitrogen tetroxide and hydrazine, respectively, were used as typical propellants on these calculations.

SMALL-SCALE SPILL TESTS

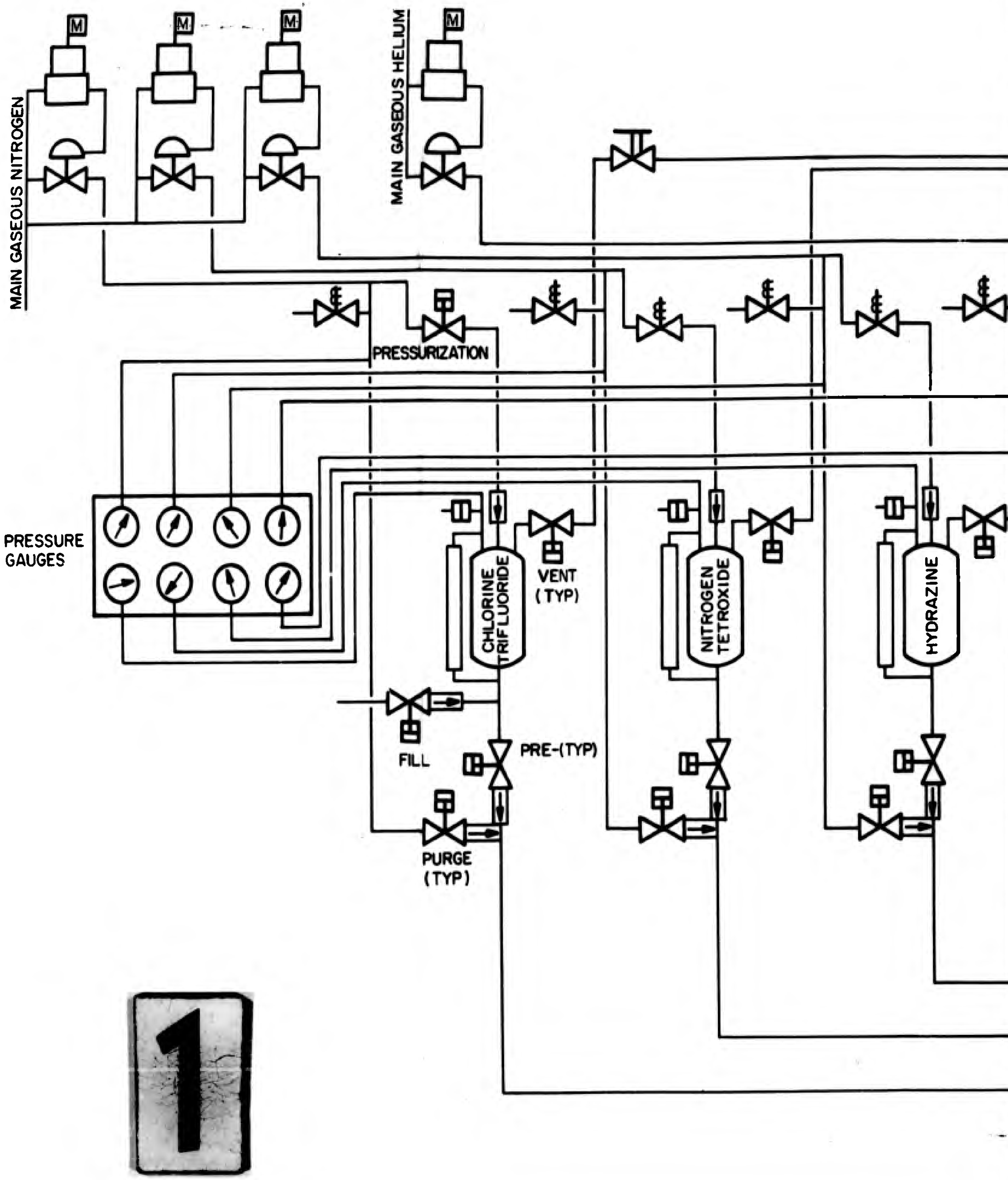
A series of small-scale spill tests were performed to: (1) describe the hazards associated with accidental spillages of hydrazine, nitrogen tetroxide, chlorine trifluoride and pentaborane, and (2) develop and/or verify safety and design criteria for the bulk storage and handling of these chemicals. These tests were conducted at the Propellant Engineering Laboratory of the Rocketdyne Propulsion Field Laboratory. The quantity of propellant used on each test was limited to a maximum of five pounds in weight.

TEST SETUP

Four similar tank systems were designed for the individual propellants (Fig. 1) and mounted on an extended, outside wall of the laboratory (Fig. 2). Each system consisted of a tank of approximately 1.5-gallon capacity, and associated plumbing. All lines in contact with the propellants were fabricated of 1/2-inch, stainless-steel AN tubing; tanks were fabricated from Type-347 stainless-steel stock. Shut-off valves were of stainless-steel construction, equipped with compatible seals.

Hydrazine and nitrogen tetroxide systems were almost identical in design detail. Both included a gaseous nitrogen pressure regulator (tank pressurization), pressurization valve, propellant tank outlet or prevalve, nitrogen purge valve, main-flow control valve, and vent valve. The purge system was operated from the pressurization regulator and located to permit purging of the propellant lines below the tank-outlet valve. All valves in contact with the propellants were pressure-operated and fabricated from compatible materials. With the exception of the nitrogen tetroxide tank vent valve and both auxiliary purge vent valves, all valves were of the "normally closed" type.

Chlorine trifluoride was stored in a system comparable to the two described above. Two vent valves were employed; however, the first was a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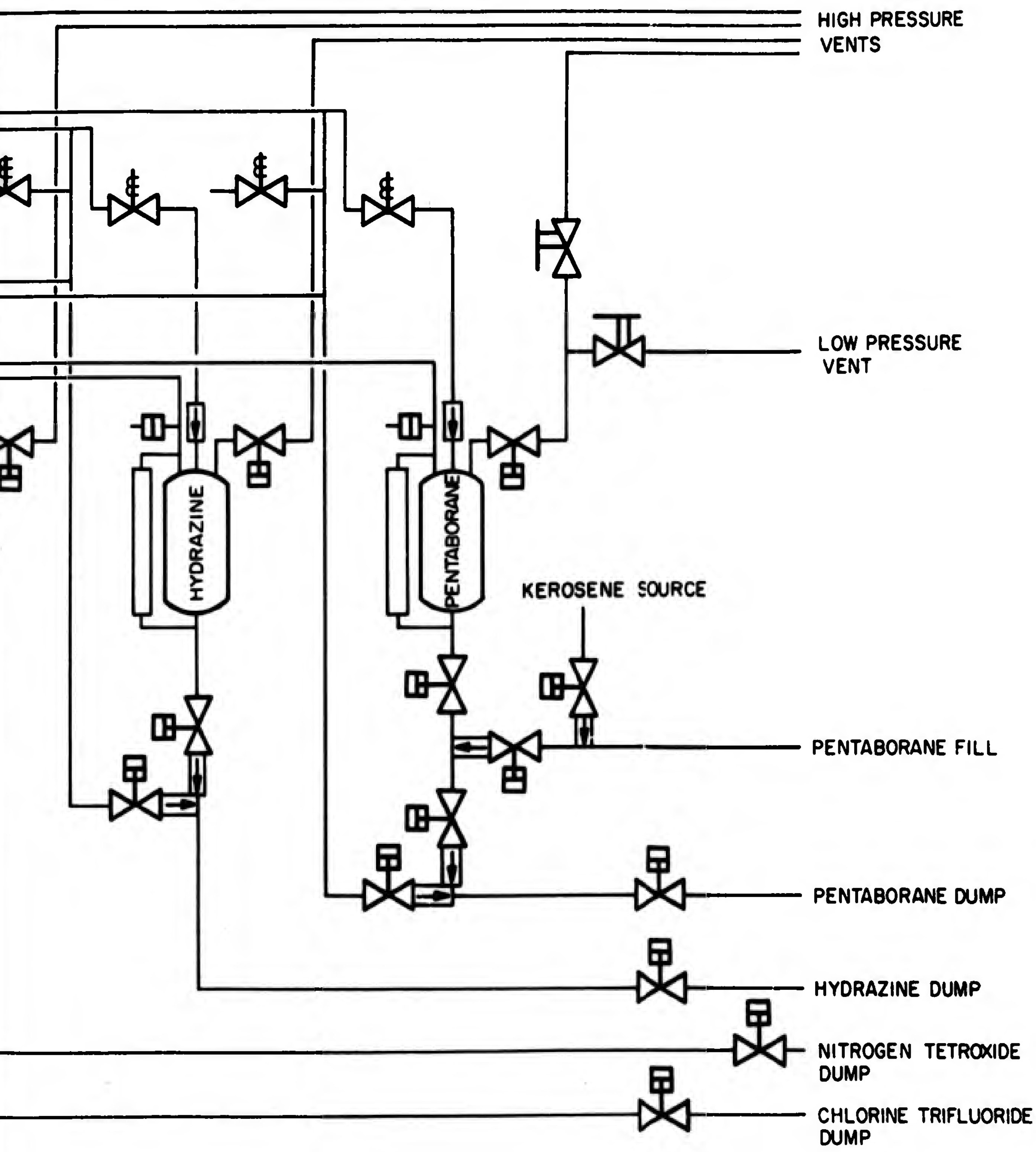

Figure 1. Schematic Diagram of Small-Scale Hazard Determination Spill System

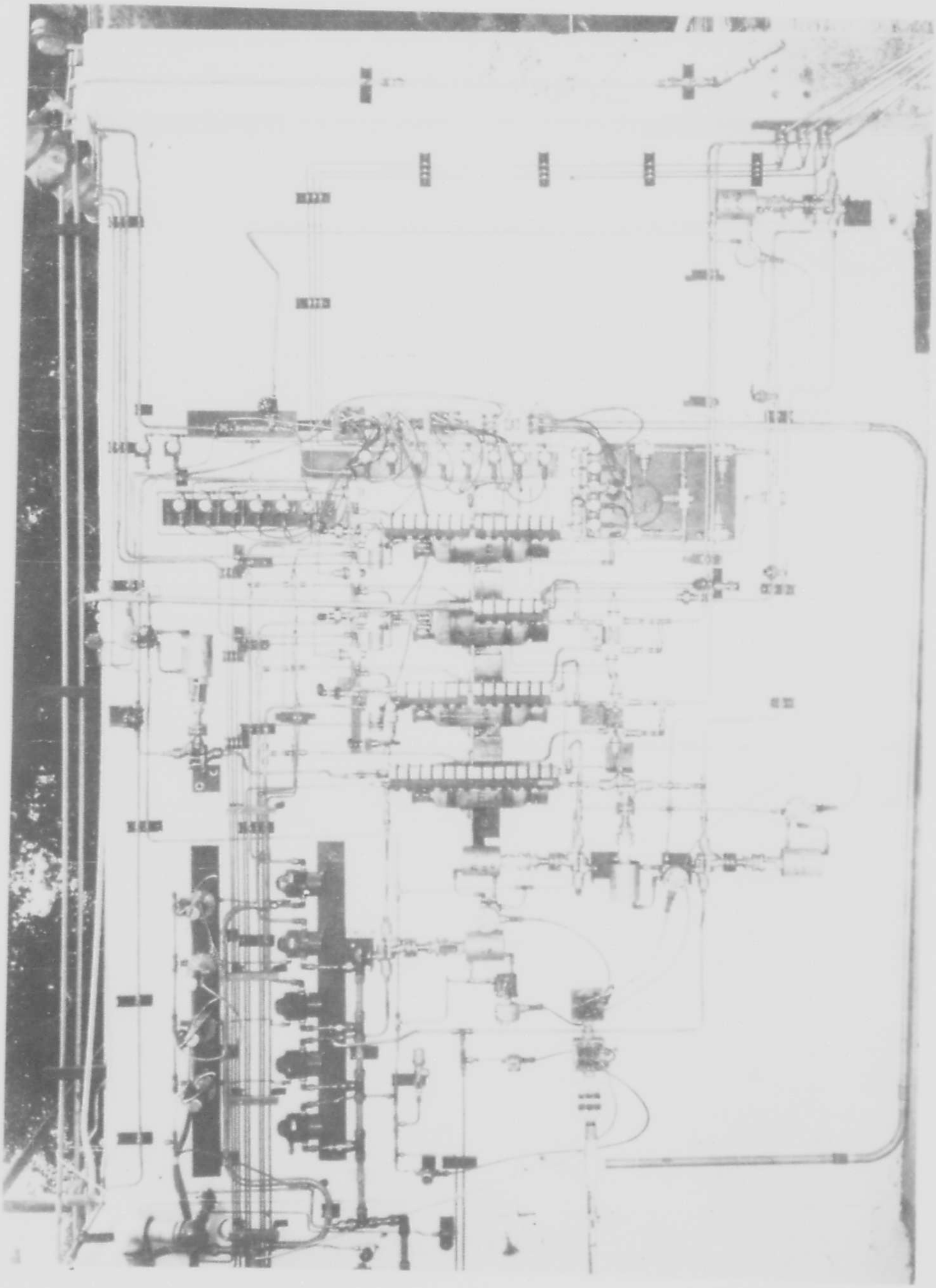

Figure 2. Small-Scale Hazard Determination Test System

standard, pressure-operated, "normally-open" valve, while the second was hand operated and was added to ensure positive sealing and exclusion of moisture during periods of system inactivity. The purge system was of particular importance for operations with chlorine trifluoride, because the main "spill" line could become hot enough to ignite the metal with residual propellant and create a fuse effect. All valves, except the hand vent and auxiliary purge vent, were pressure-operated valves equipped with soft copper seats.

The design of the pentaborane tank system was based on previous designs employed in small thrust chamber test stand operations utilizing this propellant. A helium pressure regulator supplied gas for tank pressurization and purge purposes. In addition to the usual valve arrangement for propellant flow control, a second prevalve was installed between the tank outlet valve and the main flow-control valve. Pentaborane tank venting was accomplished in two ways. Immediately downstream of the main pressure-operated vent valve, the vent line was split into two lines controlled separately by hand valves. One line was terminated in air, the other was terminated in a 55-gallon drum that was partially filled with kerosene. Pressures greater than 30 psig were vented directly to the atmosphere. Lower pressures, encountered during loading and disposal operations were vented to the kerosene drum.

Pentaborane was transferred from the shipping cylinder to the test-stand tank through a filling valve located between the first and second prevalves. In addition, a complete kerosene flush system was connected to the storage system by means of the same filling valve and an auxilliary flush valve. All valves employed in the pentaborane system, with the exception of the hand valves, were pressure-operated and "normally closed". As in the case of chlorine trifluoride, the purge was important as it prevented residual pentaborane from reacting with air and plugging the line downstream of the main flow control valve.

The propellants spill lines were extended from the main flow control valves to a point about 1 foot in height over a special spill test basin. Discharged liquids from these lines impinged within a radius of 2 inches on the test basin surface. The basin (Fig. 3) was fabricated of concrete and has a 2 foot by 2 foot square cross-section and is 6 inches deep. It was designed to provide some degree of confinement for the reacting propellants, and to retain unreacted material and combustion products for safe disposal.

Special contact surfaces required for the test program were placed in the concrete spill basin, as needed. Water was supplied to the basin with a laboratory deionized water line, terminated in a spray nozzle at a point 3 feet above the basin surface. A drain connecting the basin to the main laboratory effluent trench permitted flushing and decontamination of the basin following testing.

INSTRUMENTATION

During the early portion of the Small-Scale Program, test results were observed visually and recorded on color film with three high-speed motion picture cameras. A Fastax camera was focused on the immediate spill contact area and operated at 1000 frames per second; a Traid camera was used to scan the entire test area at 200 frames per second. Selected still photographs of the results were printed from 70 mm film taken by a Hulcher camera, operated over a range of 6 to 20 frames per second, overlooking the test site. Ambient air temperature was measured with thermometers suspended in the general laboratory area, while humidity and wind velocity were monitored and recorded by the Rocketdyne Test Operations Control Center.

Because of unexpected complexities in the interpretation of initial test results, pressure sensing devices and photocells were installed for the greater portion of the program. Two Photocon microphone transducers (Fig. 4), with ranges of approximately 5 psi, were employed to detect overpressure shocks. Sensor No. 1 (M-1) was located 10 feet from the point of contact with the face oriented directly toward the origin. Sensor No. 2 (M-2) was located 15 feet from the origin in a direct line with M-1.

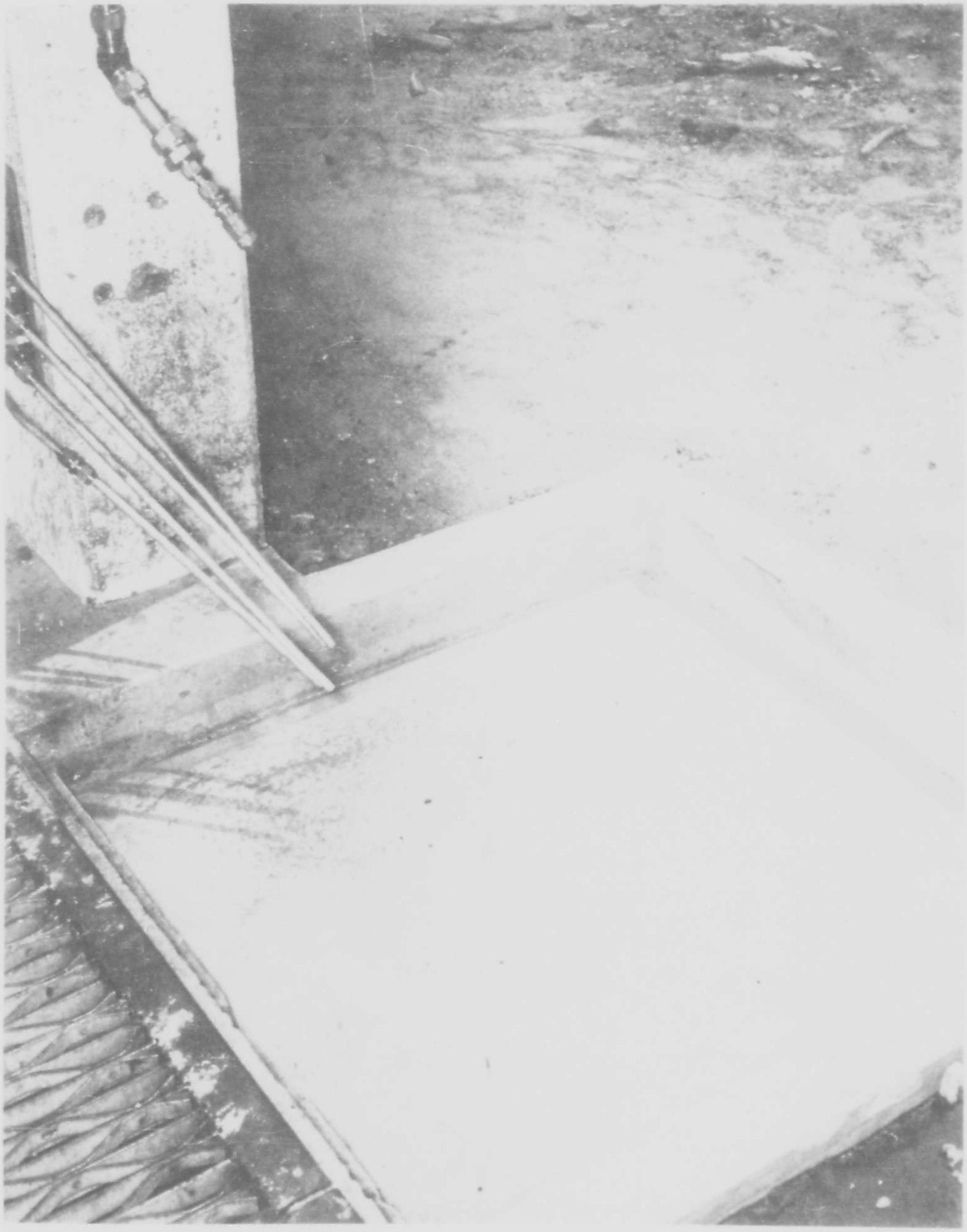

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Figure 3. Concrete Spill Test Basin

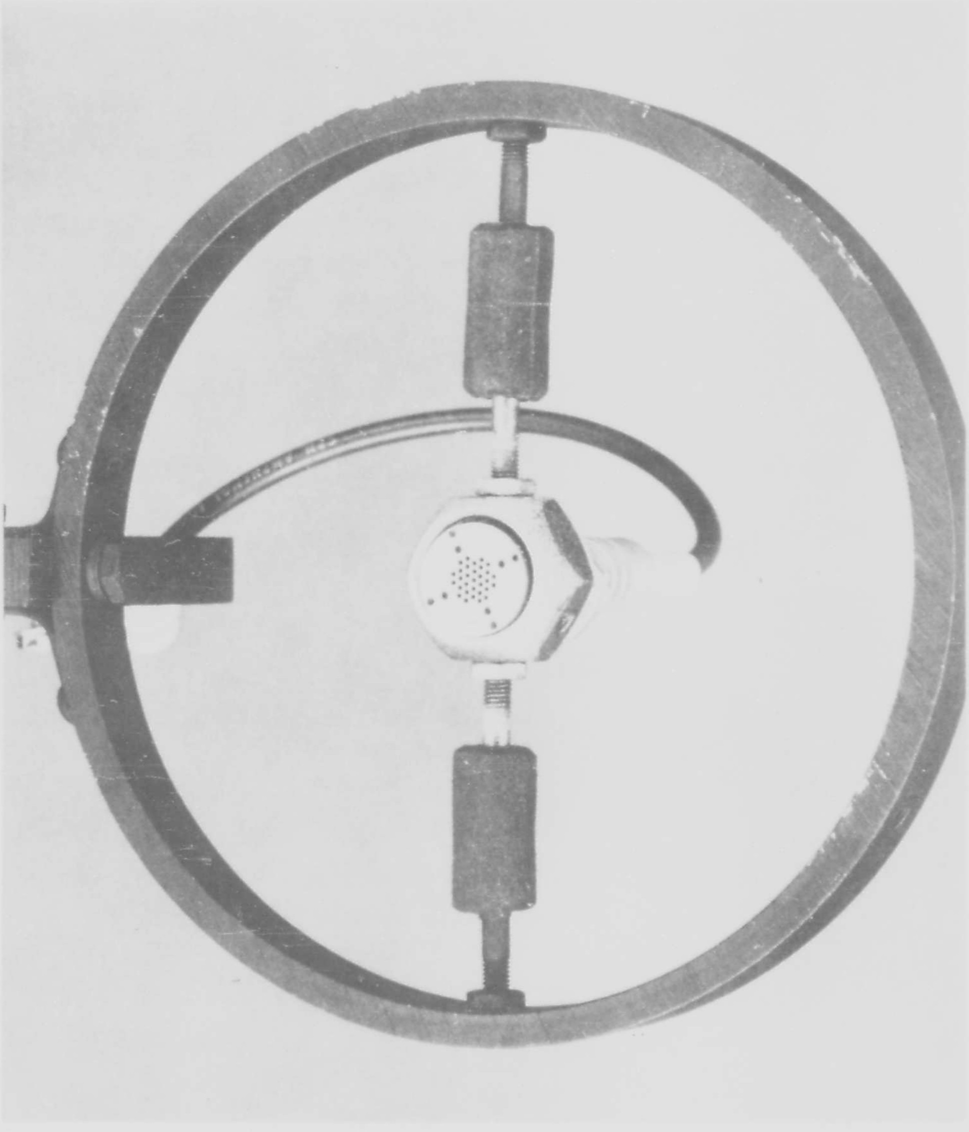


Figure 4. Photocon Microphone Transducer and Mounting Assembly

Both transducers were mounted approximately 1 foot above ground level, i.e., in a plane about 14 to 18 inches above the actual contact surface. A Photocon 505 (lead sulfide) photocell was located about 10 feet from the point of origin.

Ignition or first flame of the reacting propellants was sensed by the photocell, while overpressure shocks were sensed by the microphone transducers. Signals generated by these devices were recorded on magnetic tape with an Ampex FR-107 FM recorder. The sound tape was replayed through a Tektronix 535A oscilloscope; photographs were taken of data of interest with a Polaroid Land Camera attachment to the oscilloscope. In addition, the tape was replayed at slow speed and significant data were rerecorded with a CEC galvanometer oscillograph. Ignition and overpressure data were compared with high-speed Fastax film to establish the sequence of significant events in the test results.

SAFETY PRECAUTIONS

Because of hazards associated with the use of propellants in this program, propellant handling and testing were confined to certain well defined "safe" time periods. These periods were determined by numerous factors. A primary consideration was a minimum air flow of 4 knots; this condition insured continuous removal and diffusion of propellant vapors from the laboratory environs. A second consideration was control of unprotected personnel stationed downstream of the test site. As a result of these limitations, most handling and testing were accomplished in the evening and early morning.

Test schedules were established on the basis of meteorological predictions by the Rocketdyne Test Operations Control Center. Propellant loading commenced with the onset of favorable wind velocity and direction. Continuity of favorable conditions was assured through use of direct telephone communication between the Propellant Engineering Laboratory and the Control Center. Finally, during actual testing, road blocks were established to provide absolute control on personnel movements, and emergency equipment was positioned for rapid and efficient access to the test site.

The laboratory was equipped with a manifold breathing-air system capable of supplying 32 manhours of air to personnel working at maximum exertion. From the manifold, low pressure breathing air was supplied to numerous "quick-disconnect" terminals located at convenient places in and around the laboratory. The test team, consisting of a maximum of five persons was provided with flexible air hose extensions and Scott air masks equipped with two-way communication systems. In addition, three self-contained Scott-Paks and seven small Escape Bottles were available for special situations.

Two workers were required for direct propellant handling operations. These personnel were equipped with air hose extensions capable of a 60-foot radius from the nearest manifold disconnect terminal. For work with pentaborane, hydrazine and nitrogen tetroxide, they were dressed in complete Gra-Lite suits and hoods, rubber boots and Charco Hy-Sol gloves. With chlorine trifluoride, protective clothing was limited to face shields, fire resistant asbestos aprons, and loose-fitting Charco Hy-Sol gloves.

LOADING PROCEDURES

Hydrazine and nitrogen tetroxide were loaded into the respective tank systems by pouring propellants directly from small intermediate storage vessels, through a funnel, into pressure ports at the tops of the tanks. Chlorine trifluoride was transferred by attaching a 200-pound shipping cylinder to the tank system fill valve with 1/4-inch, copper AN tubing. The main cylinder hand valve was opened and propellant was admitted to the test stand system by remote operation of the fill valve. Pentaborane was transferred through a connection between a 125-pound shipping cylinder and the fill valve of the tank system; all operations, with the exception of opening the shipping container hand valve, were controlled remotely. Storage and shipping vessels were removed from the test stand area prior to the start of testing.

TEST PROCEDURES

All test stand valves, except the hand valves noted, were actuated from a control panel located inside the laboratory control center at a distance of approximately 20 feet from the spill basin. After all of the propellants for a test series were loaded, pre-valves were opened and propellants were dropped to the main-flow control valves. All vents were closed and pressurization valves opened; each tank was pressurized from 30 to 50 psig.

Appropriate main-flow control valves were actuated and sequenced manually. The magnetic tape recorder was started approximately 10 seconds prior to the spill; cameras were started 1 second before actuation of the flow-control valves. For simultaneous spills of two propellants, both flow-control valves were actuated together. Lead-lag situations were simulated by actuation of the first flow-control valve 1 second before actuation of the second. In singular spills, flow was maintained for 1 second; in combination spills, flow was continued until some evidence of reaction was detected visually. Tests were terminated by deactivation of the appropriate flow-control valves. In situations requiring purges, pre-valves were deactivated and purges were carried out with the flow-control valves remaining open.

Residual propellants were usually disposed of by reacting them in the spill test basin. Chlorine trifluoride, nitrogen tetroxide and hydrazine tank systems were freed of propellant by purging with gaseous nitrogen. Pentaborane was removed from the system with a kerosene purge, and disposed of by burning in an adjacent pit.

TEST RESULTS

Initial Combined Spill Tests

The initial small-scale hazard classification tests were simultaneous spills of nitrogen tetroxide and hydrazine, hydrazine and pentaborane, and nitrogen tetroxide and pentaborane on a dry concrete surface. Calibrations established that about 0.7 pounds of pentaborane, 1.0 pound of hydrazine, and 1.5 pounds of nitrogen tetroxide were involved in each test employing these particular propellants. All of the combinations resulted in an apparent immediate reaction at the point of contact. Weak explosions were indicative of some shock generation by the nitrogen tetroxide and hydrazine and nitrogen tetroxide and pentaborane combinations; however, hydrazine and pentaborane led to only a fire with no distinguishable shock effect. The latter fire is shown in Fig. 5.

None of the tests in this first series resulted in any damage to the test area other than some general discoloration of the paint. Some trouble was encountered with the pentaborane tank system. During the first test involving pentaborane, there was no post-test purge and deposits of boric oxide were formed in the main-flow control valve. The valve permitted no flow, even in the fully open position. This problem was solved by "blowing" the valve with a high-pressure purge and employing a low-pressure, post-test purge in all subsequent tests.

A second series of tests employed the same propellant combinations with dry asphalt as the spill contact surface. The surface consisted of several large pieces of asphalt fitted together in the concrete spill basin. Oxidizer leads with these combinations allowed some puddling of nitrogen tetroxide or hydrazine prior to the appearance of the fuel. About 2.0 pounds of nitrogen tetroxide and 1.0 pound of hydrazine produced several explosions, but no apparent damage to the asphalt surface. Tests utilizing 0.5 pounds of pentaborane, with either 1.3 pounds of hydrazine or 2.0 pounds of nitrogen tetroxide, yielded very sharp explosions. The large pieces of asphalt surfacing

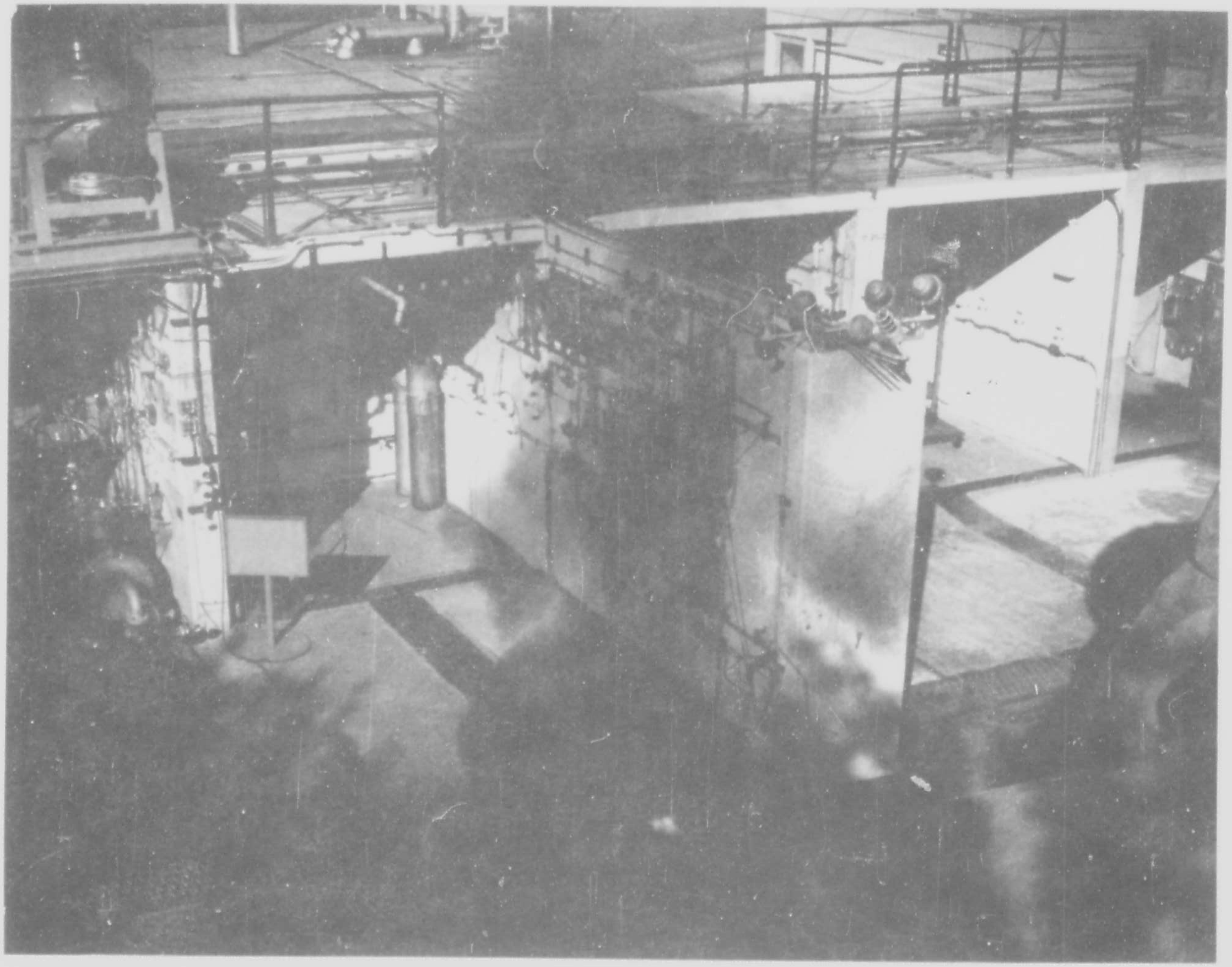


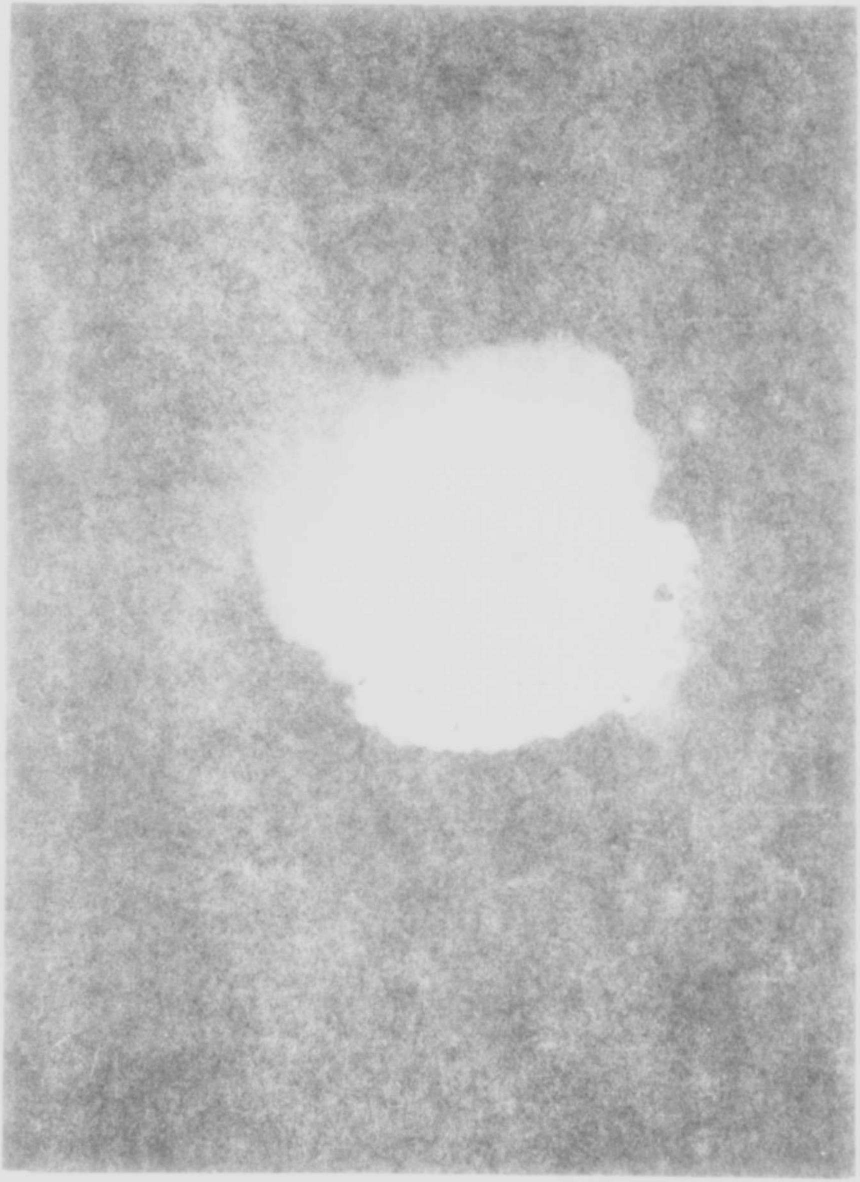
Figure 7. Spill of Nitrogen Tetroxide and Hydrazine on Dirt --1-sec Fuel Lead

were fractured into small pieces that were scattered over a 20-yard radius; one piece of burning asphalt started a small brush fire about 60 feet from the spill basin. These explosions appeared to occur sometime after the initial reaction of the propellants and were audible to personnel at a distance of as much as 0.5 miles from the test site. Figure 6 is a photograph of the hydrazine and pentaborane spill.

In a third series of tests, the spill basin was filled with 1/4 to 1/2-inch of water and the three combinations were evaluated with simultaneous injection of the two propellants into the water. In all cases, reaction was delayed. Nitrogen tetroxide and hydrazine had the shortest delay of the combinations. Audible explosions occured after ignition, but there was no damage to the test area. A louder explosion, which caused some damage to adjacent photofloods, occurred with hydrazine and pentaborane. Nitrogen tetroxide and pentaborane produced, by far, the most severe explosion of the entire test program. Propellants were spilled for two to three seconds before any evidence of reaction. Ignition appeared to trigger an explosion which shook the control center, damaged several exterior lighting fixtures, broke gage faces and a metal relay box, and cracked the concrete spill basin.

Two to three inches of dirt were placed in the concrete spill basin for the fourth series of tests. A 1-second lead of hydrazine in association with nitrogen tetroxide caused a weak explosion and a small fire. A large quantity of oxidizer boiled away without reacting (Fig. 7). Pentaborane led hydrazine and nitrogen tetroxide, respectively, onto the dirt in the next two tests. Both sequences resulted in instantaneous fires. The pentaborane appeared to ignite in ambient air, at 98 F, before coming in contact with the dirt spill surface. None of these tests generated significant shock effects.

In the fifth series of tests, the dirt was thoroughly wetted with water. Simultaneous spills of the three propellant combinations produced slight reaction delays in each case. These delays were not of the same order



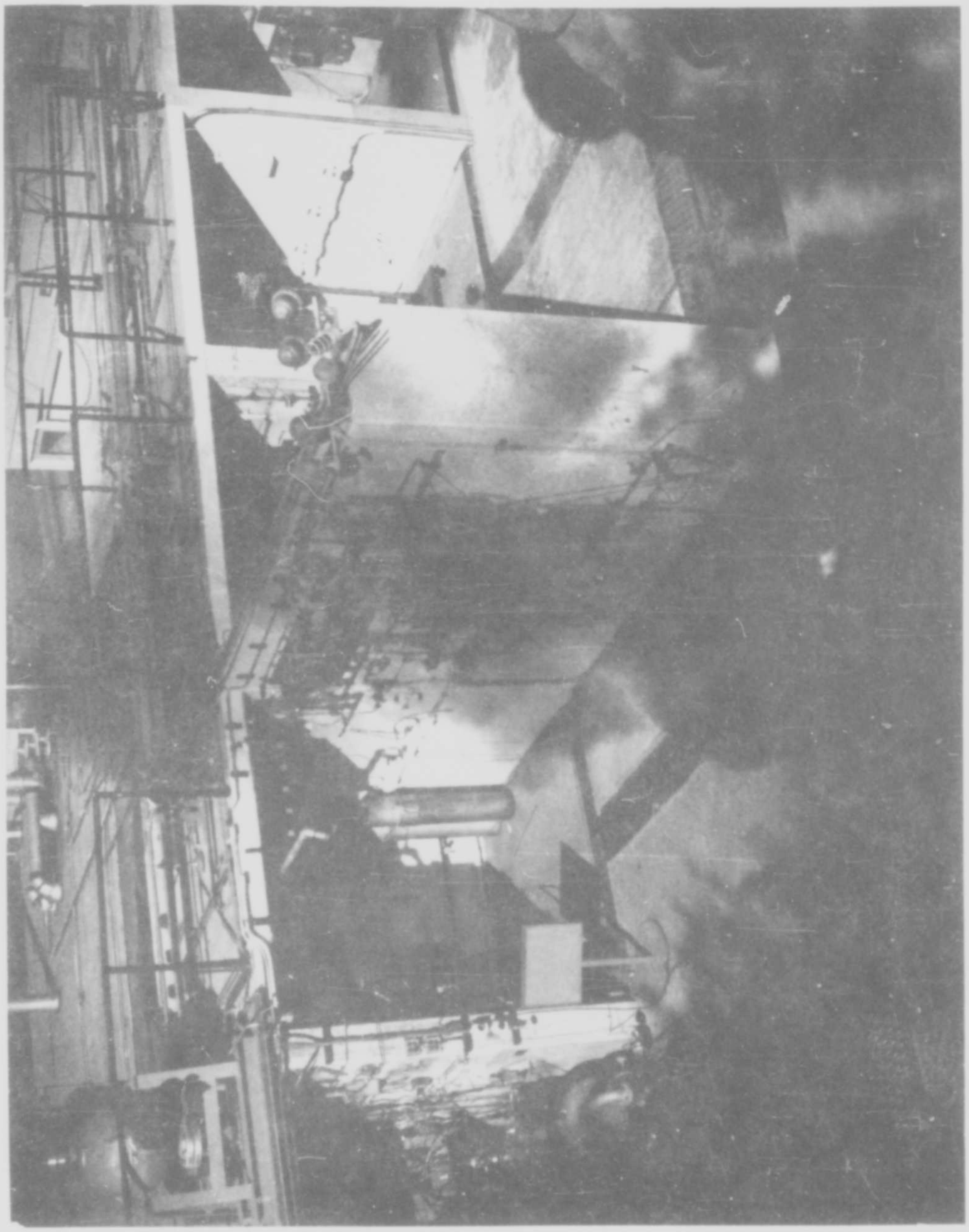


Figure 7. Spill of Nitrogen Tetroxide and Hydrazine on Dirt --1-sec Fuel Lead

as those experienced with water only in the spill basin. It is probable that the dirt absorbed enough of the water to preclude an extended reaction delay. Although pentaborane was ignited in air at the high ambient temperature, the nitrogen tetroxide and pentaborane combination produced a loud explosion and threw dirt around the surrounding test area. Motion pictures gave further evidence of the phenomena associated with pentaborane combination spills. Figure 8 is a photograph of a hydrazine and pentaborane fire on wet dirt. In all instances, similar large fires occurred; however, streamers of liquid pentaborane were ejected from the combustion zone and burned in the surrounding air. These observations were suggestive of delays in mixing and reaction of pentaborane with nitrogen tetroxide or hydrazine and simultaneous, rapid reaction in air.

Hydrazine was spilled with pentaborane on a wood surface insert. This test was intended as a hydrazine lead; however, because of a leak, the fuel actually led. Ignition of the pentaborane in air resulted in immediate reaction and subsequent smooth burning at the contact surface. A 1-second nitrogen tetroxide lead, in conjunction with hydrazine, was also attempted on the wood insert. Several explosions were detected. In both tests, the wood continued to burn after all of the spilled propellant had been exhausted.

Singular Spill Tests

During the period of the initial combined spills, hydrazine was spilled singly on dry concrete, dry asphalt, dry rust, dirt and wet concrete. Simple spills on asphalt, concrete and rust resulted in the immediate formation of a vapor cloud over the contact surface; there was no evidence of appreciable monopropellant decomposition. Dirt absorbed hydrazine to some extent and delayed formation of a vapor cloud for several seconds. Vapors were also noted over the wetted concrete surface; however, the cloud was very diffuse and persisted only until the spill was

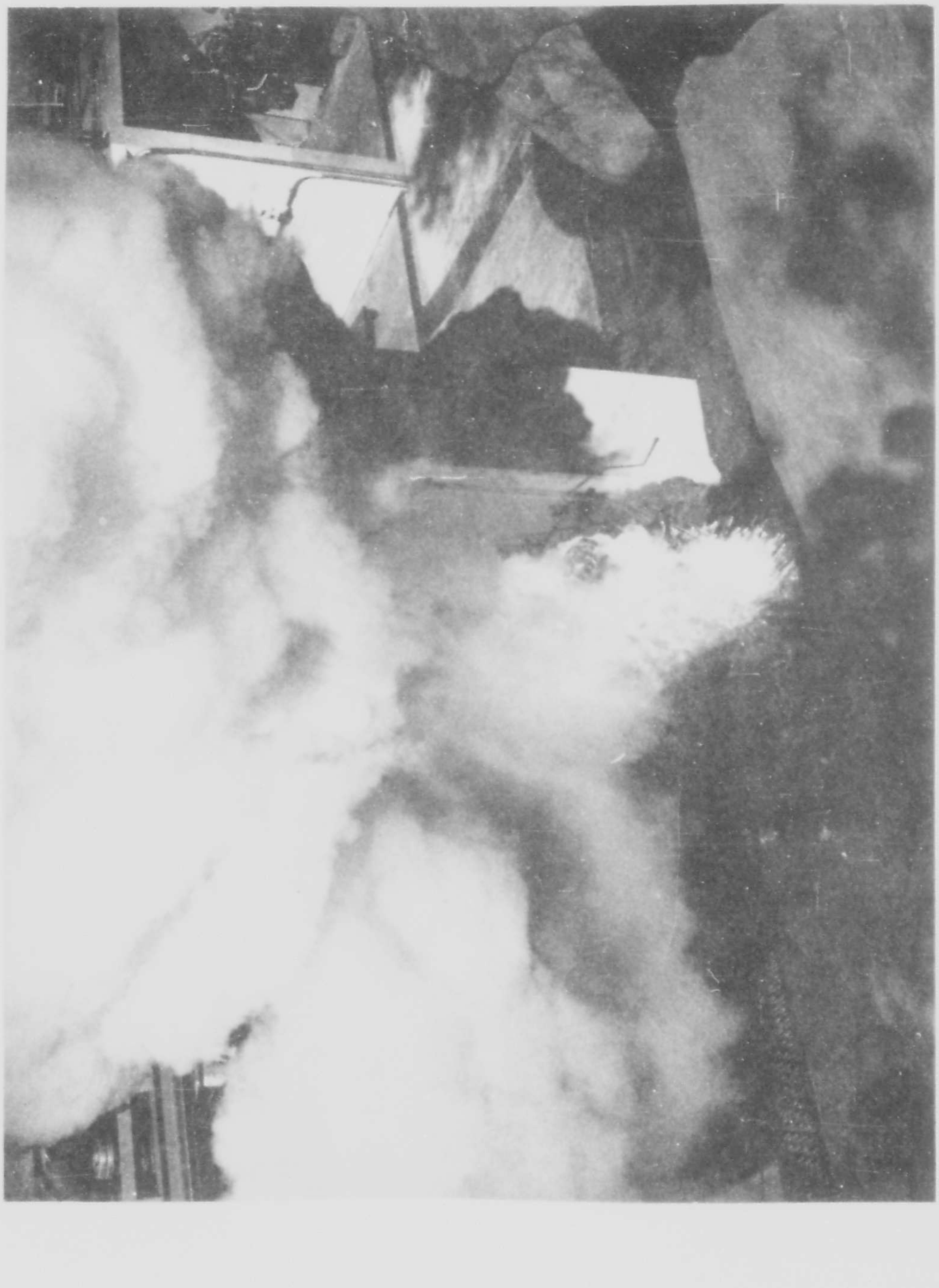


Figure 8. Simultaneous Spill of Hydrazine and Pentaborane on Wet Dirt

terminated. Finally, hydrazine was spilled onto a painted wood surface that had been saturated previously with nitrogen tetroxide. Instantaneous ignition and smooth burning accompanied this test.

Several single tests with nitrogen tetroxide were made during the initial combination spills. The oxidizer readily boiled off from dry asphalt, dry concrete and painted wood surfaces without damage to the material. A spill into water resulted in extremely rapid evaporation. Nitrogen tetroxide was also spilled onto a rusted surface saturated with hydrazine; it ignited instantaneously and burned until the hydrazine was consumed.

Single spills of pentaborane were made on dry concrete (at 85 F and 18 percent relative humidity, and at 98 F and 17 percent relative humidity), and on dry asphalt (at 83 F and 18 percent relative humidity). At the lower temperatures, pentaborane ignited with air upon contact with the spill basin surface. At 98 F, ignition occurred upon the appearance of fuel at the end of the propellant system dump line.

Initial Chlorine Trifluoride Tests

The chlorine trifluoride tank system was completed some time after the beginning of tests with the other propellants. The tank system was degreased, dried and passivated prior to operations with chlorine trifluoride. Passivation consisted of a continuous gaseous fluorine purge for several minutes followed by retention of 200 psig fluorine gas pressure, in the entire system,for one hour.

Hydrazine spilled simultaneously with chlorine trifluoride, on concrete, resulted in immediate ignition, smooth combustion and no audible explosions. Nitrogen tetroxide was spilled into the basin from which about 1 pound of chlorine trifluoride was evaporating slowly. No reaction occurred and the two oxidizers continued to boil off until all of the liquid was depleted. A single spill of chlorine trifluoride on concrete had no gross effect on the surface; however, it did result in some erosion of exposed cracks. Similar tests were conducted on wet dirt and dry sandstone; both were accompanied by weak explosions as propellants streams and droplets contacted these surfaces.

As a result of premature depletion of chlorine trifluoride, it became convenient to spill larger quantities of nitrogen tetroxide and hydrazine than had previously been planned. About 11 pounds of oxidizer and 8 pounds of fuel were spilled into the dry concrete basin. After ignition, several strong explosions occurred. With continued burning, the explosions appeared to diminish in frequency and strength. There was no damage to the spill basin or surrounding area.

Results of initial combined hazard classification tests are summarized in Table 1. Table 2 is a summary of observations made during the singular spill tests.

Pentaborane System Failure

The standard pentaborane operating procedure included provision for scrubbing low-pressure vent gases, during loading, in a 55-gallon drum filled with approximately 40 gallons of kerosene. Immediately prior to the pentaborane system failure, difficulty was encountered in determining fuel liquid level in the test stand tank system; the sight gage did not indicate liquid until the tank was filled completely. It was assumed that either (1) the bottom connection of the sight gage was plugged with boric oxide or (2) the inside surface of the sight gage was coated with boric oxide. In either case, the boric oxide was formed by reaction of residual pentaborane with air or moisture that leaked into the tank system. As a consequence it became evident that some pentaborane had overflowed through the low-pressure vent and into the kerosene scrubber during loading.

TABLE 1

RESULTS OF COMBINATION PROPELLANT SPIL

Test No.	Propellants	Approximate Quantities, (lb)	Sequence	Surface	Temperature, F
1	NTO/HZ	1.5/1.0	Simultaneous	Dry concrete	85
2	HZ/PB	1.0/0.67	Simultaneous	Dry concrete	85
3	NTO/PB	1.5/0	Simultaneous	Dry concrete	85
4	NTO/PB	1.5/0	Simultaneous	Dry concrete	84
5	NTO/PB	1.5/0.67	Simultaneous	Dry concrete	84
6	NTO/HZ	2.0/1.0	NTO Lead	Asphalt	84
7	HZ/PB	1.33/0.67	HZ Lead	Asphalt	84
8	NTO/PB	2.0/0.67	NTO Lead	Asphalt	80
9	NTO/HZ	1.5/1.0	Simultaneous	Water-covered concrete	80
10	HZ/PB	1.0/0.67	Simultaneous	Water-covered concrete	76
11	NTO/PB	1.5/0.67	Simultaneous	Water-covered concrete	76
12	NTO/HZ	1.5/1.33	HZ Lead	Dry dirt	100
13	HZ/PB	1.00/0.90	PB Lead	Dry dirt	98
14	NTO/PB	1.50/0.90	PB Lead	Dry dirt	98
15	NTO/HZ	1.50/1.0	Simultaneous	Wet dirt	98
16	HZ/PB	1.00/0.67	Simultaneous	Wet dirt	98

TABLE 1

OMBINATION PROPELLANT SPILL TESTS

	Temperature, F	Relative Humidity, percent	Results
e	85	18	Several small overpressures
e	85	18	Instantaneous burning
e	85	18	PB line plugged,NTO boiled off
e	84	18	PB line plugged, NTO boiled off
e	84	18	Several small overpressures
	84	18	Several small overpressures
	84	18	Large overpressure, scattering asphalt
	80	18	Large overpressure, scattering asphalt
ed	80	18	Slight ignition delay, several small overpressures
ed	76	18	Slight ignition delay, large overpressure
ed	76	18	Large ignition delay, very large overpressure
	100	17	Some small overpressure
	98	17	PB ignited in air, small overpressure
	98	17	PB ignited in air, small overpressure
	98	17	Small overpressures
	98	17	PB ignited in air, small overpressure

Test No.	Propellants	Approximate Quantities, (lb)	Sequence	Surface
17	NTO/PB	1.50/0.07	Simultaneous	Wet dirt
18	HZ/PB	1.33/0.07	HZ Lead	Dry wood
19	NTO/HZ	2.0/1.0	NTO Lead	Dry wood
20	CTF/HZ	1.8/1.0	Simultaneous	Dry concrete
21	CTF/NTO	1.8/1.5	Simultaneous	Dry concrete
22	NTO/HZ	11/8	Simultaneous	Dry concrete
23	NTO/HZ	1.5/1.0	Simultaneous	Dry concrete
24	NTO/HZ	2.0/1.0	NTO Lead	Dry concrete
25	NTO/HZ	1.5/1.0	HZ Lead	Dry concrete
26	NTO/HZ	1.5/1.0	Simultaneous	Water-covered concrete

1

TABLE 1
(Continued)

Surface	Temperature, F	Relative Humidity, percent	Results
Wet dirt	98	17	PB ignited in air, large overpressure scattered dirt
Dry wood	98	17	PB leaked prior to HZ valve opening, fire
Dry wood	98	17	Several small overpressures
Dry concrete	70	40	Instantaneous ignition, smooth burning
Dry concrete	60	44	Boiloff of both propellants
Dry concrete	60	44	Several small overpressures
Dry concrete	64	74	Several small overpressures
Dry concrete	64	73	Several small overpressures
Dry concrete	64	73	Several small overpressures
Water-covered concrete	64	72	Small overpressure, after slight ignition delay

TABLE 2

RESULTS OF SINGLE PROPELLANT SPILL TESTS (1-18)

Test	Propellant	Surface	Temperature, F	Relative Humidity, percent	Results
1	Hydrazine	Dry asphalt	98	18	Rapid formation of dense vapors over surface
2	Hydrazine	Dry concrete	98	18	Same as 1
3	Hydrazine	Dirt	98	18	Slow formation of dense vapors over surface
4	Hydrazine	Water	98	18	Light vapors over surface
5	Hydrazine	Dry rust	98	18	Rapid formation of dense vapors over surface
6	Hydrazine	Wood, saturated with NTO	98	18	Instantaneous flame
7	Nitrogen Tetroxide	Dry asphalt	98	18	Rapid boil-off, no surface damage
8	Nitrogen Tetroxide	Dry concrete	98	18	Rapid boil-off, no surface damage
9	Nitrogen Tetroxide	Dirt	98	18	Same as 8
10	Nitrogen Tetroxide	Dry painted wood surface	98	18	Same as 8

TABLE 2
(Continued)

Test	Propellant	Surface	Temperature, F	Relative Humidity, percent	Results
11	Nitrogen Tetroxide	Water	98	18	Very rapid boil-off
12	Nitrogen Tetroxide	Rust, saturated with hydrazine	98	18	Instantaneous flame
13	Pentaborane	Dry concrete	85	18	Instant ignition on surface
14	Pentaborane	Dry asphalt	83	18	Instant ignition on surface
15	Pentaborane	Dry concrete	98	17	Instant ignition in air
16	Chlorine Trifluoride	Dry concrete	70	80	Rapid boil-off of liquid, no damage to concrete surface
17	Chlorine Trifluoride	Wet Dirt	70	80	Several small pops, no damage
18	Chlorine Trifluoride	Sandstone	70	80	Several small pops, no damage

As one of the operating technicians was removing the low-pressure vent line from the kerosene drum, the content of the drum exploded and sprayed burning kerosene over the test area. The sequence of events that followed the overfilling of the fuel tank system, resulting in the kerosene scrubber explosion, was believed to have been as follows:

1. A quantity of pentaborane overflowed into the kerosene drum at a rate which prevented thorough mixing and the formation of a solution. Some of the pentaborane floated and formed a thin film on the surface of the kerosene.
2. Pentaborane vaporized in the ullage space of the kerosene drum. The resultant gas mixture was not spontaneously flammable, but fell within the explosive limits for air-pentaborane mixtures.
3. When the dip-leg section of the low-pressure vent line was removed from the kerosene, a drop of residual liquid pentaborane ignited in air. In turn, the mixture in the ullage space was ignited and the overpressure from the explosion ruptured the drum. Heat and burning solid particles, generated by the reaction, were sufficient to ignite the kerosene as it was ejected from the damaged drum.

The two technicians in the loading team suffered extensive burns through their protective clothing. A major portion of the pentaborane tank system was destroyed; the other propellant tank systems sustained severe fire damage. In addition, the explosion and fire resulted in failure of the pentaborane tank safety head. Leakage of fuel vapors through the relief device ensued. Vapors ignited with air at the safety head outlet and a small secondary fire persisted for several minutes, but boric oxide deposits eventually sealed the relief port. It was found to be impossible to drain the pentaborane tank of its contents, because associated valves and control wiring had been destroyed or badly damaged (Fig. 9). It was necessary to pierce the tank by rifle fire to dispose of residual propellant and remove the hazard of fires and toxic vapors.

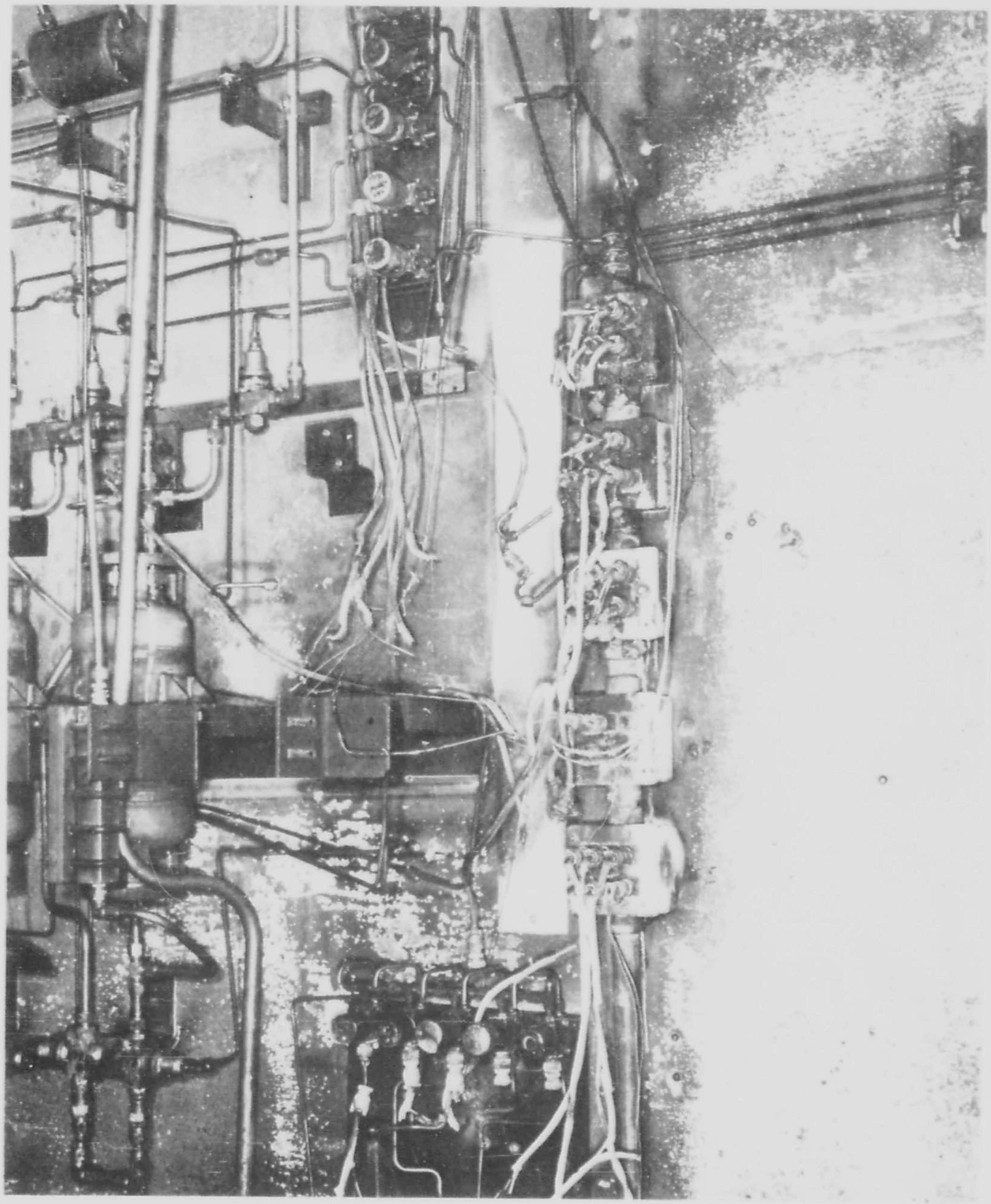


Figure 9. Damage to Valves and Control Wiring Following Pentaborane System Failure

The test area was decontaminated by spray washing with a water solution of ammonia (3 percent) and detergent (1 percent). The entire pentaborane system was dismantled and placed in a large vat of decontamination solution. It proved possible to salvage many of the fuel system valves by careful disassembly and decontamination of the individual components.

System Reconstruction and Program Analysis

Because of the severe damage sustained by the entire hazard classification test stand (Fig. 10), all four propellant tank systems were dismantled, cleaned, serviced and remounted. During reconstruction, the pentaborane tank system was redesigned to prevent recurrence of the above failure and explosion. The vent system, which had consisted of one remotely operated valve and two hand valves, was revised to be operated remotely. The kerosene scrubber was moved to the opposite side of the reinforced concrete mounting wall, to be divorced from the immediate vicinity of loading operations. Finally, a low-pressure helium purge system was provided for the ullage space of the scrubber drum.

Redesign of the pentaborane system permitted test spills to be carried out without disconnecting the low-pressure tank vent and removing the scrubber drum. In turn, this enabled the operating personnel to flush the entire system with kerosene and helium prior to disconnecting any lines that could have come in contact with the propellant. With this revision in the fill and decontamination procedures, periods in which personnel were required to attend the operation were reduced to a minimum.

During the reconstruction period, the over-all test program and its objectives were subjected to critical analysis. It was concluded that visual observation and motion picture documentation were valuable aids in the evaluation of tank failure and leakage hazards. However, more quantitative measurements were necessary to establish an adequate basis for classification, comparison and interpretation of results. Accordingly, it was decided to install pressure and light sensing equipment. Two

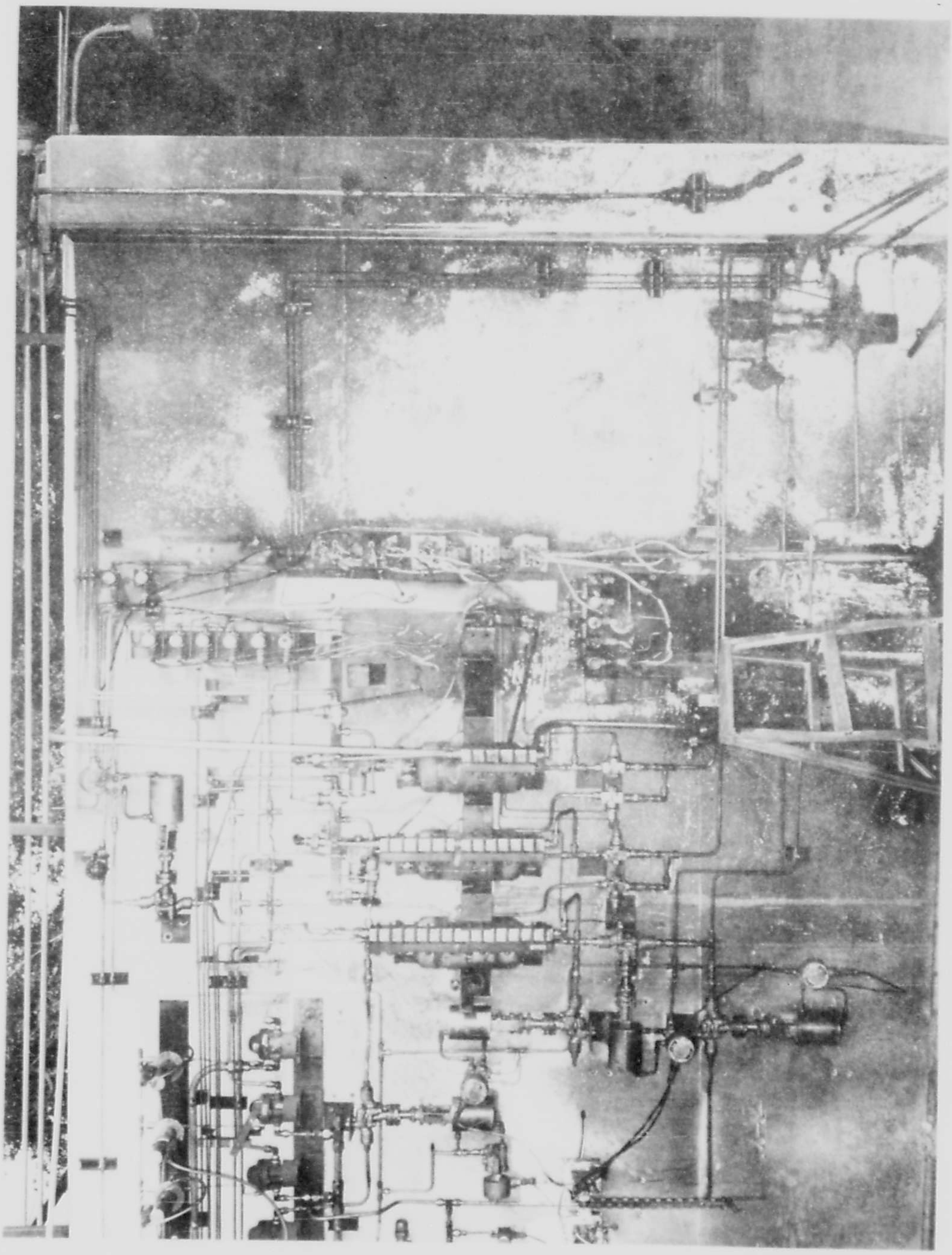


Figure 10. Hazard Classification Test Stand Following Pentaborane System Failure

microphone pressure transducers and a photocell were added to the test stand in the manner previously described. With these devices, in conjunction with continuing film instrumentation, it was possible to provide an adequate quantitative description of propellant reactions and related blast phenomena.

Chlorine Trifluoride and Hydrazine

Chlorine trifluoride was spilled with hydrazine on dry concrete; in each of the three sequence variations, ignition occurred upon contact of the fuel and oxidizer. With simultaneous arrival, four distinct overpressure shocks were detected at each of the microphone transducer stations. The largest overpressure, ca. 0.171 psi (Fig. 11), was detected at M-1 near the end of the actual propellant flows. A 1-second lead of hydrazine produced comparable effects; the peak overpressure was 0.230 psi (Fig. 12). In both cases, overpressure amplitude at M-2 was 50- to 60-percent of that at M-1, on the average. No overpressure shock was detected for a spill on dry concrete with an oxidizer lead.

A layer of dirt, 2 inches in depth, was placed in the spill basin and spills of this combination were continued. Both a simultaneous spill and a hydrazine lead test exhibited immediate ignition, smooth burning and very slight overpressure effects at M-1. Reaction with no measurable overpressure was observed with a chlorine trifluoride lead.

The dirt layer was removed and replaced with 2 inches of water. The simultaneous spill ignited and produced a series of overpressure shocks which reached a peak amplitude of 0.490 psi (Fig. 13). A lead of hydrazine generated several minor overpressure disturbances over a period of several hundred milliseconds. Maximum overpressure of 0.126 psi occurred about midway through the propellant flow interval (Fig. 14). Overpressures as high as 0.178 psi (Fig. 15) were observed near the end of the test with a chlorine trifluoride lead. In the latter test, the frequency of overpressure shocks was higher than for the simultaneous spill and hydrazine lead test.

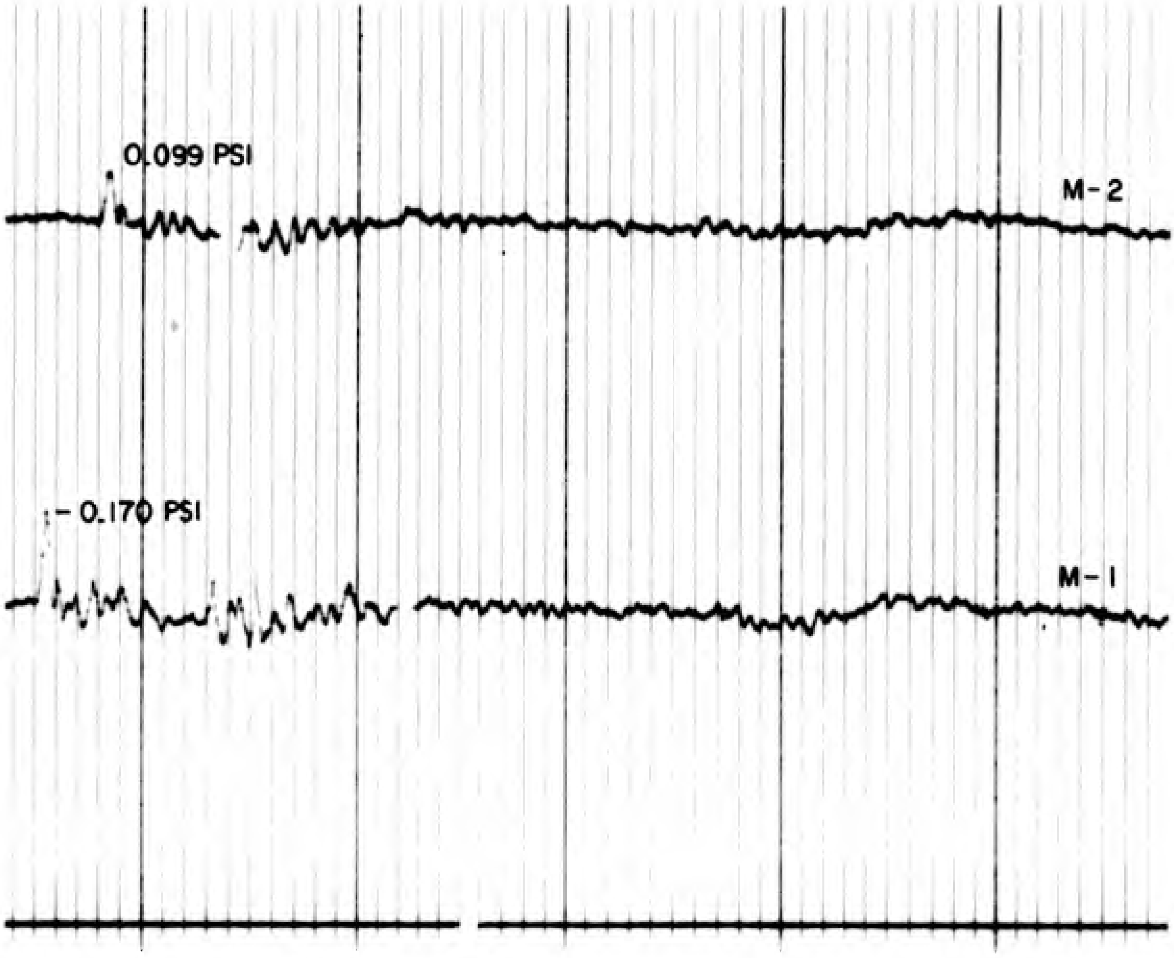


Figure 11. Overpressures from Simultaneous Spill of Chloride Trifluoride and Hydrazine on Concrete

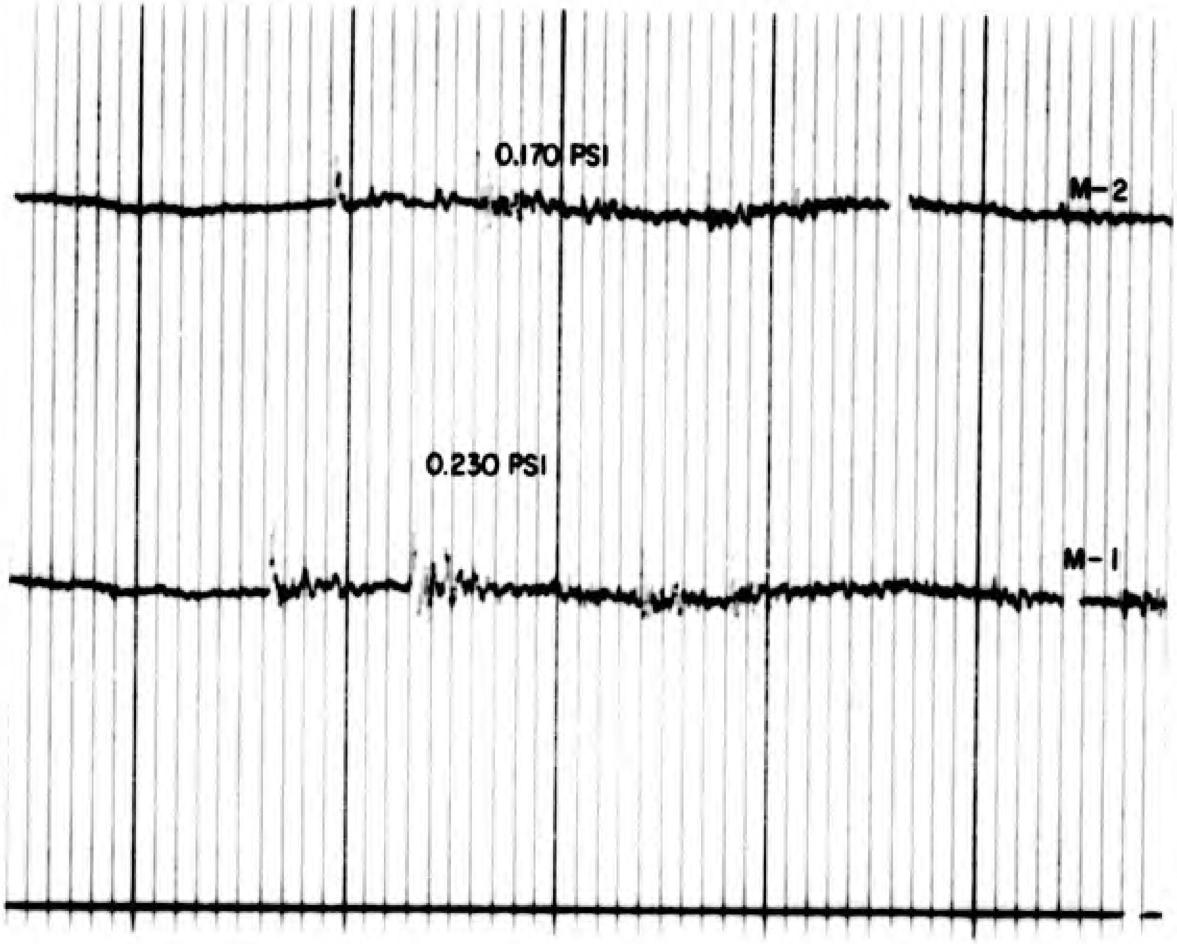


Figure 12. Overpressures from Hydrazine Lead of Chlorine Trifluoride on Concrete

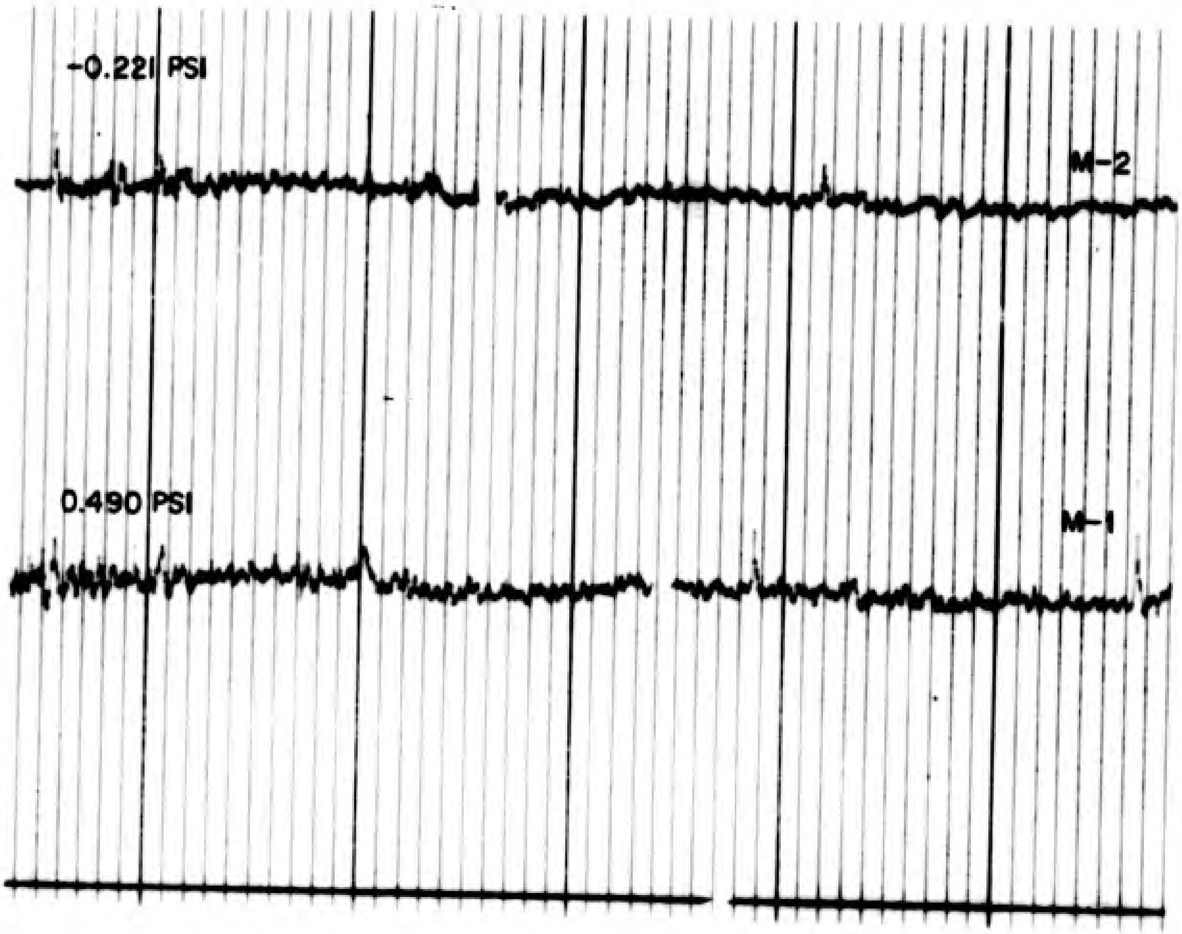


Figure 13. Overpressures from Simultaneous Spillage of Chlorine Trifluoride and Hydrazine on Water

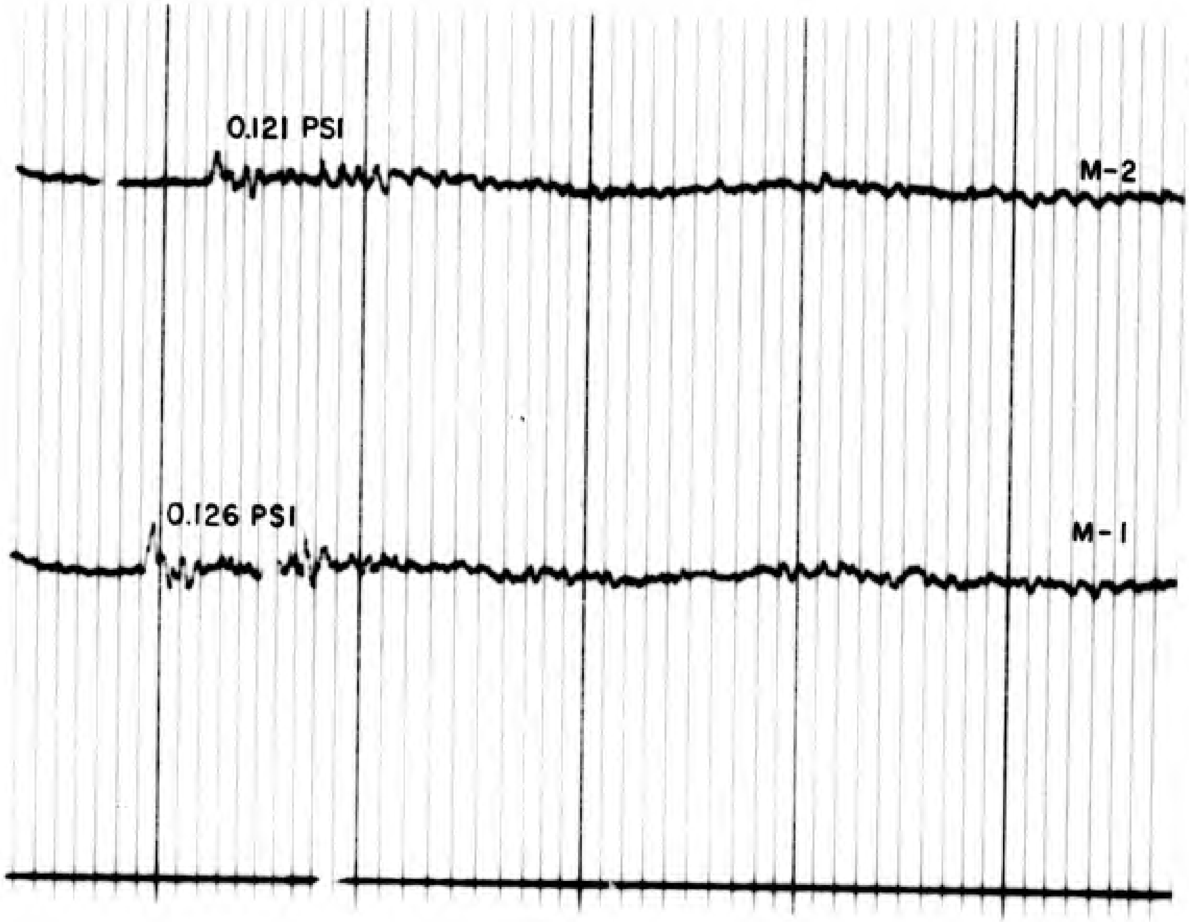


Figure 14. Overpressures from Hydrazine Lead of Chlorine Trifluoride on Water

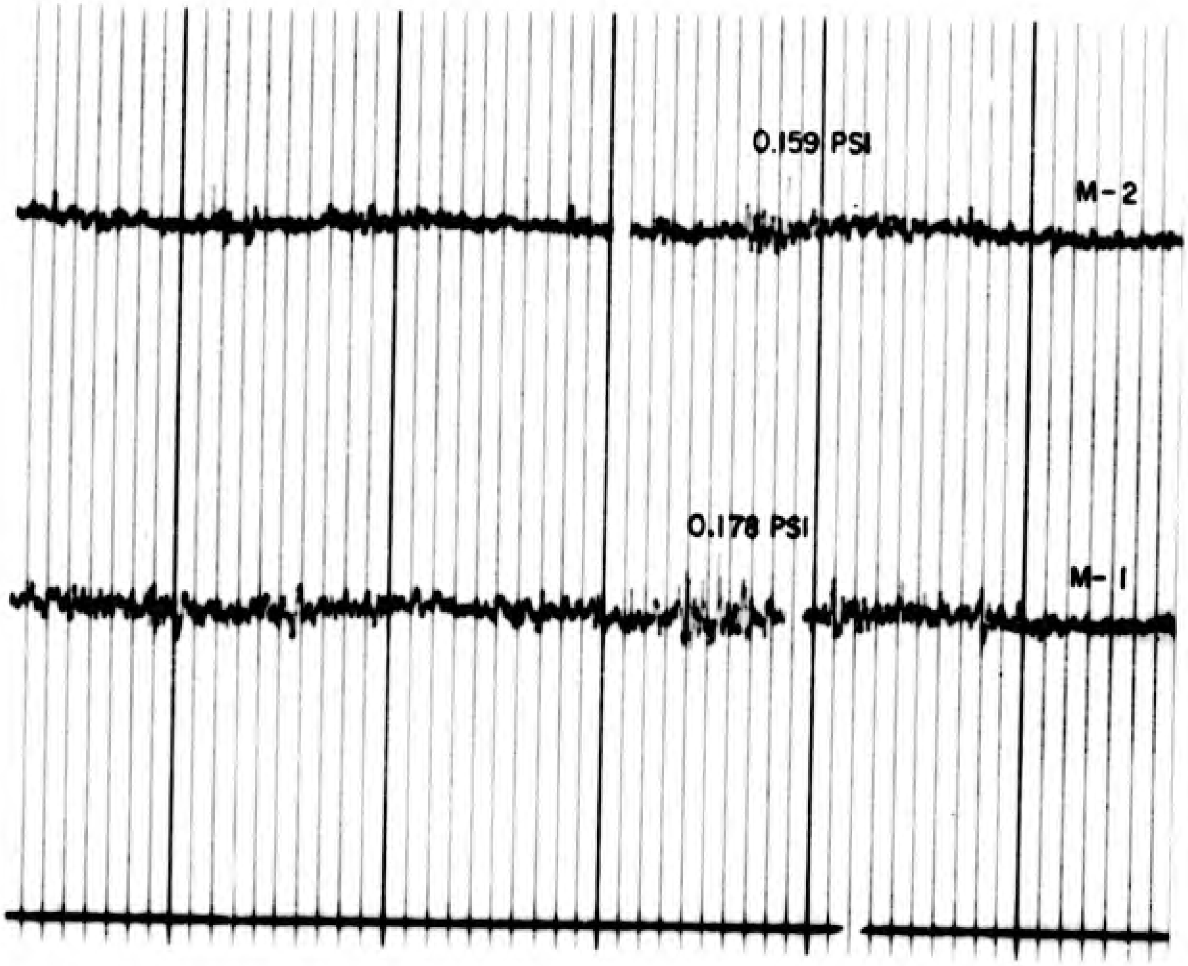


Figure 15. Overpressures from Chlorine Trifluoride Lead with Hydrazine on Water

A simultaneous spill of chlorine trifluoride and hydrazine on asphalt resulted in several minor overpressure shocks; the largest was 0.141 psi. A test with a 1-second hydrazine lead generated only one measurable overpressure, while the subsequent test with an oxidizer lead produced only trace overpressures. In all sequences, chlorine trifluoride appeared to react with the asphalt and caused disintegration and burning at the surface.

In all tests with the chlorine trifluoride/hydrazine propellant combination, the photocell employed to detect reaction failed to function properly. Thus, it was not possible to identify the time sequence of initial reaction and overpressure shocks. However, photographic records indicate that the overpressure shocks were the result of reactions occurring several feet above the spill surface. Further, these reactions were characterized by bright flashes in the product gas cloud above the spill basin, starting a few milliseconds after ignition.

Chlorine Trifluoride and Nitrogen Tetroxide

A combined spill of the two oxidizers failed to exhibit any reaction on dry concrete. Both propellants were depleted by boil-off a few minutes after spilled. The three lead sequences showed no differences whatsoever. The combination was spilled simultaneously on water, also. There was no visible or detectable reaction; even the characteristic "crackling" of the chlorine trifluoride-water reaction was not evidenced. With these tests, it was concluded that no reaction of any consequence would be observed when mixing these propellants. Therefore, further testing of this combination was cancelled.

Chlorine Trifluoride and Pentaborane

This combination was spilled first on a dry concrete surface. Simultaneous spillage and an oxidizer lead on this surface resulted in instantaneous ignition, smooth burning, and no measurable overpressures. A one-second lead of pentaborane produced three, distinct, minor overpressure shocks. However, the first peak was the result of pentaborane ignition with air at the concrete surface, prior to the appearance of chlorine trifluoride (Fig. 16). The reaction of pentaborane at the spill contact surface was attributed, in part, to the fact that the surface was still warm from the preceding test.

A simultaneous spill of chlorine trifluoride and pentaborane and a fuel lead on dirt resulted in immediate ignition, smooth burning, and no evidence of overpressure. Several small overpressure peaks, of which only three were measurable, were observed during a combined spill with a one-second oxidizer lead.

Similar results were recorded when the dirt was replaced by an asphalt surface. No overpressure shocks were encountered following a simultaneous spill and a test with a pentaborane lead. Overpressures as high as 0.147 psi (Fig. 17) resulted from a chlorine trifluoride lead. As noted before, the oxidizer reacted with asphalt to produce some deterioration of the surface.

All three sequences employing this combination, on water, resulted in a series of overpressure shocks during the tests. Maximum overpressure amplitudes of 0.114, 0.048 and 0.106 psi were recorded for the simultaneous spill, pentaborane lead and chlorine trifluoride lead, respectively. In each of these tests, the propellants appeared to burn on the surface of the water until pentaborane was depleted.

The photocell failed again to operate properly during this series of tests. As before, accurate over-all sequencing of the data was not possible. The photographic evidence for reactions taking place in the product cloud above the spill basin was repeated.

Nitrogen Tetroxide and Hydrazine

Although several uninstrumented spills of nitrogen tetroxide and hydrazine had been made previously, it was decided that this series should be repeated for the purpose of making measurements of overpressure amplitudes.

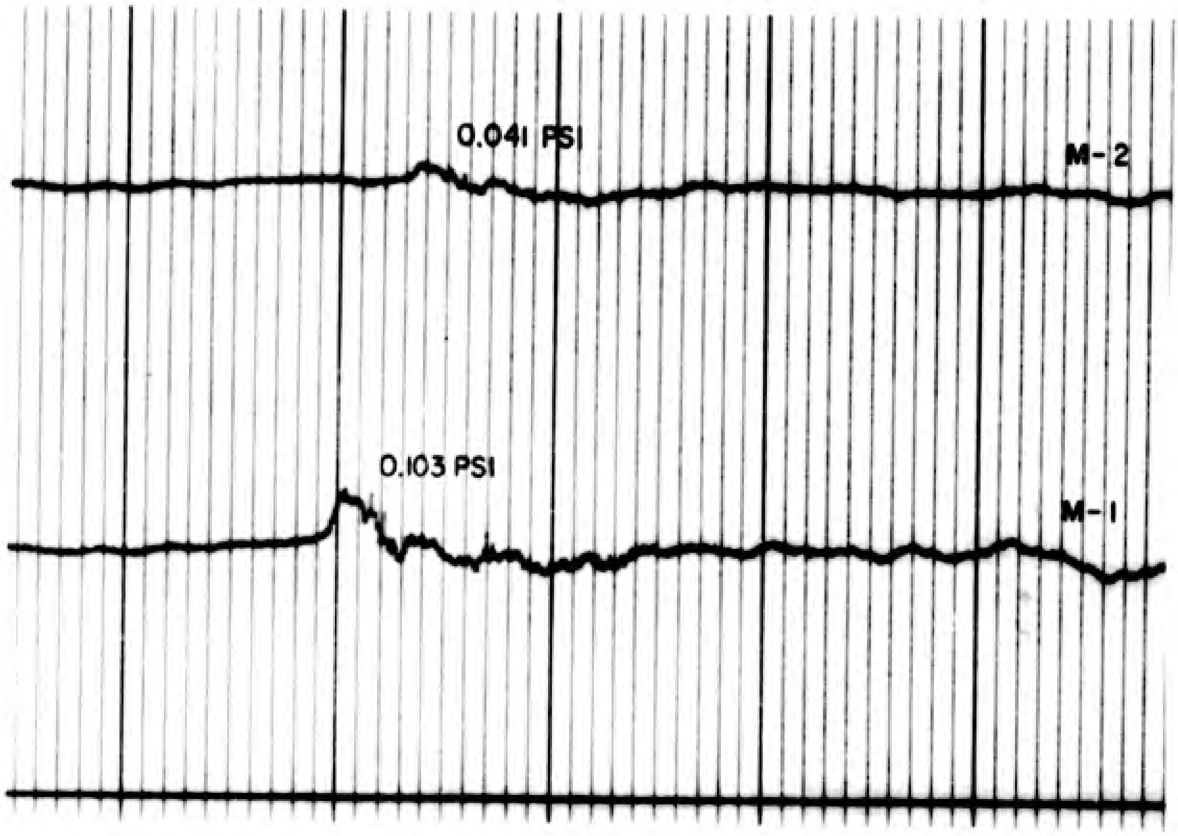


Figure 16. Overpressure Resulting from Pyrophoric Ignition of Pentaborane

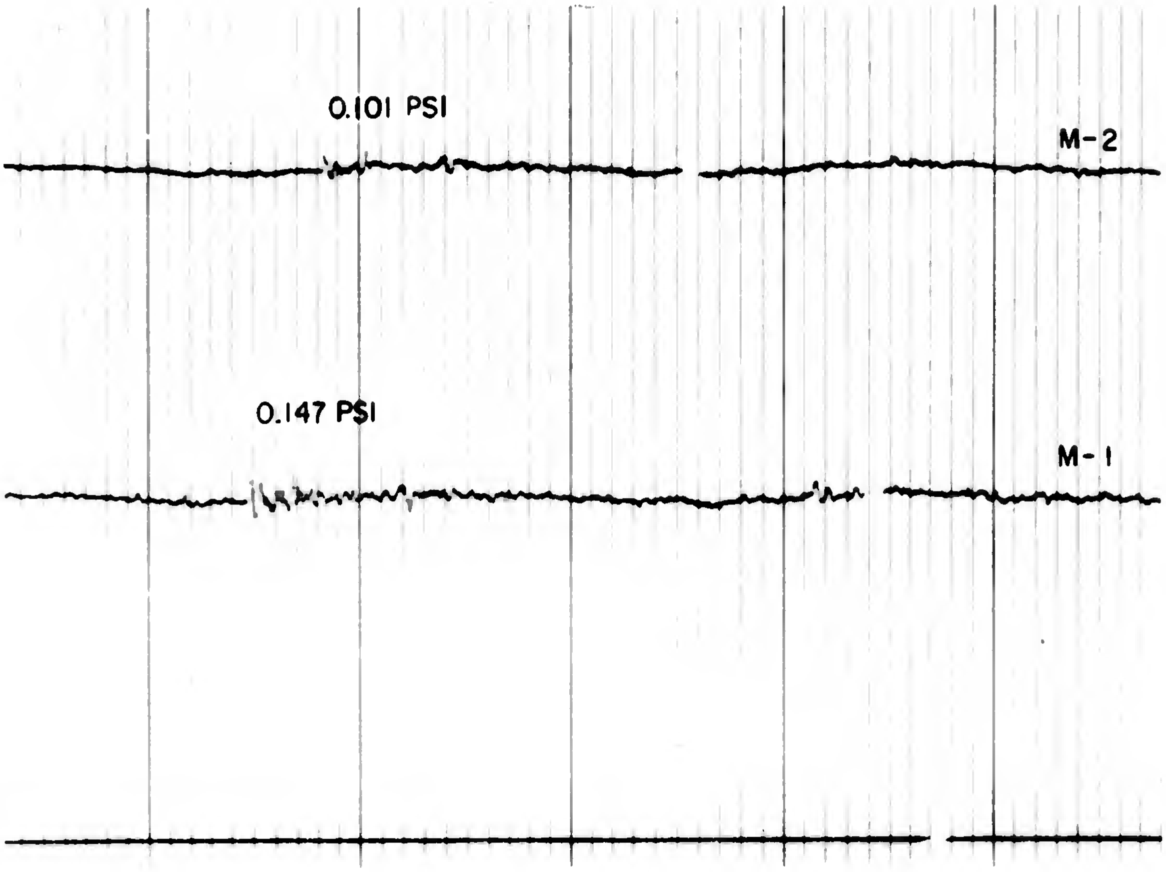


Figure 17. Overpressure Resulting from Chlorine Trifluoride Lead with Pentaborane on Asphalt

Combination spills were made first on dry concrete. Approximately 8.75 milliseconds after the photocell recorded ignition in a simultaneous spill, an overpressure of 0.454 psi was detected at M-1 (Fig. 18). The speed of sound under the ambient test conditions was 1127 feet per second, corresponding to an interval of 8.88 milliseconds for sound to traverse the 10 feet between the origin and M-1. A shock strength of 0.191 psi was recorded at M-2, 4.45 milliseconds later. This time delay was in good agreement with the speed of sound computation, also. Two additional shocks of 0.182 and 0.819 psi were detected by M-1 at 0.113 and 0.430 seconds after ignition (photocell), respectively.

A hydrazine lead on the concrete surface generated a series of overpressure shocks in the time interval between 0.075 and 0.536 seconds after ignition. Amplitudes as great as 2.000 psi were attained at two points in this test. Several weak shocks were recorded in a spill of the combination with an oxidizer lead. A trace overpressure was detected at 9.25 milliseconds after photocell activation; shock amplitudes of 0.910 psi were encountered at 38 and 56 milliseconds, successively (Fig. 19), and a peak of 1.00 psi was recorded 217 milliseconds after ignition.

The same spill sequences were repeated on an asphalt surface. No pressure effects were recorded during a test beginning with a simultaneous spill of nitrogen tetroxide and hydrazine. A fuel lead resulted in a series of overpressure shocks, which reached an amplitude of 1.545 psi several hundred milliseconds after ignition. A combined spill with a nitrogen tetroxide lead produced immediate ignition and a series of overpressure shocks (Fig. 20); these were concluded approximately 60 milliseconds after initial appearance.

An overpressure was recorded 38 milliseconds after the ignition of a simultaneous spill on dirt. A few hundred milliseconds later, a series of shocks that reached 1.455 psi were observed. Five overpressure shocks, with amplitudes as high as 1.910 psi (Fig. 21), were recorded after a hydrazine lead on dirt. A nitrogen tetroxide lead on dirt generated a series of shocks that continued until 0.825 seconds after ignition. A maximum overpressure of 1.728 psi occurred 0.533 seconds after ignition.

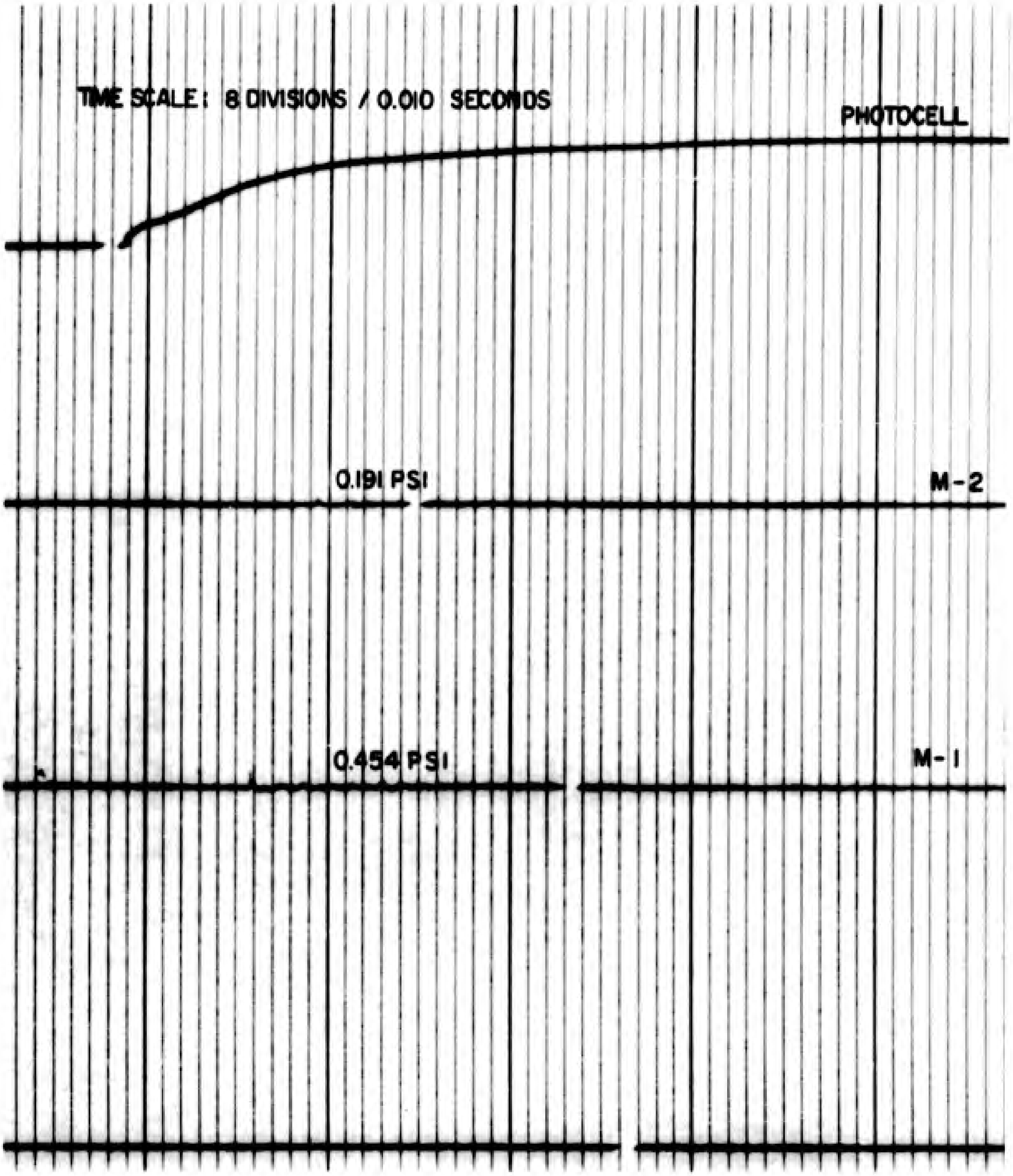


Figure 18. Overpressure Resulting from Simultaneous Spill of Hydrazine and Nitrogen Tetroxide on Dry Concrete

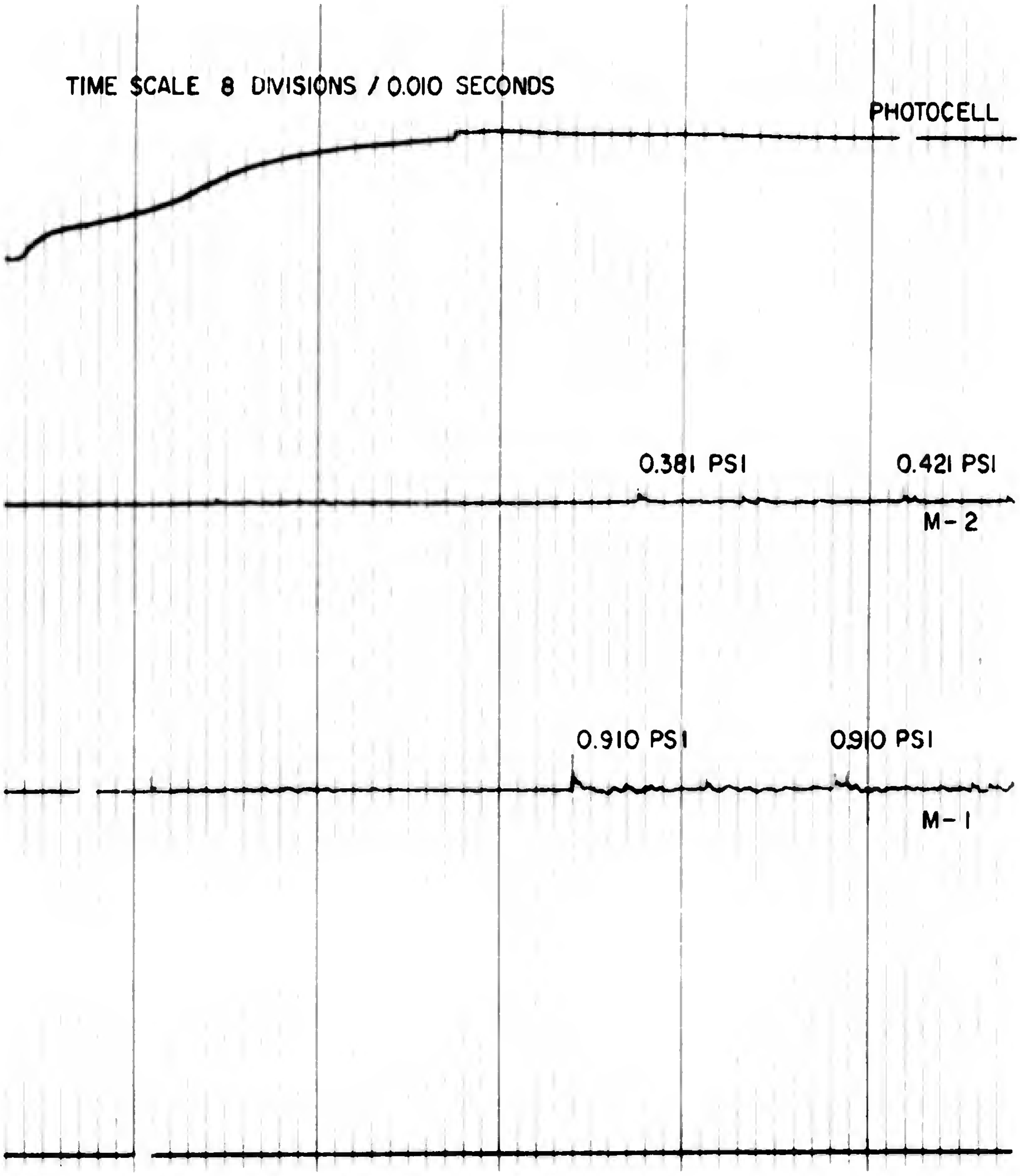


Figure 19. Overpressure Resulting from Nitrogen Tetroxide Lead with Hydrazine on Dry Concrete

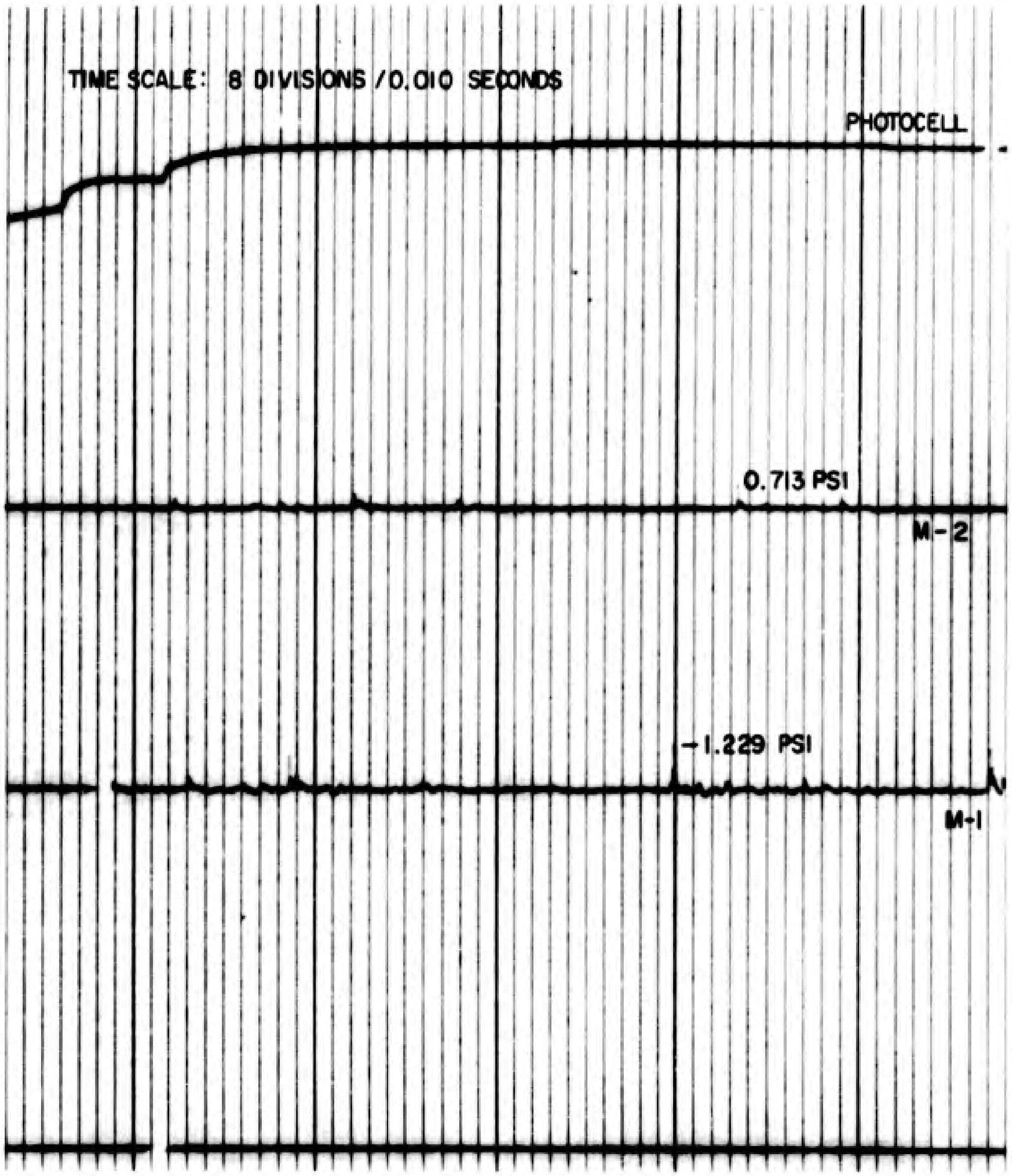


Figure 20. Overpressure Resulting from Nitrogen Tetroxide Lead with Hydrazine on Asphalt

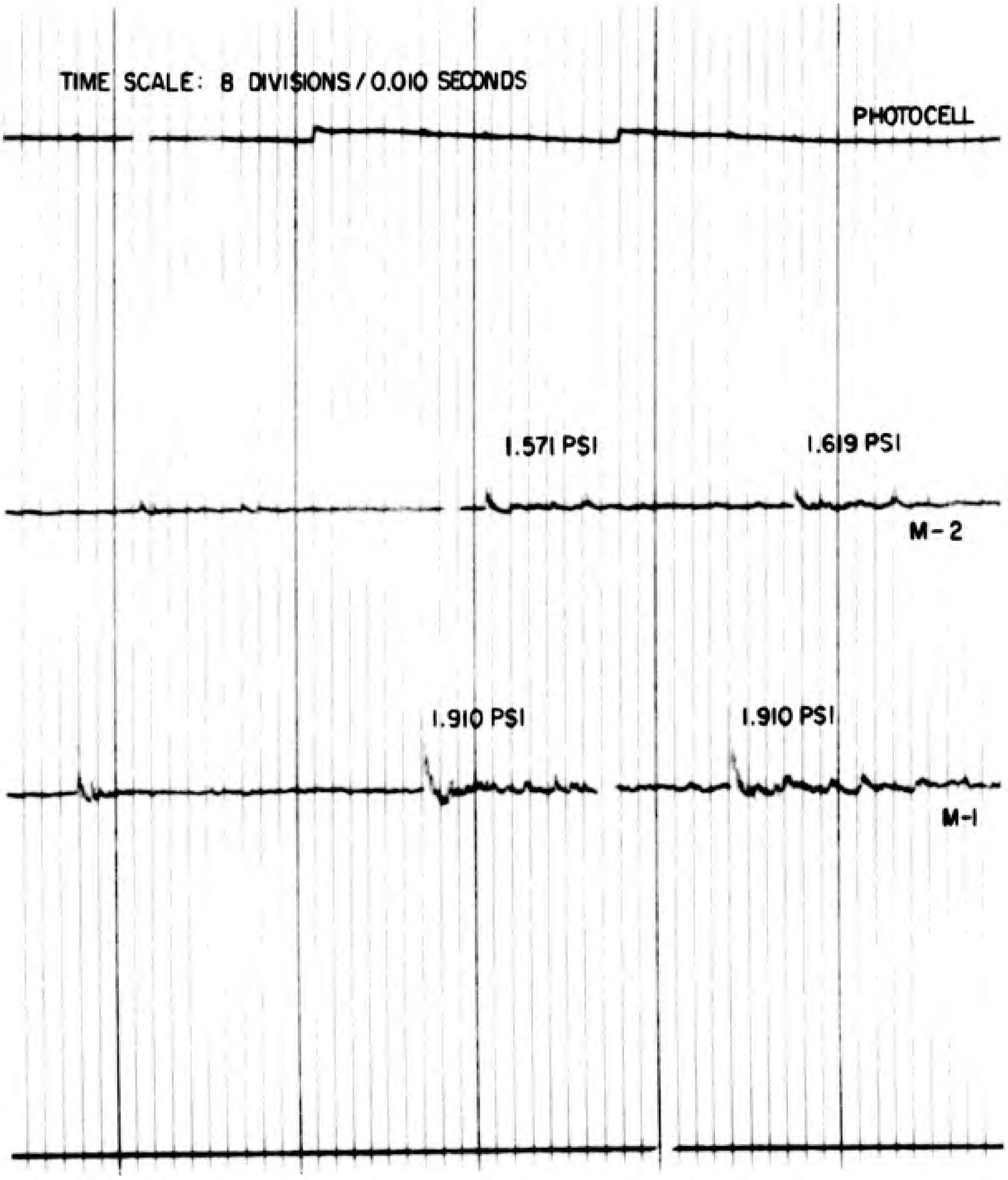


Figure 21. Overpressure Resulting from Hydrazine Lead with Nitrogen Tetroxide on Dirt

The concrete spill basin was flushed thoroughly and filled with 2 inches of water. A simultaneous spill of nitrogen tetroxide and hydrazine yielded five overpressure shocks at 52, 108, 326, 382 and 419 milliseconds after ignition, respectively; the maximum overpressure was 1.819 psi. Several overpressure shocks, in the period from 49 to 485 milliseconds after ignition, accompanied a combined spill on water with a hydrazine lead. The test on water with an oxidizer lead employed twice as much total propellant as had been used previously. Thus, overpressures were observed as late as 0.969 seconds after ignition. However, the maximum overpressure of 1.046 psi occurred only 46 milliseconds after ignition.

In all of the nitrogen tetroxide and hydrazine spill tests, ignition occurred immediately upon contact. The majority of these tests were accompanied by an extended series of overpressure shocks. The source of the explosions appeared to be an area about two to four feet above the spill contact surface. Color motion pictures clearly defined bright, white flashes originating in the product gas cloud above the actual propellant fire. Data was correlated by comparison of the time bases for the magnetic tape and Fastax film. In every instance, it was found that the flashes recorded photographically were related directly to the overpressures sensed by the microphone transducers.

Hydrazine and Pentaborane

Several of the initial spills with this combination were repeated with full instrumentation. First, the combination was spilled simultaneously on concrete; ignition occurred after a short delay and a slight overpressure was detected at M-1. Subsequent burning was rapid and smooth. A lead of pentaborane on the same surface produced identical results. With a hydrazine lead on concrete, the propellants appeared to ignite on contact and began to burn smoothly. About 2 seconds after, the photocell detected a second increase in radiation intensity, and overpressures of 2.635 and 2.155 psi were observed at M-1 and M-2, respectively (Fig. 22). However, the shock wave was recorded at M-1 only 6 milliseconds after the step-change in intensity at the photocell. As noted previously, a shock

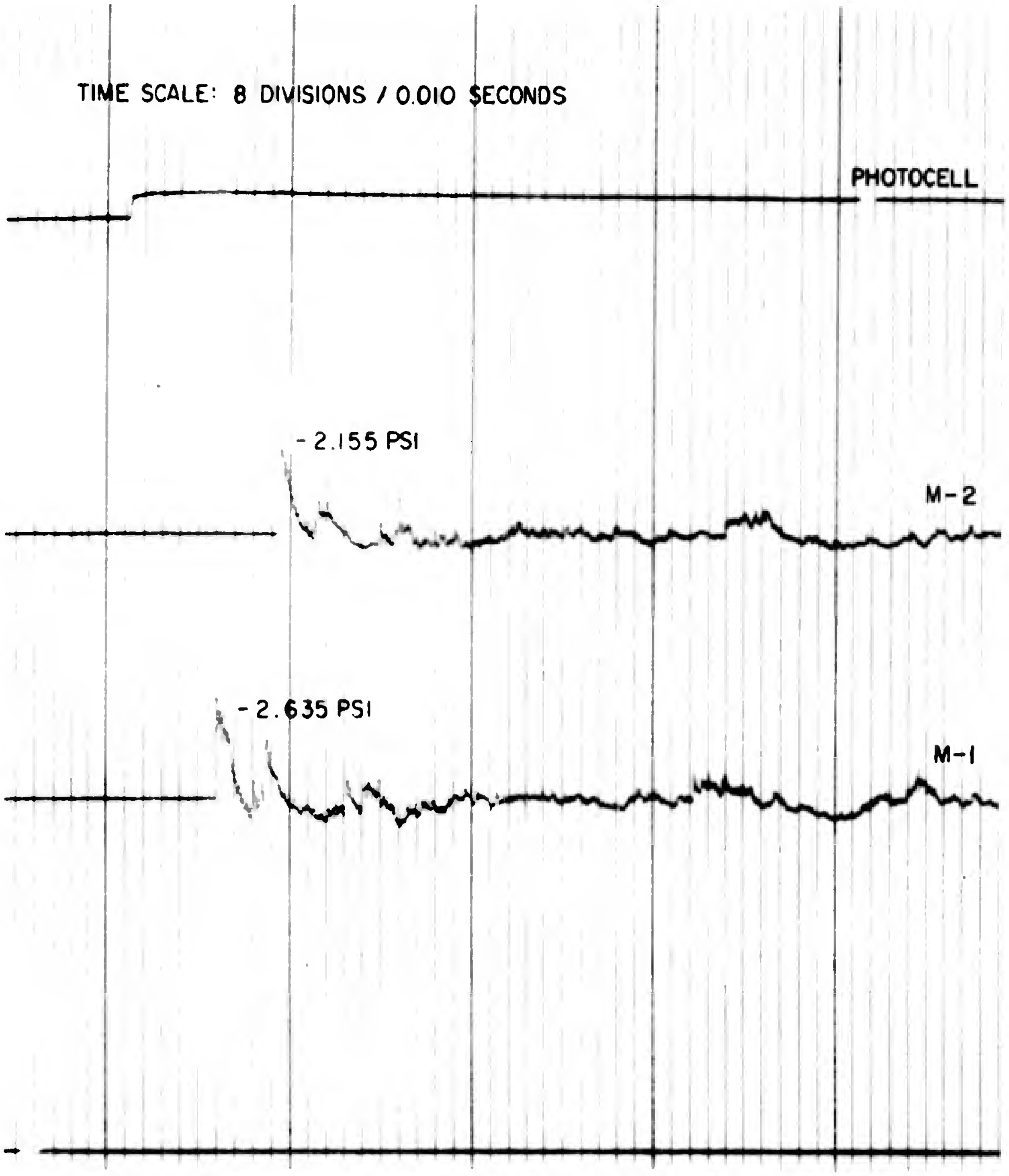


Figure 22. Overpressure Resulting from a Hydrazine Lead with Pentaborane on Dry Concrete

travelling at the speed of sound requires 8.8 milliseconds to traverse the 10 feet between the spill basin and M-1. In this case, also, the time delay between detection at M-1 and M-2 agreed with the calculated value of 4.5 milliseconds; see Fig. 22. Later examination of motion pictures showed that this explosion took place in conjunction with the post-test propellant purges.

Two combined hydrazine and pentaborane spills were carried out on an asphalt surface. Simultaneous spillage resulted in a large explosion after an appreciable delay in reaction; overpressure was recorded at M-1 6.25 milliseconds after photocell activation (Fig. 23). The explosion threw asphalt several feet through the surrounding test area. Overpressure amplitudes of 2.365 and 2.423 psi were observed at M-1 and M-2, respectively. A lead of pentaborane on asphalt resulted in a comparable ignition delay and large explosion. An overpressure of 2.455 psi was detected at M-1, 12.5 milliseconds after the photocell sensed ignition; the shock strength at M-2 was 2.463 psi (Fig. 24). The asphalt was fragmented and scattered as before. In both these tests, the shock transit time between stations M-1 and M-2 was the theoretical 4.5 milliseconds.

The asphalt was replaced by 2 inches of dirt in the concrete spill basin. Simultaneous spillage of hydrazine and pentaborane on dirt produced a slight ignition delay and smooth burning until 0.205 seconds after photocell activation. At that time, the photocell sensed a second increase in intensity; 5.25 milliseconds later, M-1 sensed an overpressure of 2.365 psi. An overpressure of 2.230 psi was recorded at M-2, 4.5 milliseconds later (Fig. 25). A pentaborane lead gave the same sequence of events. An overpressure of 2.500 psi was observed at M-1, 10.5 milliseconds after the photocell indicated ignition (Fig.26). The same shock was recorded as 2.650 psi at M-2 after the usual delay.

All tests with hydrazine and pentaborane were characterized by an appreciable delay in the initial reaction, ca. 30 to 40 milliseconds. In tests of other combinations, the origin of overpressure shocks appeared to be in the product gas cloud above the spill basin. With this combination, however, the origin appeared to be located at the contact surface or within

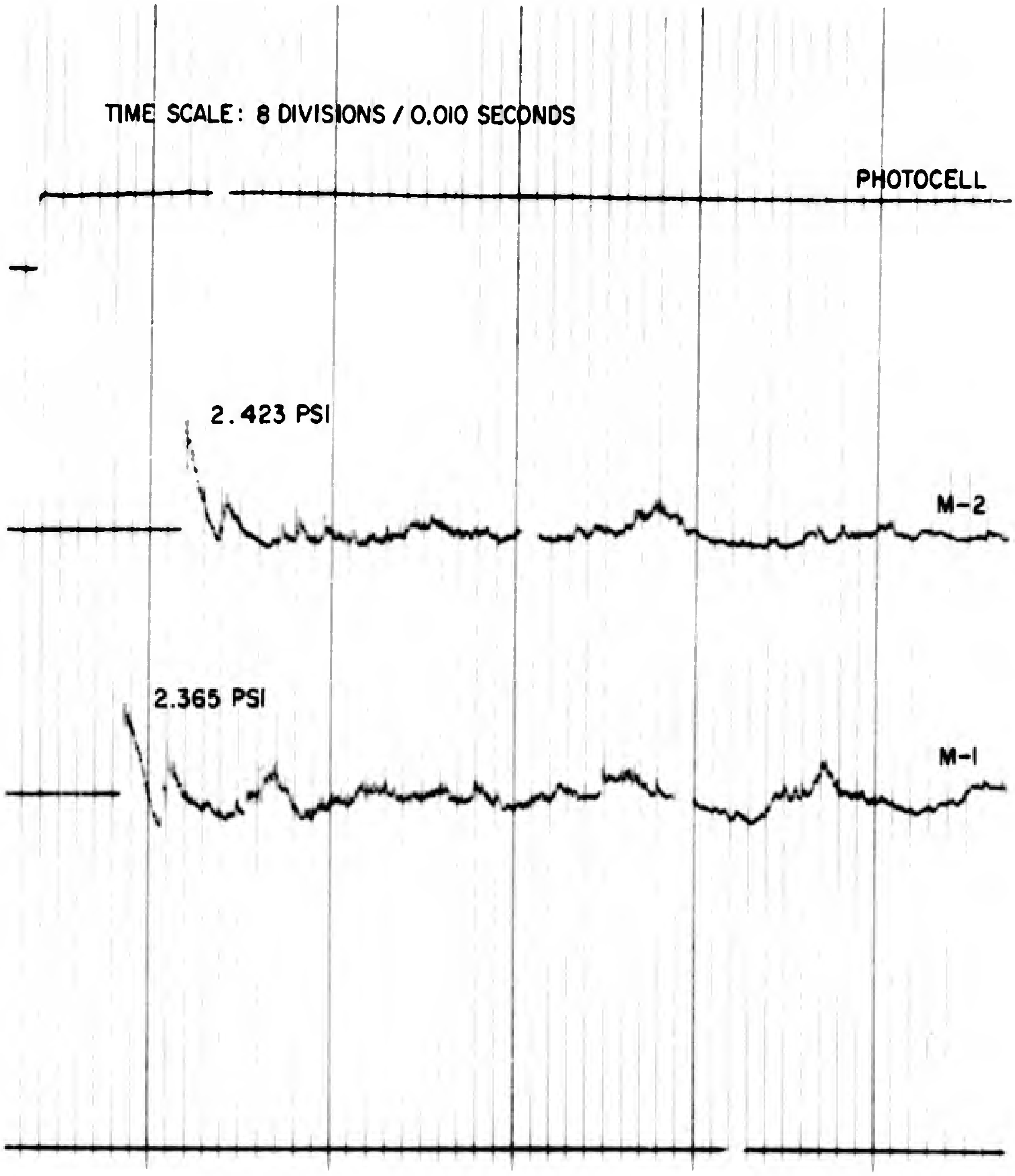


Figure 23. Overpressure Resulting from a Simultaneous Spill of Hydrazine and Pentaborane on Asphalt

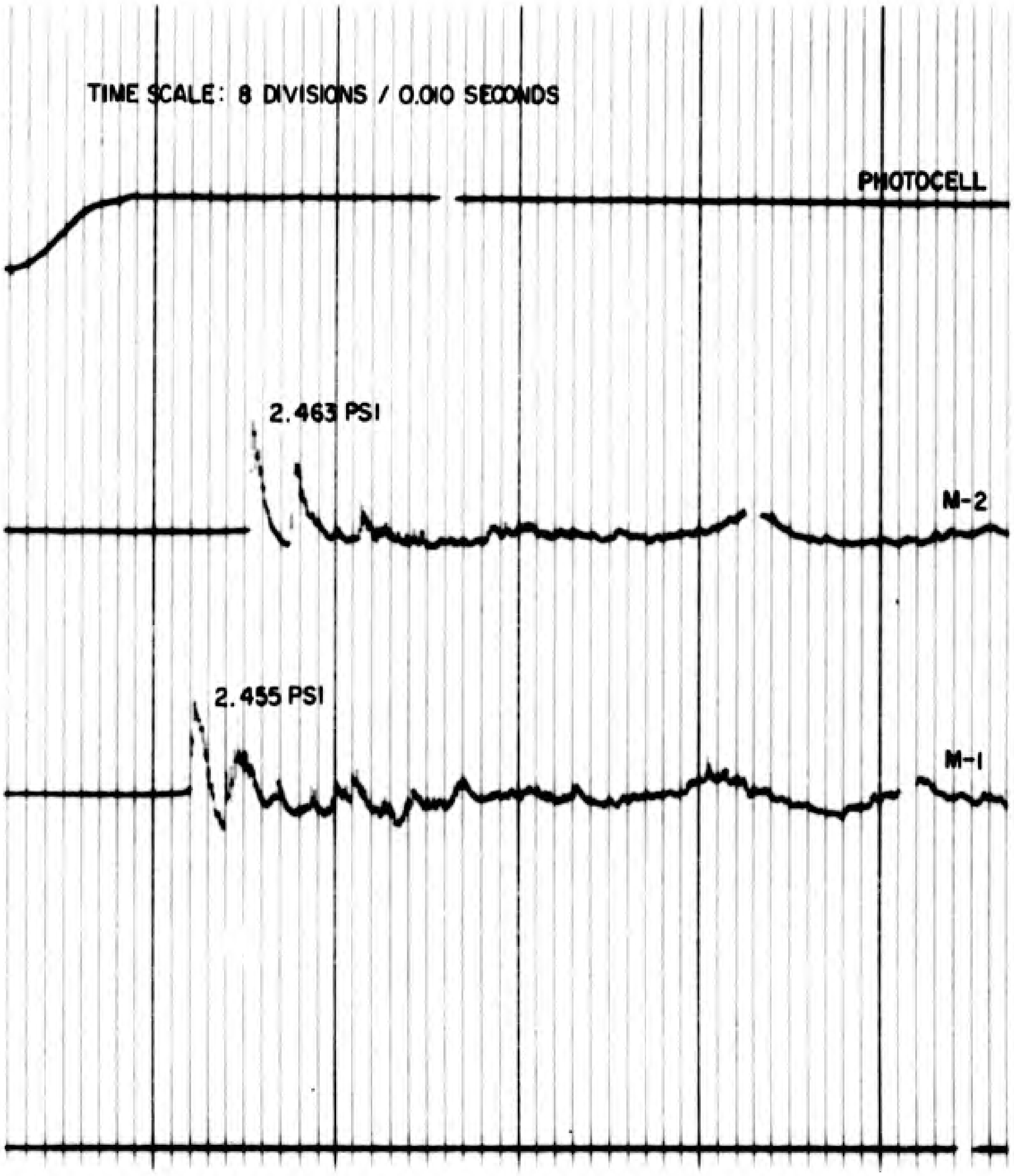


Figure 24. Overpressure Resulting from a Pentaborane Lead with Hydrazine on Asphalt

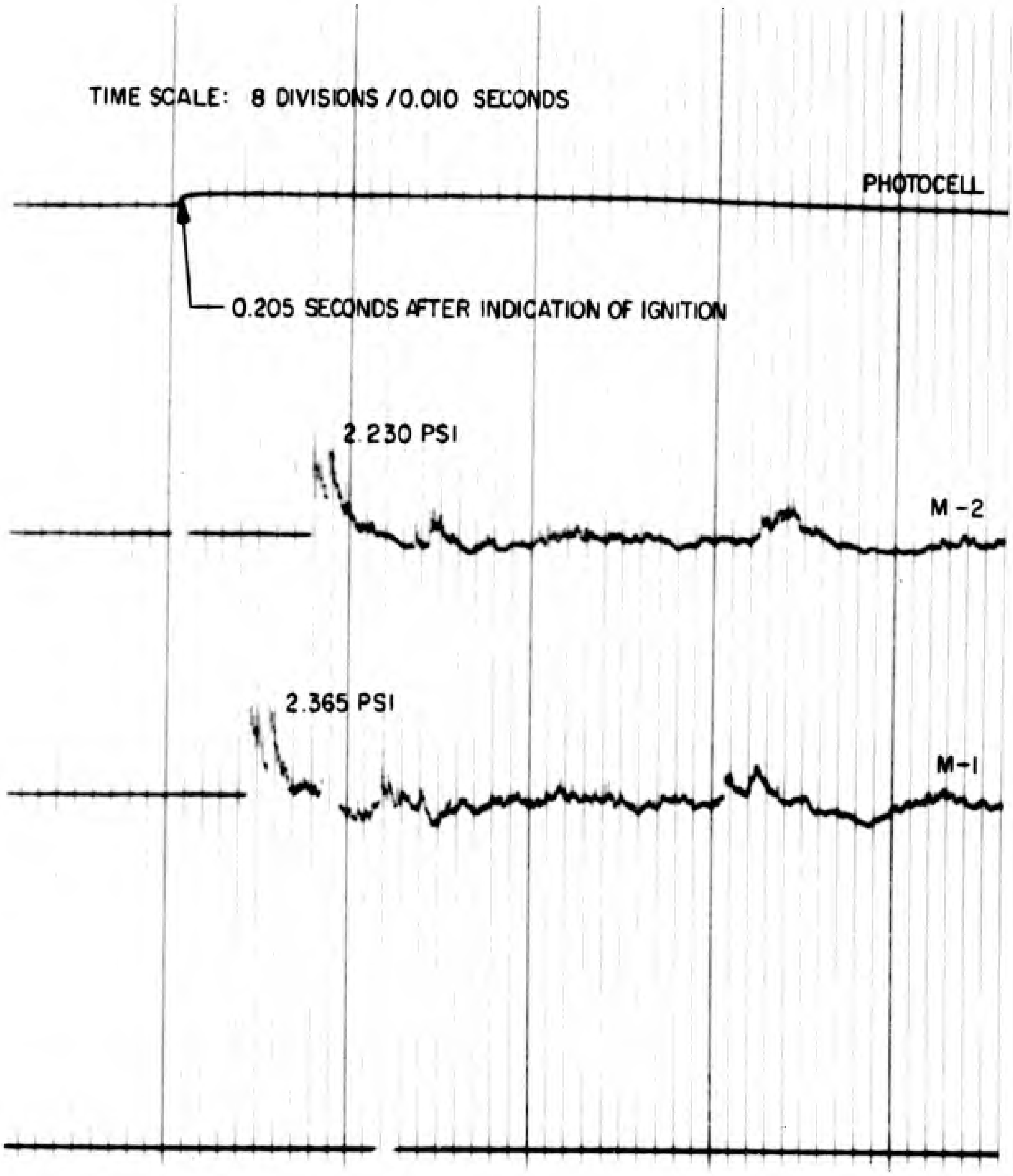


Figure 23. Overpressure Resulting from Simultaneous Spill of Hydrazine and Pentaborane on Dirt

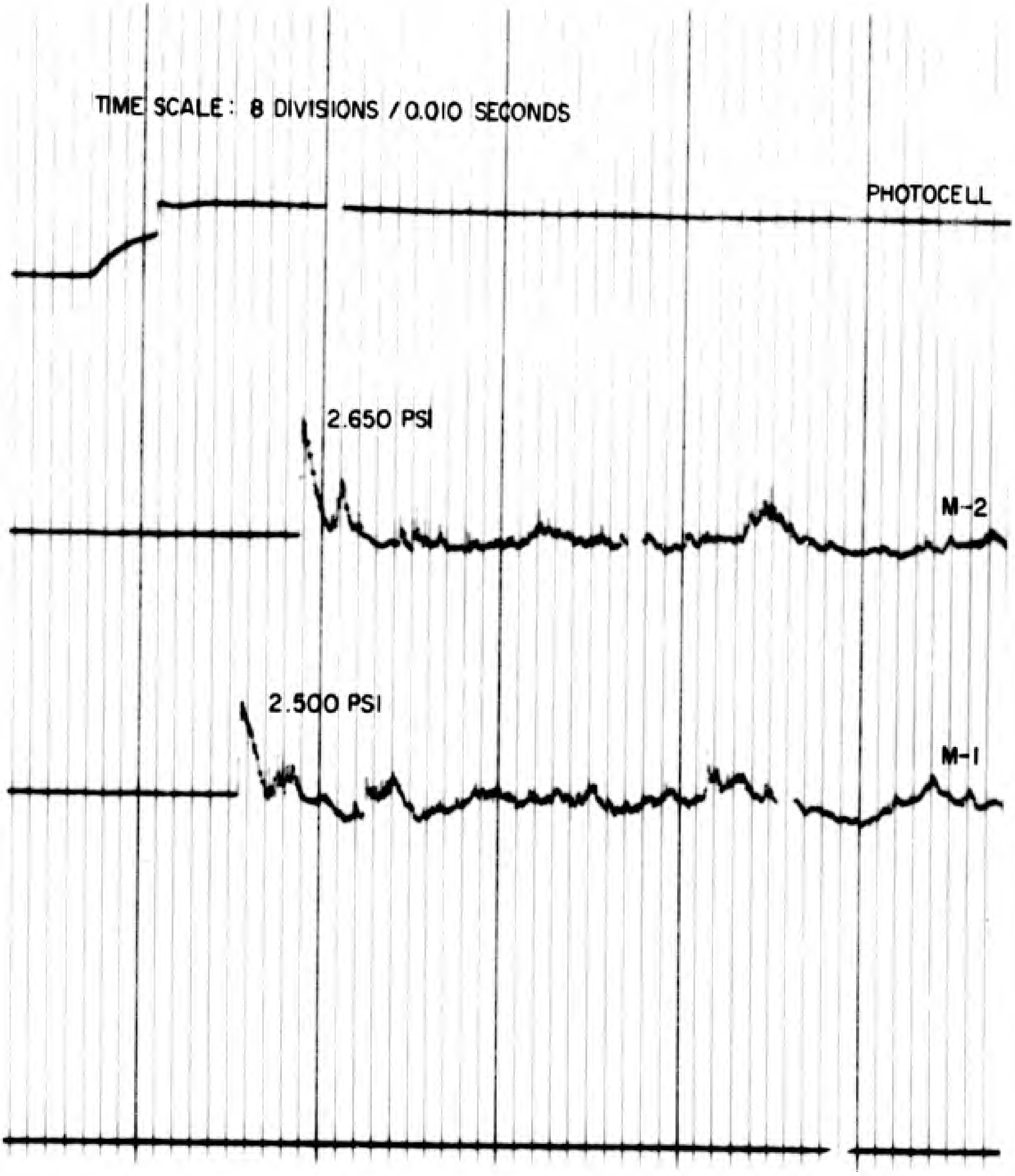


Figure 26. Overpressure Resulting from Pentaborane Lead with Hydrazine on Dirt

the confines of the spill basin. Certain other anomalies were encountered also. Time delays between photocell activation and shock interaction at M-1 were consistently less than the predicted 8.8 milliseconds. Conversely, shock transition times between M-1 and M-2 were in good agreement with theory. Finally, shock strengths were equal at stations M-1 and M-2, rather than 40- to 60-percent less as observed for other propellant combinations and as predicted from TNT equivalence tables.

The results of all instrumented combined spill tests are summarized in Table 3.

Additional Single Spills

Additional single spills of chlorine trifluoride, on various surfaces, were made during tests of this oxidizer with hydrazine and nitrogen tetroxide. A spill on dry concrete resulted in rapid evaporation of the liquid and no damage to the concrete surface. However, the propellant appeared to further erode cracks that were already present in the surface. Dirt and painted steel reacted to some extent with chlorine trifluoride; reaction was evident as sparks and weak explosions. Spills into water generated several weak overpressure shocks with amplitudes as high as 0.037 psi, at M-1, and 0.023 psi, at M-2. Wood was ignited immediately upon contact.

Single spills of pentaborane were made on concrete, dirt, asphalt, and water at an ambient temperature of 70 F and 9 percent relative humidity. The fuel floated on the surface of the water for several seconds; it was ignited with a brief chlorine trifluoride purge and burned on the water until exhausted. Ignition occurred on the other surfaces, after delays of a few seconds, with weak explosions.

Pentaborane spilled on dry concrete at 64 F and 10 percent relative humidity failed to ignite; evaporation was complete in several seconds. Dirt and asphalt caused ignition of the propellant after slight delays under the same

TABLE 3

RESULTS OF INSTRUMENTED COMBINED SPILL TESTS

Chlorine Trifluoride and Hydrazine

Test No. 27 - Simultaneous Spill on Dry Concrete
Temperature, 62 F; Rel. Humidity, 13 percent
W_{CTF}, 1.8 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.030	0.015
t_2	0.111	0.061
t_3	0.156	0.076
t_4	0.171	0.099

Test No. 28 - Hydrazine Lead on Dry Concrete
Temperature, 62 F; Rel. Humidity, 13 percent
W_{CTF}, 1.8 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.047	0.030
t_2	0.096	0.046
t_3	0.130	0.092
t_4	0.230	0.107

TABLE 3
(Continued)

Test No. 29 - Chlorine Trifluoride Lead on Dry Concrete

Temperature, 62 F; Rel. Humidity, 13 percent

W_{CTF}, 2.5 lb; W_{HZ}, 1.0 lb

No Detectable Overpressure

Test No. 33 - Simultaneous Spill on Dirt

Temperature, 60 F; Rel. Humidity, 14 percent

W_{CTF}, 1.8 lb; W_{HZ}, 1.0 lb

Trace Overpressure

Test No. 34 - Hydrazine Lead on Dirt

Temperature, 60 F; Rel. Humidity, 14 percent

W_{CTF}, 1.8 lb; W_{HZ}, 1.3 lb

Trace Overpressure

Test No. 35 - Chlorine Trifluoride Lead on Dirt

Temperature, 60 F; Rel. Humidity, 15 percent

W_{CTF}, 2.5 lb; W_{HZ}, 1.0 lb

No Detectable Overpressure

Test No. 36 - Simultaneous Spill on Water

Temperature, 59 F; Rel. Humidity, 15 percent

W_{CTF}, 1.8 lb; W_{HZ}, 1.0 lb

Test No. 36 (Continued)

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.044	0.030
t_2	0.490	0.221
t_3	0.237	0.099
t_4	0.133	0.091
t_5	0.156	0.099
t_6	0.104	0.053
t_7	0.319	0.168

Test No. 37 - Hydrazine Lead on Water

Temperature, 58 F; Rel. Humidity, 15 percent

W_{CTF}, 1.8 lb; W_{HZ}, 1.5 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.096	0.057
t_2	0.082	0.069
t_3	0.126	0.121
t_4	0.119	0.107
t_5	0.067	0.046

Test No. 38 - Chlorine Trifluoride Lead on Water

Temperature, 58 F; Rel. Humidity, 16 percent

W_{CTF}, 2.5 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.033	0.023
t_2	0.081	0.053
t_3	0.100	0.083
t_4	0.148	0.068
t_5	0.156	0.076
t_6	0.178	0.149
t_7	0.174	0.129

Test No. 40 - Simultaneous Spill on Asphalt

Temperature, 57 F; Rel. Humidity, 16 percent

W_{CTF}, 1.8 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.104	0.046
t_2	0.104	0.061
t_3	0.141	0.083

Test No. 41 - Hydrazine Lead on Asphalt

Temperature, 56 F; Rel. Humidity, 16 percent

W_{CTF}, 1.8 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	Trace	Trace
t_2	0.082	0.038
t_3	Trace	Trace

Test No. 42 - Chlorine Trifluoride Lead on Asphalt

Temperature, 56 F; Rel. Humidity, 16 percent

W_{CTF}, 2.4 lb; W_{HZ}, 1.3 lb

Trace Overpressure

Chlorine Trifluoride and Nitrogen Tetroxide

Test No. 30 - Simultaneous Spill on Dry Concrete

Temperature, 61 F; Rel. Humidity, 13 percent

W_{CTF}, 1.8 lb; W_{NTO}, 1.5 lb

No Reaction

Test No. 31 - Nitrogen Tetroxide Lead on Dry Concrete

Temperature, 61 F; Rel. Humidity, 14 percent

W_{CTF}, 1.8 lb; W_{NTO}, 2.0 lb

No Reaction

Test No. 32 - Chlorine Trifluoride Lead on Dry Concrete

Temperature, 61 F; Rel. Humidity, 14 percent

W_{CTF}, 2.4 lb; W_{NTO}, 1.5 lb

No Reaction

Test No. 39 - Simultaneous Spill on Water

Temperature, 57 F; Rel. Humidity, 16 percent

W_{CTF}, 1.8 lb; W_{NTO}, 1.5 lb

No Reaction

Chlorine Trifluoride and Pentaborane

Test No. 43 - Simultaneous Spill on Dry Concrete

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.7 lb

No Detectable Overpressure

Test No. 44 - Pentaborane Lead on Dry Concrete

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.9 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.103	0.041
t_2	0.082	0.030
t_3	0.139	0.101

Test No. 45 - Chlorine Trifluoride Lead on Dry Concrete

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 2.4 lb; W_{PB}, 0.7 lb

No Detectable Overpressure

Test No. 46 - Simultaneous Spill on Dirt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.7 lb

No Detectable Overpressure

Test No. 47 - Pentaborane Lead on Dirt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.9 lb

No detectable Overpressure

Test No. 48 - Chlorine Trifluoride Lead on Dirt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 2.4 lb; W_{PB}, 0.7 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.051	0.030
t_2	0.066	0.041
t_3	0.103	0.051

Test No. 49 - Simultaneous Spill on Asphalt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.7 lb

No Detectable Overpressure

Test No. 50 - Pentaborane Lead on Asphalt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.9 lb

No Detectable Overpressure

Test No. 51 - Chlorine Trifluoride Lead on Asphalt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 2.4 lb; W_{PB}, 0.7 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.103	0.061
t_2	0.147	0.101
t_3	0.051	0.051
t_4	0.114	0.086
t_5	0.059	0.041

Test No. 52 - Simultaneous Spill on Water

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 017 lb

Test No. 52 - (Continued)

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.066	0.041
t_2	0.073	0.046
t_3	0.114	0.071
t_4	0.059	0.035

Test No. 53 - Pentaborane Lead on Water

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 1.8 lb; W_{PB}, 0.9 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.048	0.035
t_2	0.037	0.020

Test No. 54 - Chlorine Trifluoride Lead on Water

Temperature, 70 F; Rel. Humidity, 9 percent

W_{CTF}, 2.4 lb; W_{PB}, 0.7 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.106	0.071
t_2	0.092	0.061
t_3	0.106	0.071
t_4	0.070	0.061
t_5	0.051	0.041
t_6	0.103	0.066

Nitrogen Tetroxide and Hydrazine

Test No. 55 - Simultaneous Spill on Dry Concrete

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.00875	0.454	0.191
0.113	0.182	0.048
0.430	0.819	0.333

Test No. 56 - Hydrazine Lead on Dry Concrete

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.075	0.346	0.191
0.117	1.955	1.381
0.143	2.000	1.620
0.187	0.728	0.619
0.264	0.818	0.904
0.299	1.455	0.762
0.371	1.685	1.142
0.399	2.000	1.810
0.456	1.639	1.142
0.536	1.639	0.953

Test No. 57 - Nitrogen Tetroxide Lead on Dry Concrete

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 2.0 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.00925	Trace	Trace
0.038	0.910	0.381
0.056	0.910	0.428
0.217	1.000	0.667

Test No. 58 - Simultaneous Spill on Asphalt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.0 lb

No Detectable Overpressure

Test No. 59 - Hydrazine Lead on Asphalt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.409	0.143
t_2	0.682	0.333
t_3	1.545	0.667

Test No. 60 - Nitrogen Tetroxide Lead on Asphalt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 2.0 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.0089	0.636	0.286
0.048	1.229	0.713
0.069	1.091	0.666

Test No. 61 - Simultaneous Spill on Dirt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.038	0.546	0.238
0.356	0.454	0.191
0.379	1.455	0.762
0.403	0.773	0.381
0.446	1.091	0.524

Test No. 62 - Hydrazine Leadon Dirt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.118	0.500	0.286
0.322	0.910	0.381
0.410	1.273	0.857
0.433	1.910	1.571
0.455	1.910	1.619

Test No. 57 - Nitrogen Tetroxide Lead on Dry Concrete

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 2.0 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.00925	Trace	Trace
0.038	0.910	0.381
0.056	0.910	0.428
0.217	1.000	0.667

Test No. 58 - Simultaneous Spill on Asphalt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.0 lb

No Detectable Overpressure

Test No. 59 - Hydrazine Lead on Asphalt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
t_1	0.409	0.143
t_2	0.682	0.333
t_3	1.545	0.667

Test No. 60 - Nitrogen Tetroxide Lead on Asphalt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 2.0 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.0089	0.636	0.286
0.048	1.229	0.713
0.069	1.091	0.666

Test No. 61 - Simultaneous Spill on Dirt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.038	0.546	0.238
0.356	0.454	0.191
0.379	1.455	0.762
0.403	0.773	0.381
0.446	1.091	0.524

Test No. 62 - Hydrazine Lead on Dirt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.3 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.118	0.500	0.286
0.322	0.910	0.381
0.410	1.273	0.857
0.433	1.910	1.571
0.455	1.910	1.619

Test No. 63 - Nitrogen Tetroxide Lead on Dirt

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 2.0 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.0975	0.318	0.095
0.436	1.091	0.524
0.465	1.363	0.666
0.533	1.728	1.238
0.669	1.091	0.476
0.720	1.091	0.476
0.825	0.728	0.286

Test No. 64 - Simultaneous Spill on Water

Water, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.052	1.363	0.762
0.108	0.910	0.381
0.326	1.272	0.666
0.382	1.819	1.285
0.419	0.819	0.286

Test No. 65 - Hydrazine Lead on Water

Temperature, 67 F; Rel. Humidity, 12 percent

W_{NTO}, 1.5 lb; W_{HZ}, 1.3 lb

Test No. 65 - (Continued)

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.049	1.137	0.950
0.297	1.046	0.476
0.332	0.364	0.190
0.363	0.636	0.190
0.395	1.046	0.428
0.415	0.773	0.333
0.485	1.228	0.619

Test No. 66 - Nitrogen Tetroxide Lead on Water
Temperature, 67 F; Rel. Humidity, 12 percent
W_{NTO}, 4.0 lb; W_{HZ}, 2.0 lb

Time, Sec	Overpressure, psi	
	Station M-1	Station M-2
0.046	1.046	0.428
0.825	0.955	0.381
0.902	0.546	0.190
0.969	0.854	0.381

Hydrazine and Pentaborane

Test No. 67 - Simultaneous Spill on Dry Concrete
Temperature, 70 F; Rel. Humidity, 9 percent
W_{HZ}, 1.0 lb; W_{PB}, 0.7 lb
Trace Overpressure at Ignition

Test No. 68 - Pentaborane Lead on Dry Concrete

Temperature, 70 F; Rel. Humidity, 9 percent

W_{HZ}, 1.0 lb; W_{PB}, 0.9 lb

Trace Overpressure at Ignition

Test No. 69 - Hydrazine Lead on Dry Concrete

Temperature , 70 F; Rel. Humidity, 9 percent

W_{HZ}, 1.3 lb; W_{PB}, 0.7 lb

Overpressures of 2.635 psi (Station M-1) and 2.155 psi (Station M-2) after 2.011 Seconds

Test No. 70 - Simultaneous Spill on Asphalt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{HZ}, 1.0 lb; W_{PB}, 0.7 lb

Overpressures of 2.365 psi (Station M-1) and 2.423 psi (Station M-2) after 0.00625 Seconds

Test No. 71 - Pentaborane Lead on Asphalt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{HZ}, 1.0 lb; W_{PB}, 0.9 lb

Overpressures of 2.455 psi (Station M-1) and 2.463 psi (Station M-2) after 0.01250 Seconds

Test No. 72 - Simultaneous Spill on Dirt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{HZ}, 1.0 lb; W_{PB}, 0.7 lb

Overpressures of 2.365 psi (Station M-1) and 2.230 psi (Station M-2) after 0.21025 Seconds

Test No. 73 - Pentaborane Lead on Dirt

Temperature, 70 F; Rel. Humidity, 9 percent

W_{HZ}, 1.0 lb; W_{PB}, 0.9 lb

Overpressures of 2.500 psi (Station M-1) and 2.650 psi (Station M-2) after 0.01050 Seconds

NOTES:

1. Total weight values are approximate quantities of propellant spilled during a test.
2. Time is taken from the point of first photocell signal generation; "t" notations signify photocell failure.
3. Time recorded is taken for the observation at Station M-1; shocks were detected at Station M-2 approximately 4.5 milliseconds later.

ambient conditions. In the latter cases, there was some question of surface contamination as hydrazine had been burned on the same surfaces some time prior to the pentaborane tests.

Results of instrumented single spills are summarized in Table 4.

ANALYSIS

The evaluation of blast effects from propellant explosions is usually based on the relative effects of equivalent quantities of TNT. Overpressure or blast effects of TNT detonations have been examined and reported in detail; Eq. (1) is the result of statistical analysis of extensive test data (Ref. 1).

$$P_{s(TNT)} = \left[4120/(R/Y^{1/3})^3\right] - \left[105/(R/Y^{1/3})^2\right] + \left[39.5/(R/Y^{1/3})\right] \qquad (1)$$

where

P_s = Average side-on overpressure (behind the shock front), psi

R = Distance from origin, ft

Y = Quantity of TNT, lb

Side-on pressure, p_s, is defined as the static overpressure behind the blast shock front. This parameter is commonly measured by mounting a sensing element with its face parallel to shock flow. A position normal to shock flow results in a measurement of reflected pressure, p_r. Overpressure measurements in the Small-Scale Hazard Classification Program were carried out with the latter technique. This less common approach to the identification of shock waves was selected for two reasons.

TABLE 4

RESULTS OF INSTRUMENTED SINGLE SPILLS OF CHLORINE TRIFLUORIDE AND PENTABORANE (19-31)

Test	Propellant	Surface	Temperature, F	Relative Humidity, percent	Results
19	Chlorine Trifluoride	Dry concrete	62	13	Rapid boil-off of liquid, no reaction with or damage to the concrete surface
20	Chlorine Trifluoride	Dirt	60	14	Slight reaction with small sparks and "pops"
21	Chlorine Trifluoride	Water	59	15	Several small overpressures, reaching 0.037 psi on M-1 and 0.023 psi on M-2, were recorded
22	Chlorine Trifluoride	Asphalt	57	16	Vigorous burning and rapid deterioration of surface
23	Chlorine Trifluoride	Painted steel	56	16	Same as 20
24	Chlorine Trifluoride	Wood	56	16	Smooth and rapid burning of surface
25	Pentaborane	Dry concrete	70	9	Ignited with small "pop" on surface after delay of a few seconds
26	Pentaborane	Dirt	70	9	Same as 25

TABLE 4
(Continued)

Test	Propellant	Surface	Temperature, F	Relative Humidity, percent	Results
27	Pentaborane	Asphalt	70	9	Same as 25
28	Pentaborane	Water	70	9	Floated on top of water without ignition; however, it burned on top of the water after ignition with chlorine trifluoride
29	Pentaborane	Dry concrete	64	10	No ignition - finally evaporated
30	Pentaborane	Dirt	64	10	Ignited after slight delay; however, residual hydrazine might have been on surface
31	Pentaborane	Asphalt	64	10	Same as 30

Reflected shock pressure is two to eight times greater than side-on shock pressure. Since preliminary tests had indicated that the majority of propellant reactions would result in relatively slight overpressures, the reflective technique was employed to increase the sensitivity of the measurement system. Also, the early experiments indicated that overpressure shocks were originating over a range of vertical positions. The lowest position of origin was the surface of the spill basin, which was 4 to 6 inches below the lowest parallel plane in which a sensing element could be mounted. Higher sources varied from 1 to 4 feet about the spill basin surface. As a consequence of random source orientation, the angle of incidence error for side-on measurements was found to be greater than for reflected pressure detection.

A simple relation is reported for the conversion of reflected to side-on shock overpressures (Ref. 2); this relation is as follows:

$$p_r = (2p_s)\left[(7P_o - 4p_s) / (7P_o + p_s)\right] \tag{2}$$

where p_r = Reflected overpressure, psi

P_o = Ambient pressure (ahead of shock), psia

As noted above, the ratio of reflected to side-on overpressure varies from two, for weak shocks with p_s approaching zero, to eight, for strong shocks with p_s approaching infinity. Thus, for the practical purposes of this program, reflected overpressures can be converted to side-on pressures by the equation

$$p_s = p_r/2 \tag{3}$$

without introduction of significant error. This simplification is correct for very weak shocks only; however, conversion of the highest overpressure detected during this study results in about four percent error.

For comparison of overpressure shocks generated by reactions accompanying liquid propellant spills, a basis of standard TNT equivalents was selected. Equation (1) was reduced to a log-log plot of side-on overpressure, p_s, versus quantity, Y, and has been reproduced as Fig. 27. Distances, R, of 10 and 15 feet from the explosive origin were calculated for direct comparison purposes. Because the observed overpressures were quite small, TNT quantities, Y, in the range of 0.00001 to 0.1 pounds were considered.

For the evaluation of singular and combined liquid propellant spills and reactions, directly measured reflected overpressures have been converted to side-on overpressures with Equation (3). In turn, quantities of TNT have been read from the appropriate curve of Fig. 27. Finally, the weight ratio of TNT to total propellant spilled has been computed as a percent yield or efficiency.

Single Spill Tests

Single spill tests demonstrated that nitrogen tetroxide will not react with common facility construction materials over relatively short periods of contact. Because of a low boiling point, 70 F, the liquid vaporizes rapidly at normal ambient temperatures. Nitrogen tetroxide becomes highly corrosive when diluted with even traces of moisture; therefore, some corrosion might be expected after a spill and decontamination unless removal or neutralization were complete.

Hydrazine did not react on any of the surfaces on which it was spilled. Spills on hard, non-absorbent surfaces resulted in the typical vapor cloud over the test basin; this cloud is indicative of a reaction between the fuel and carbon dioxide in air. Contact with porous surfaces retarded the formation of this cloud to some extent. None of the hydrazine single spills resulted in a reaction fire or explosion. However, hydrazine-air mixtures have well-defined flammability and explosion limits. An ignition source in a hydrazine-type fuel spill area could lead to one or the other of these undesirable reactions.

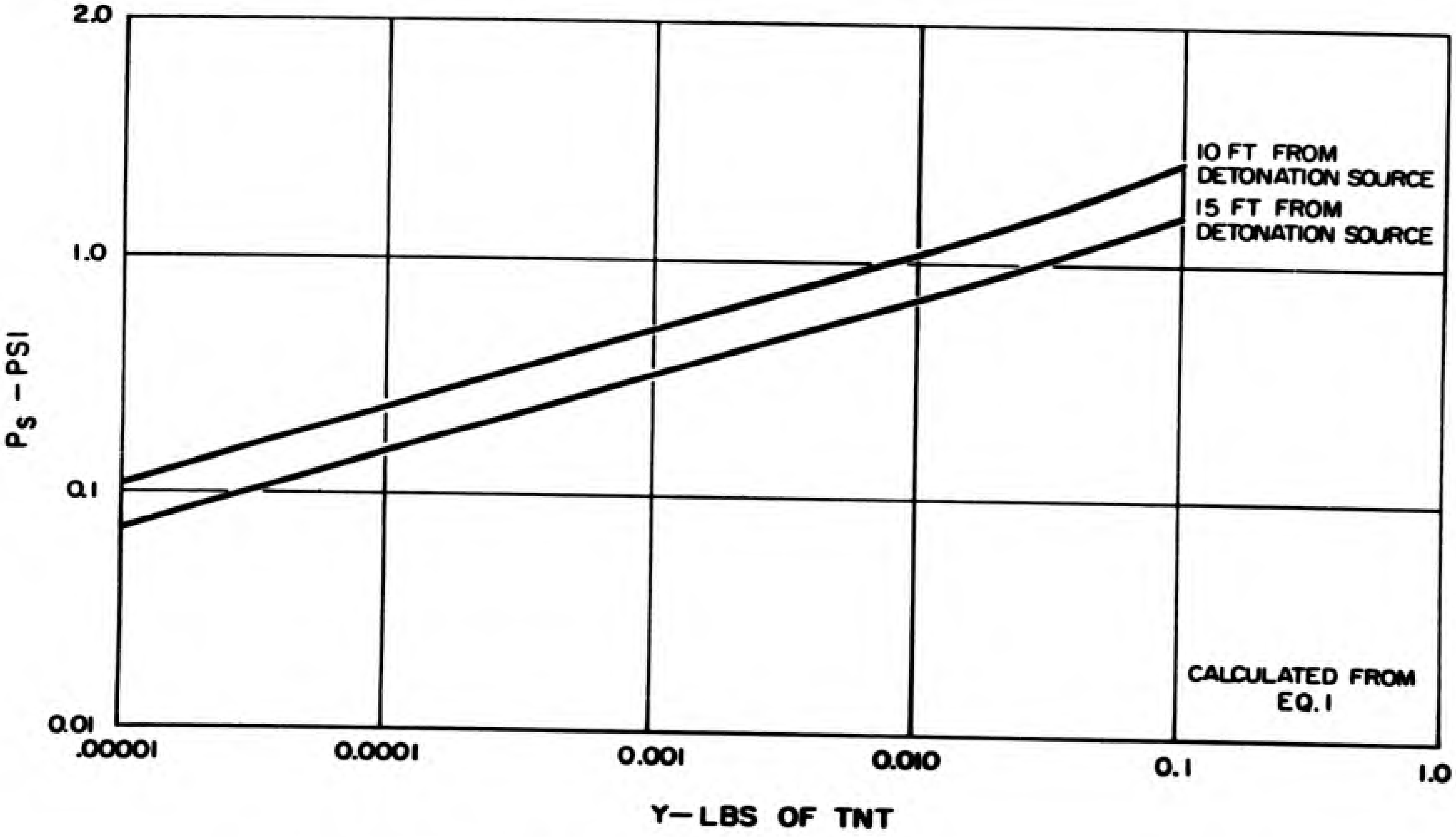


Figure 27. Side-on Overpressure Resulting from Detonation of TNT

Concrete appeared to resist attack by chlorine trifluoride; however, most other surfaces studied showed some evidence of reaction. In general, these reactions could be attributed to organic matter that was on or formed an integral part of the spill surface. Reactions were evidenced by sparks and weak explosions. Except for the case of water, all overpressure shocks were insignificant. Recorded chlorine trifluoride/water shocks were less than 0.001 percent efficient, based upon a TNT equivalent. Asphalt deteriorated rapidly and burned in the presence of chlorine trifluoride.

Spills of pentaborane in air resulted in immediate ignition and burning at temperatures greater than 80 F. There is good evidence from these hazard classification tests and from other Rocketdyne experience that the ignition of pentaborane at temperatures below 70 F, is catalyzed by a variety of surfacing materials; e.g., dirt. Slow decomposition and heat evolution may result in delayed pyrophoric reactions, also. It has been observed that pentaborane ignited spontaneously, at 40 to 50 F, about one-half hour after a spill onto dirt.

Pentaborane ignition occurred with an audible explosion that became stronger as the ignition delay increased. This shock generation was probably the consequence of a secondary reaction between hydrogen and air. The hydrogen was assumed to arise from pyrolysis of pentaborane. Generally, it is desired that pentaborane ignite rapidly to mitigate the formation and accumulation of toxic vapors. During this program, a boron hydride vapor detector was employed in the test area; no positive measurements were obtained in the general area of the spill basin, after ignition and burning had occurred.

Combination Spill Tests

Nitrogen Tetroxide and Chlorine Trifluoride. When spilled together, these two oxidizers exhibited no unusual reactions. In all cases, the results were comparable to the results of single chlorine trifluoride spills.

Chlorine Trifluoride and Hydrazine. Under some conditions, combination spills of chlorine trifluoride and hydrazine resulted in weak overpressure shocks. The maximum overpressure was equivalent to a 0.0045-percent yield based upon TNT. Photographic records showed that shocks originated from disturbances at points a few feet above the actual spill contact surface. On the average, shock strength diminished by 40 to 50 percent during the 5-foot transition between stations M-1 and M-2. This relationship is approximately correct for spherical shock propagation.

Maximum overpressure amplitudes were recorded for simultaneous spillage on water. Lesser amplitude shocks were encountered after simultaneous spills on concrete and asphalt, and hydrazine leads on concrete, asphalt and water. Insignificant trace overpressures were observed for tests on dirt and oxidizer leads on dry surfaces. A modest overpressure was detected during the test with an oxidizer lead on water; however, this result was attributed to reaction between chlorine trifluoride and water.

From the high-speed motion pictures of these tests it was possible to establish that shocks were originating from vapor phase reactions in the product gas cloud. This shock source, as well as the general effects of sequence and surfaces, suggested that these explosive reactions were taking place between fuel vapors and air; hydrazine was vaporized from the spill surface, mixed with air diffusing into the product cloud and initiated by hot combustion gases. Hard, nonporous surfaces, such as concrete and asphalt, contributed to this condition by permitting rapid fuel vapor formation. On the other hand, dirt retarded vapor phase explosion by absorbing the fuel and retaining vapors until reaction with chlorine trifluoride could take place. The water surface dissolved hydrazine and repressed vapor formation; however, it appeared to react with chlorine trifluoride in much the same way as in a single spill of the oxidizer. Finally, an oxidizer lead resulted in the rapid formation of oxidizer vapors and immediate reaction with fuel vapor as formed.

Chlorine Trifluoride and Pentaborane. Spills of these propellants produced immediate reaction and large, intense fireballs; however, overpressure effects were minor. There was some difficulty in locating the origin of trace shocks because of the brilliance of the bipropellant reaction. Shock initiation appeared as a more brilliant flash within the fireball that seemed to extend to the fringes of the reacting cloud. The entire process occurred about 4 feet above the spill surface.

Trace overpressures were detected in all spills on water, with oxidizer leads on dirt and asphalt, and with a fuel lead on dry concrete. Pentaborane ignited on the concrete before the appearance of chlorine trifluoride. As a whole, the results exhibited no discernible pattern. It appeared likely that these spurious overpressures were originating from pentaborane-air or hydrogen-air reactions. Hydrogen can be liberated by a reaction between pentaborane and water or pyrolysis of the fuel in contact with hot gases and/or surfaces.

Nitrogen Tetroxide and Hydrazine. The maximum TNT equivalent observed for a fuel lead on dry concrete was 0.75 percent. The largest overpressures accompanied spills on dry concrete. Lesser shocks were encountered with dirt, asphalt and water, in that order. A simultaneous spill or fuel lead produced stronger shocks than an oxidizer lead.

The first of a series of overpressure shocks occurred anytime from immediately following ignition to several milliseconds later. Once started, shocks continued at periodic intervals until the main-flow control valves were closed. As before, film demonstrated that shock sources were in the product cloud at points several feet above the spill surface. Shock initiation was characterized by intense, white flashes as with the previous hydrazine fuel spill series. Once propellant flow had been terminated, surface burning of hydrazine continued to depletion, but evaporation of scattered droplets ceased and shock generation was no longer observed.

There appeared to be little question that the vapor-phase explosions were hydrazine-air reaction phenomena associated with fuel vaporization and admixture with air diffusion into the product cloud. At this point in the program, a principle of uniform behavior had been established. Overpressures generated by fuel-air explosions were detected, with hydrazine and the common oxidizers, in all tests that favored the vaporization of fuel from the spill surface.

Hydrazine and Pentaborane. Of the instrumented spill tests, the largest overpressures were recorded during tests with hydrazine and pentaborane. Further, these tests were characterized by several conditions that were typical of the prior combination spills. Strong overpressures were sensed on five of seven instrumented spills and observed on four of six uninstrumented tests. However, only one discrete shock was encountered in each case. All of the earlier tests exhibited either no shock effects or a series of shocks of variable strength.

The maximum overpressure detected for a hydrazine and pentaborane reaction was 3.15 percent based upon the standard TNT equivalent. The result accompanied a pentaborane lead on dirt. Other than the dry concrete surface, which in a few instances produced smooth burning without shock generation, the nature of the spill surface and/or the spill sequence had little effect on the amplitude of the resultant shock.

The explosive origin of shocks from hydrazine and pentaborane reactions, unlike the other combinations studied, appeared to be located within the confines of the spill basin. In addition, these shocks were observed at times varying from slightly after ignition to the moment of post-test purge. In all cases, the initiation of the shock was signaled by initial activation of the photocell or an increase in the amplitude of the photocell signal. In several instances, the shock wave was detected at station M-1 within about 6 milliseconds of photocell actuation or signal step-up; thus, the shock had traversed the 10 feet to station M-1 at an average speed of 1.3 to 1.5 times the speed of sound. Travel time between stations M-1 and M-2 corresponded to the speed of sound. Finally, shock strengths detected at M-2 were approximately equal in magnitude to the value observed at M-1.

These general observations were in disagreement with a model of simple spherical shock propagation. It was concluded that these shocks had not "shocked up" or reached steady state until the disturbance had covered an appreciable fraction of the distance between the source and station M-1. Further reaction was taking place and reinforcing the shock during this time interval. The behavior of the disturbance between stations M-1 and M-2 was believed to be steady and compatible with weak shock propagation theory.

It appeared probable that the driving reaction for these overpressure shocks was between hydrogen and air. Hydrogen is evolved by the reaction between hydrazine and pentaborane and by the pyrolysis of pentaborane as well. Under ideal conditions, hydrogen ignites and burns smoothly in air. However, with only two-wall confinement it is possible to induce explosive reaction. In these tests, the spill basin provided such confinement; further, the origin of shocks within the spill basin, peculiar to this combination, agreed with this process model. Tests with dirt and asphalt contributed additional confinement, through absorption and covering actions. It was concluded that shocks generated by hydrazine and pentaborane, arise as a result of hydrogen evolution and ignition with air, and require a minimum confinement.

Nitrogen Tetroxide and Pentaborane. Tests involving this propellant combination were uninstrumented. However, it was concluded from visual and photographic observation that this combination was potentially the most hazardous of those tested. Because of the severe nature of the explosions and damage associated with the uninstrumented tests, a decision was made to forego repeat experiments with pressure sensors and photocells.

All of the spills of this combination on various surfaces ignited with some audible explosions. Reports varied from a loud "pop" to an explosion that was heard for several hundred feet during a test on water. The explosion that occurred with nitrogen tetroxide and pentaborane appeared to coincide with ignition on the spill surface. It was probably the consequence of delayed ignition and accumulation of some liquid propellant mixture in the spill basin.

The effect of surface materials on the intensity of the explosion may have reflected a variation in ignition reactions. Concrete allowed rapid mixing and relatively fast ignition. Dirt and asphalt caused some scattering of propellant streams, absorption, and in addition, provided a heat sink. Thus, ignition was delayed and some accumulation took place. Water caused dilution of both propellants and quite large quantities were able to accumulate before the reactants were sufficiently concentrated to ignite.

LARGE-SCALE SPILL TESTS

A series of singular and multiple large-scale spill tests were performed to (1) describe the hazards associated with accidental bulk spillages of hydrazine, nitrogen tetroxide, chlorine trifluoride, and pentaborane, and (2) develop and/or verify safety and design criteria for the bulk storage and handling of these chemicals. These tests were performed at the Haystack Butte Spill Test Area, Edwards Air Force Base, California. The quantity of propellant used on each test ranged from 135 to 1800 pounds.

The Haystack Butte Area is ideally located for spillages of bulk quantities of high-energy propellants. The area is isolated, uninhabited, and water or soil contamination from toxic spills does not present a problem. Prevailing winds carry toxic vapors a minimum of six miles before reaching a public highway, and 30 miles to the nearest town.

TEST SETUP

The test facility was located on and adjacent to a 40 x 60 ft concrete pad. A carbon-steel tray 20 x 20 ft x 2-ft-deep, of all-welded construction was located on the downwind (east) side of the pad. Blast instrumentation, motion picture cameras, and air-sampling instruments were positioned around the pad as shown in Fig.28 and 29.

Propellant spill systems were designed to provide for safe and reliable propellant handling operations with a minimum of subsystems and components. Spill tanks were fabricated of both carbon steel and stainless steel with capacities of 150 and 165 gallons. All tanks were cylindrical in construction with a 6-inch-diameter port at the bottom. A tank setup for a singular spill test is shown in Fig.30 and for a multiple spill in Fig. 31.

A pneumatically operated rupture device was attached to the bottom flange of the spill tanks as shown in Fig. 32. This device, upon activation by

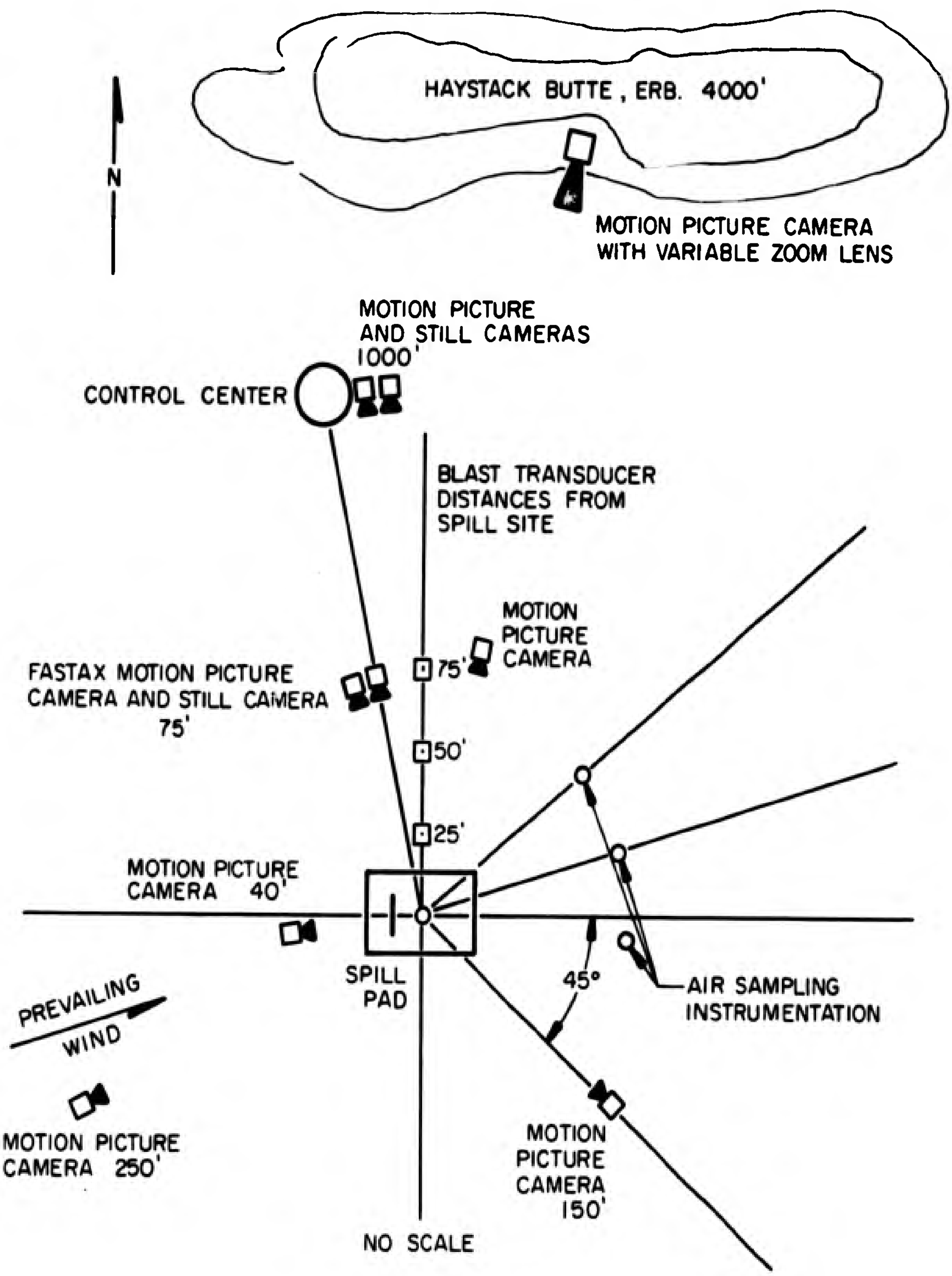


Figure 28. Blast Transducer and Motion Picture Positions at Haystack Butte, ERB

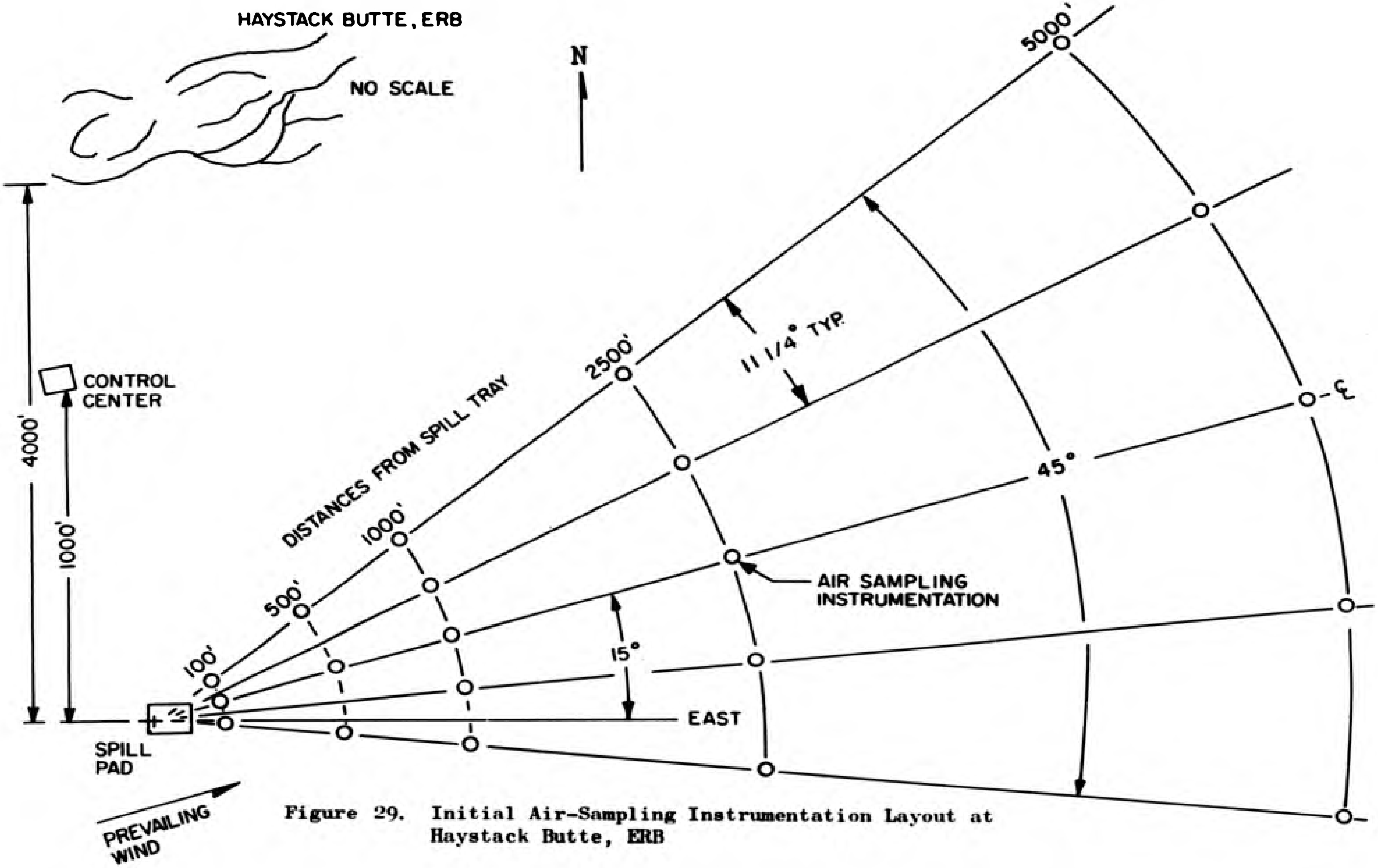


Figure 29. Initial Air-Sampling Instrumentation Layout at Haystack Butte, ERB

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Figure 30. Spill Tank for Singular Spill of Propellants

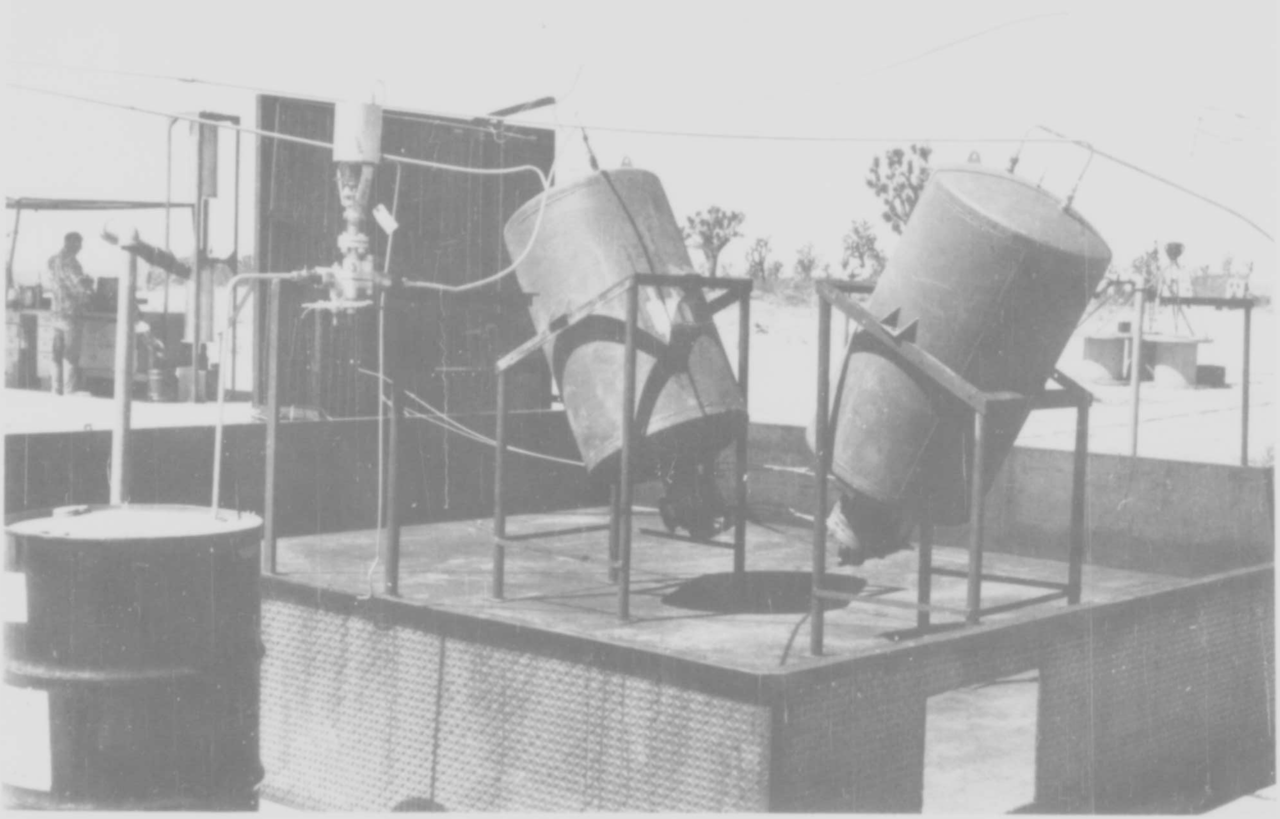

Figure 31. Spill Tanks for Simultaneous Spill of Propellants

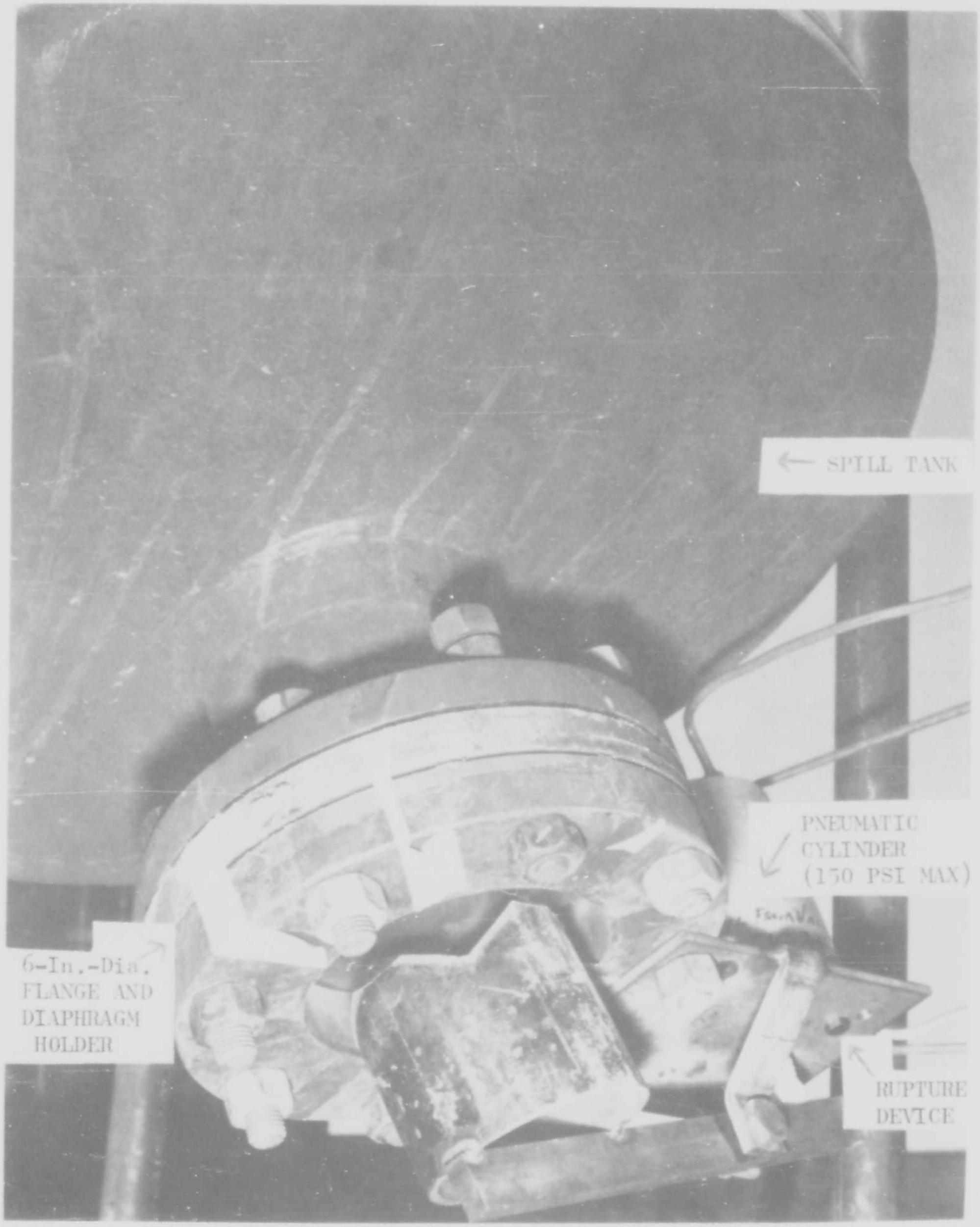

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Figure 32. Rupture Device Used For Piercing the Burst Diaphragms on the Propellant Spill Tanks

a remote electrical signal, pierced a thin metal diaphragm to give near-instantaneous spillage of the propellant on-board.

The hydrazine and nitrogen tetroxide spill systems were almost identical in configuration, and are schematically presented in Fig. 33 and 34, respectively. The setup consisted of the spill tank, rupture device, transfer system, pressurization system, vent systems, and gaseous purge system. These systems were fabricated of compatible materials and components, and arranged in a manner to prevent liquid traps and reduce to a minimum the number of joints. All valves were normally closed and remotely controlled with the exception of the nitrogen tetroxide cylinder shutoff valves which were hand-operated.

The chlorine trifluoride spill system (Fig. 35) was similar to the nitrogen tetroxide system except for the addition of a gaseous fluorine passivation system. Valves, tubing, and tanks were fabricated of stainless steel, and copper was used for gaskets and valve seats; Teflon chevrons were used for valve stem packings. All components in the system were cleaned with a dilute nitric acid-hydrofluoric acid solution, flushed with distilled water, and completely dried before assembly. The system was then purged with nitrogen gas and passivated with elemental gaseous fluorine. All valves were normally closed and remotely controlled with the exception of the chlorine trifluoride cylinder shutoff valves, which were manually operated.

The pentaborane spill sytem (Fig. 36) was similar to the hydrazine system except for the addition of a kerosene (RP-1) purge in the propellant transfer line which diluted any residual propellant in the line. Prior to system modification, repair, or teardown, the residual pentaborane-kerosene solution in the transfer line was neutralized with concentrated ethyl alcohol. The entire system was fabricated of compatible materials and components, arranged to prevent liquid traps. All valves were normally closed and remotely controlled with the exception of the pentaborane cylinder shutoff valves, which were hand-operated.

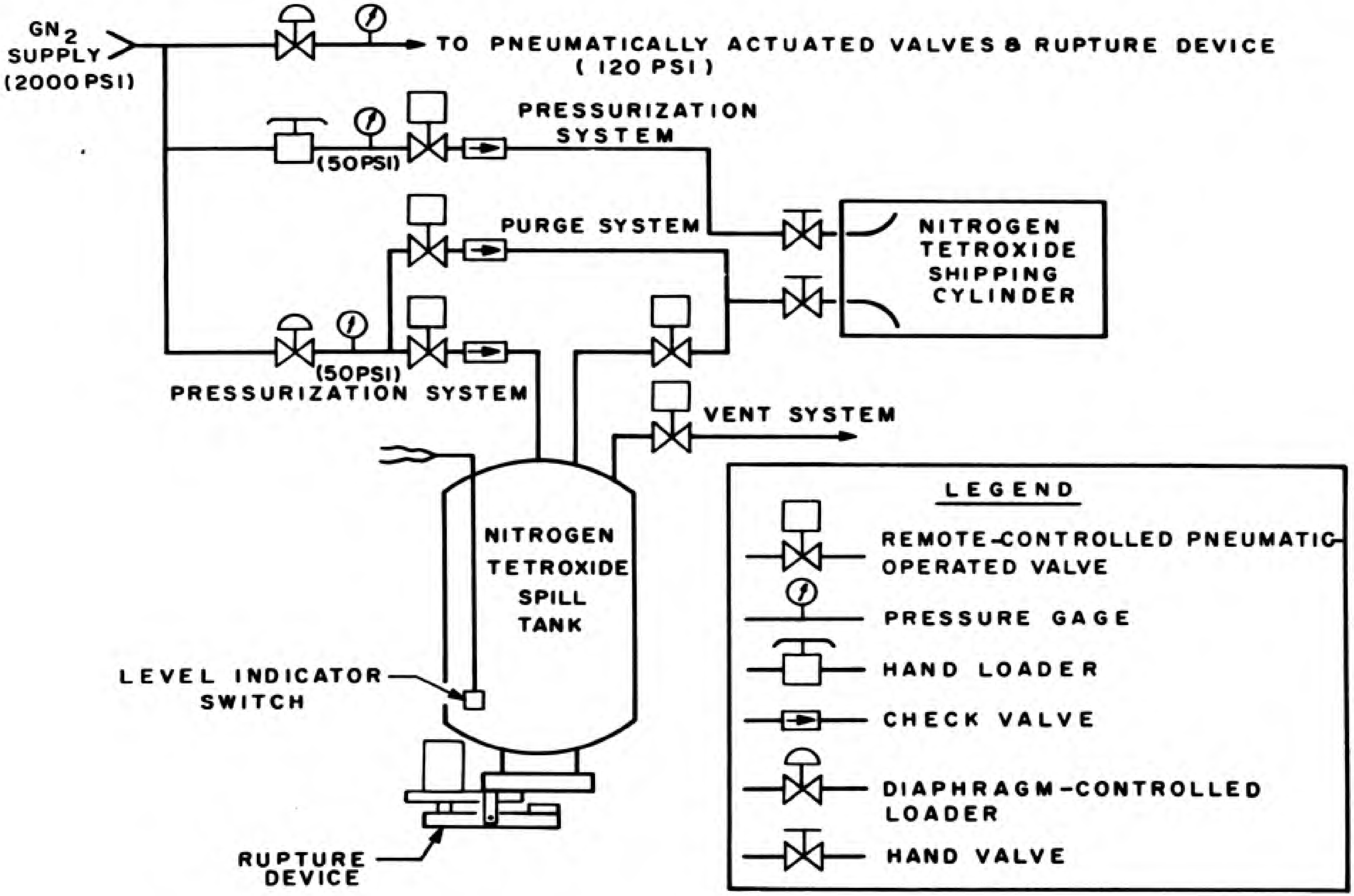

Figure 33. Schematic Diagram of the Nitrogen Tetroxide Spill System

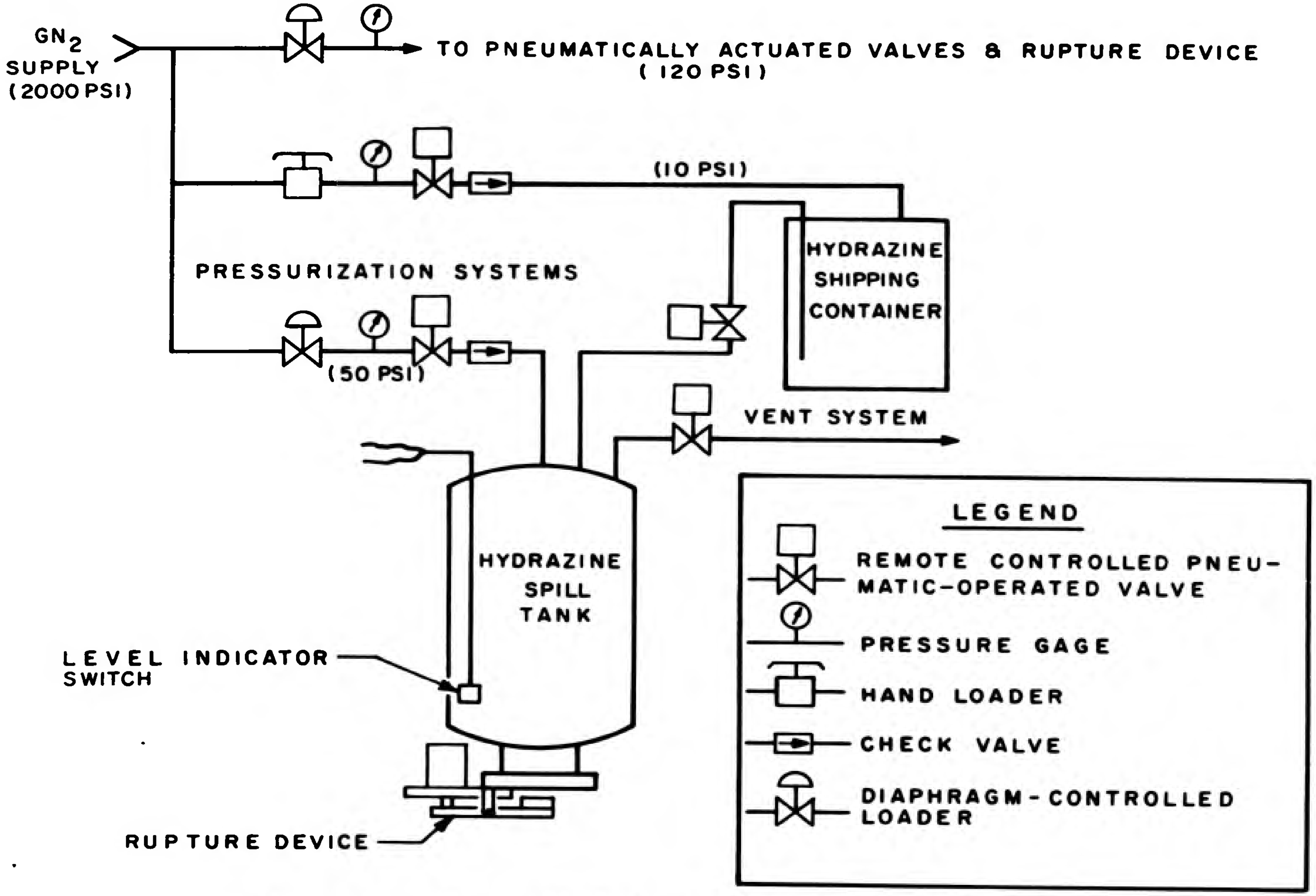

Figure 34. Schematic Diagram of the Hydrazine Spill System

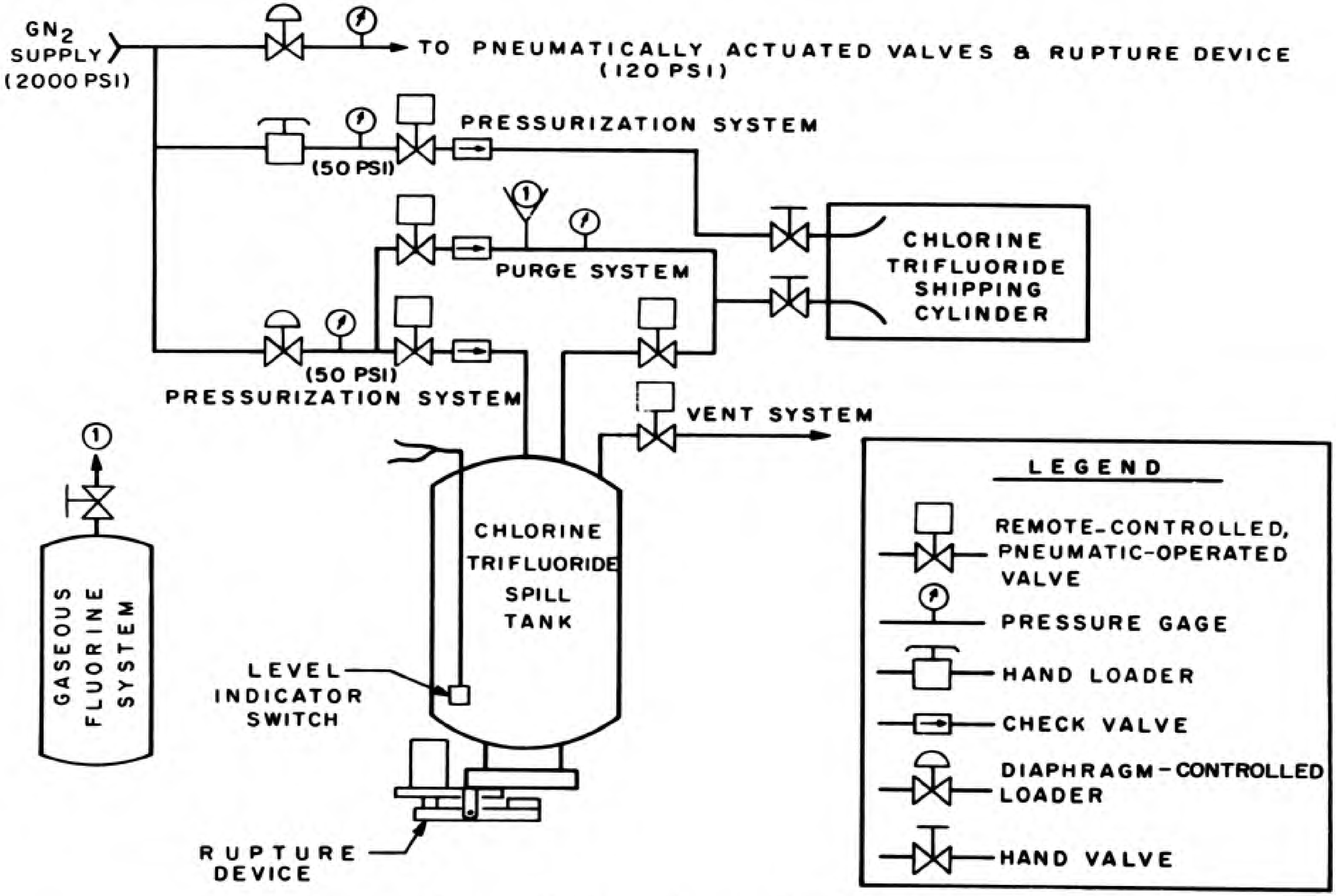

Figure 55. Schematic Diagram of the Chlorine Trifluoride Spill System

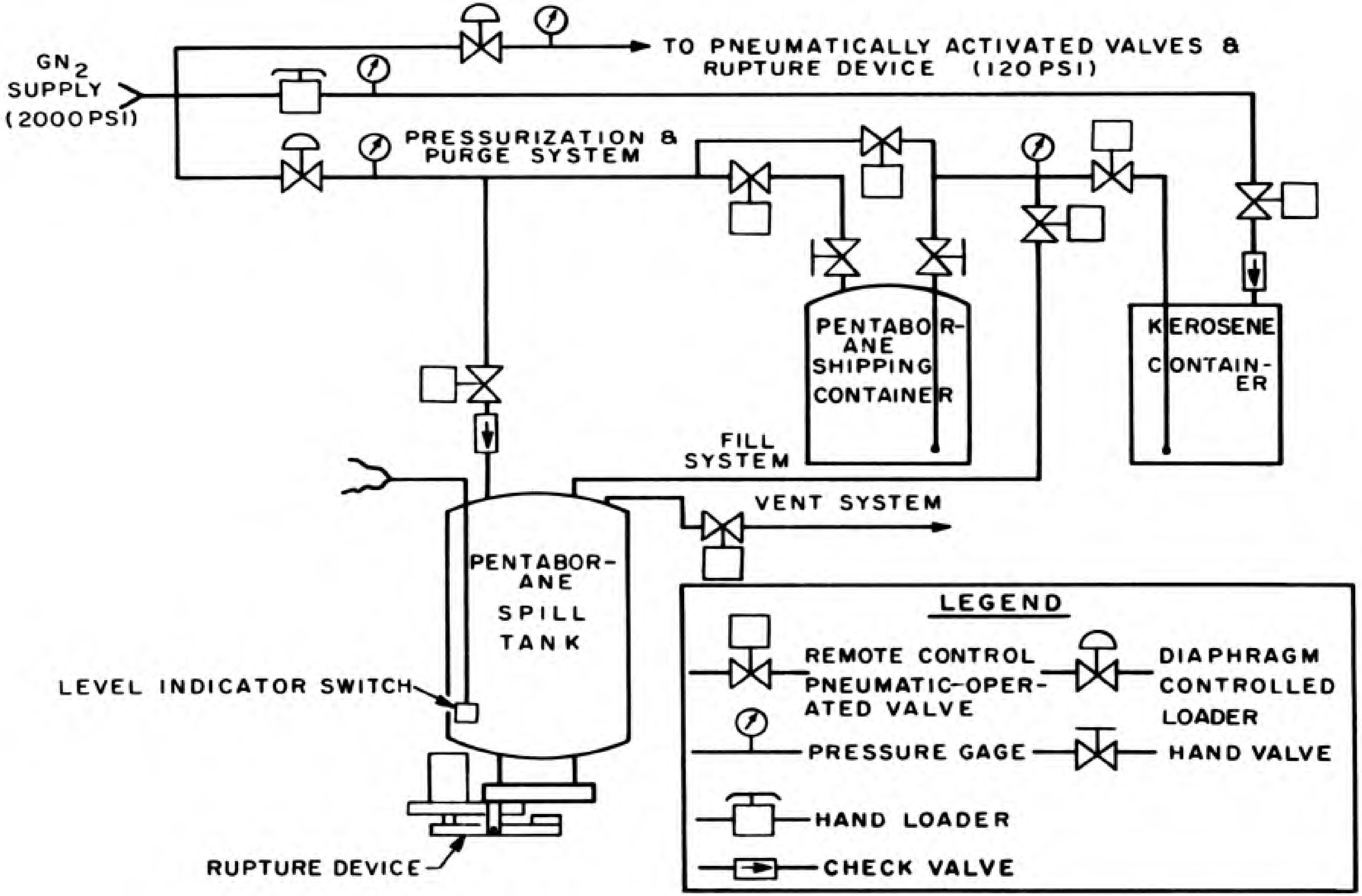

Figure 56. Schematic Diagram of the Pentaborane Spill System

The pneumatic control equipment was mounted on a vertical steel plate attached to a wall of the spill tray. Nitrogen gas at 2000 psi for pressurization, purges, and pneumatic valve operation was supplied by a gaseous nitrogen trailer. Electrical power was provided by a portable 110-volt a-c generator and wet-cell, 28-volt storage batteries.

A drain opening was provided in the spill tray to wash out residual unburned propellants and combustion products. A water-deluge system was mounted along the walls of the tray and was used during some of the tests to determine the effect of water sprays on the behavior of the spilled propellants. A water-spray system was installed also to protect the pneumatic control panel from overheating during the tests.

The control center was located 1000 feet from the spill tray and housed the instrumentation recording equipment and remote control equipment for operating valves, cameras, and air-sampling apparatus.

INSTRUMENTATION

The instrumentation used in this program consisted mainly of blast-pressure transducers, still and motion picture cameras, and air-sampling devices. These instruments were controlled remotely.

Blast Measurements

Three Photocon microphone transducers, model 304 AT, were used to detect overpressure shocks. These transducers were located 25, 50, and 75 feet from the center of the spill tray (propellant impingement point) at ground level for a "side-on" overpressure measurement. The mounting arrangement is shown in Fig. 37. Signals generated by these devices were recorded on magnetic tape with an Ampex model 306-7 recorder. The sound tape was replayed and recorded by a Miller oscillograph. The transducers were calibrated by means of a mercury manometer to the following ranges: 0 to 20 psi for that located at the 25-foot station, 0 to 15 psi for that

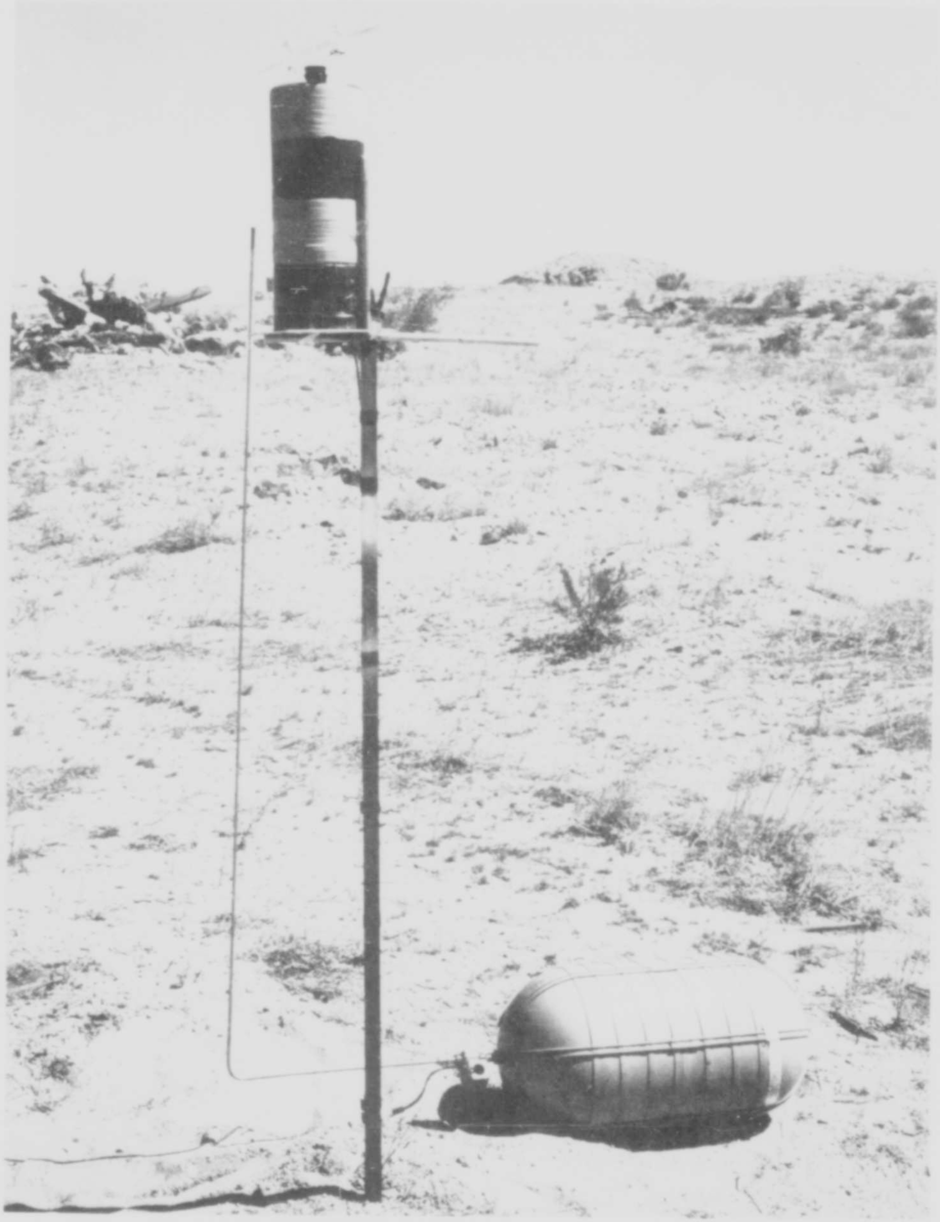

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Figure 38. Air Sampling Equipment

eight months to procure continuous-recording vapor detectors which were being developed by several companies. A limited number of vapor detectors were obtained for evaluation. These instruments were deployed at selected positions near the spill tray (100 to 600 ft) in alignment with the anticipated wind direction.

Two basic types of direct-recording vapor detectors were evaluated. Type A utilized an ionization chamber to detect an aerosol, which is formed from the propellant vapor. A very small change of particulate matter causes a drop in the flow of ionic current. Thus, the effect of the aerosol on the conductivity of the ion chamber is a measure of the concentration of the propellant vapor. Continuous ionization of the sample was provided by an alpha source. Figure 39 shows the instrument on the improvised field installation. Type B is an oxidizer vapor detector and utilizes an electrolyte. The incoming oxidizer vapor reacts with the electrolyte to reduce the internal impedance of the cell. This variation causes a corresponding change in current flow between the electrodes which is an indication of vapor concentration.

The pentaborane vapor sampling instruments were a modification of the evacuated-bottle type devices used on the first three tests. The 2100 cubic-inch, stainless-steel tanks were evacuated to pull an air sample through a "U" tube trap containing a liquid hydrocarbon solvent. The trap was immersed in a trichloroethylene dry-ice bath.

SAFETY PRECAUTIONS

Propellant handling and testing operations were restricted to periods of satisfactory wind conditions, which usually ranged from four to six hours in a working day. The spill site was arranged so that the working area was upwind of the spill tray and propellant storage during the prevailing-wind period.

Propellant transfer operations, with the exception of opening the shutoff valves in the propellant shipping cylinders, were performed remotely. Gra-Lite suits and Scott-Paks were available, and maintained in operating

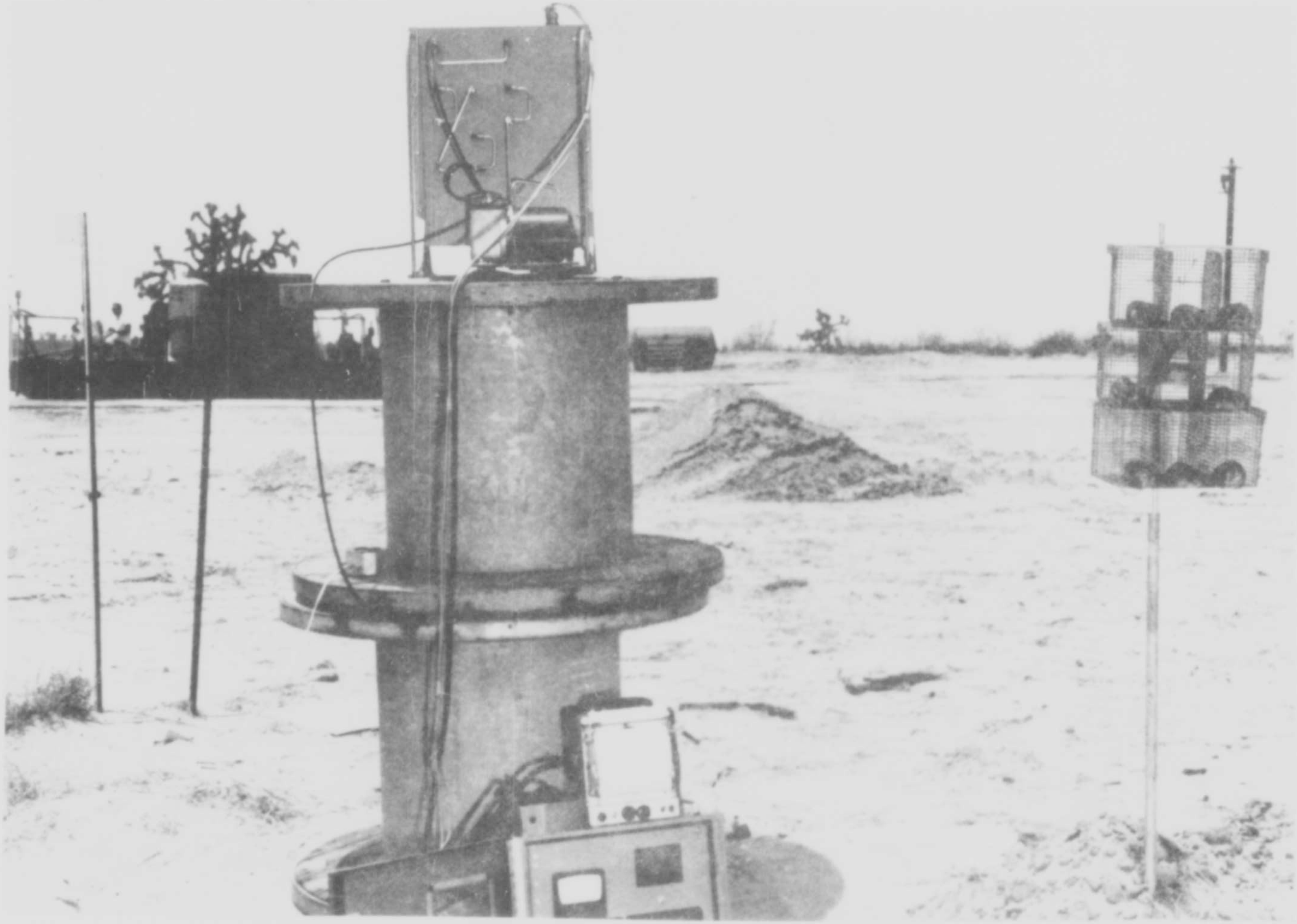

Figure 39. Typical Field Installation of Type A Vapor Detector and Test Animals

order at all times.. Air Force Rocket Base personnel provided fire and first-aid support during propellant handling and testing operations.

The spill tests were performed within five minutes after the propellant tanks were loaded. Following the tests, the propellant systems were remotely purged and the propellants disposed of by burning, diluting, or vaporizing. The shipping cylinders shutoff valves were manually closed before support personnel were allowed into the spill area. All personnel remained upwind of the spill tray until the propellant vapors had completely dissipated. A portable detector was used in those tests involving pentaborane to ensure that the spill area was not contaminated prior to and after the tests. A water hose and safety shower were available at the test area for emergency use.

LOADING PROCEDURES

The propellant loading procedures were initiated after the test area was completely secured and the operation of the various test instruments and components verified. When animal studies were required, the hamsters were placed in their cages at each air-sampling station prior to the loading operations. (A complete discussion on the animal studies is presented in Appendix C.)

The procedures utilized for loading the four propellants were basically identical. They consisted of opening the shipping cylinder shutoff valves, spill tank vent valve, fill valve and shipping cylinder pressurizing valve, in the sequence listed. When the propellant in the spill tank reached the desired level, as indicated by a red light on the control panel, the transfer operation was completed by closing the fill valve. The system was then secured by closing the spill tank vent valve and the shipping cylinder pressurizing valve. (The shipping cylinder shutoff valves were not closed until after the test.)

TEST PROCEDURE

Following the propellant trasnfer securing operation, the spill tank was pressurized to 50 psig by opening the spill tank pressurizing valve. This additional head assured a rapid expulsion of the propellant upon burst diaphragm failure. The proper wind conditions were then verified with a portable velometer.

Countdown started at X-10 seconds. This timing action provided a reference point for the instrumentation and photo personnel to synchronize their equipment. At X-0, the spill tank rupture device was actuated resulting in the spillage of the propellant. Following propellant burning and/or vaporization, the fill line was purged with gaseous nitrogen and the spill system secured.

TEST RESULTS

A total of nine large-scale spill tests was performed at the Haystack-Butte Area. These tests consisted of five singular spills, three multiple spills, and one heating test. A description of these tests is shown in Table 5.

Test No. 1

This test consisted of a singular spillage of 1800 lb of nitrogen tetroxide, immediately followed by a water deluge. Incomplete rupture of the burst diaphragm increased the duration of the spillage from the anticipated 1.5 seconds to 25 minutes. The large surface area of the spill tray (400 sq ft) coupled with the water deluge caused very rapid propellant boiloff.

The water was applied at a rate of about 30 gal/min using coarse-spray nozzles. This configuration provided a water blanket over the tray and did not visually reduce the effluent nitrogen dioxide vapor.

TABLE 5

LARGE-SCALE SPILL TESTS

Test No.	Date	Propellant Type and Quantity	Instrumentation				
			Blast	Temp and Fireball Size	Camera	Vapor Conc.	Animal Studies
1	23 August 1960	1800 lb nitrogen tetroxide with water deluge			X	X	X
2	30 August 1960	1800 lb NTO			X	X	
3	21 Sept. 1960	900 lb NTO--700 lb hydrazine			X	X	
4	25 May 1961	500 lb CTF--500 lb hydrazine	X	X	X		
5	6 June 1961	750 lb CTF			X	X	X
6	20 June 1961	750 lb CTF with water deluge			X	X	
7	3 July 1961	500 lb pentaborane	X	X	X	X	
8	18 July 1961	275 lb pentaborane-- 100 lb hydrazine	X	X	X	X	X
9	16 August 1961	135 lb hydrazine heating (90 percent ullage)		X	X		

The majority of the spilled propellant vaporized within 35 minutes after the burst diaphragm was initially ruptured. Nitrogen dioxide vapors were given off from the residual nitric acid solution in the tray until the solution was further diluted and flushed from the tray.

Analysis of the air samples taken by the evacuated-bottle method failed to indicate a significant amount of propellant vapor. These findings were considered in error since the sampling instruments were surrounded by highly concentrated vapor clouds during the sampling period.

Hamsters exposed to the effluent vapors appeared to be unaffected. A detailed hospital report on these animals is presented in Appendix C.

Test No. 2

This test consisted of a singular spill of 1800 lb of nitrogen tetroxide on a dry spill tray. Incomplete rupture of the burst diaphragm resulted in an expulsion period of 2 minutes. The propellant boiloff was relatively slow because of self-refrigeration; a period of 45 minutes was required for complete propellant evaporation.

Analysis of the air samples indicated only trace quantities of the propellant. These findings were again in disagreement with the observed phenomena. As shown in Fig. 40, the propellant vapor cloud retained its shape for several hundred yards downwind and passed across the instruments positions. Visible areas of the vapor cloud exceeded 50 ppm.

Test No. 3

This test was a multiple spill of 900 lb of nitrogen tetroxide and 700 lb of anhydrous hydrazine on a dry spill tray. Near-instantaneous release of the propellants resulted in immediate ignition. A large fireball prevailed for about 3 to 4 seconds and propellant burning was completed in about 4 to 5 minutes. The effluent vapor cloud traveled close to the ground as shown in Fig. 41 (wind velocity 20 KTS).

Figure 40. Cloud from 1800-lb Nitrogen Tetroxide Spill Under Dry Conditions (Visible areas of the cloud exceed 50 ppm)

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Figure 41. Simultaneous Spill of 900 Pounds Nitrogen Tetroxide and 700 Pounds Hydrazine on a Dry Spill Tray (Test No. 3)

Several weak hydrazine vapor-air explosions were heard throughout the test. However, these overpressures were not recorded due to a malfunction in the tape instrument.

Post-test examination of the spill area revealed only minor damage. This damage consisted of ruptured fill and vent lines in the hydrazine spill system and melting of aluminum lines within the spill tray. The failure of the hydrazine fill and vent lines was apparently caused by the thermal decomposition of residual hydrazine within these lines.

Analysis of the air samples taken during the test gave negative results again.

Instrumentation Changes

Some instrumentation changes were made in the test setup after the first three tests were performed. First, the evacuated-bottle type sampling devices were replaced by the continuous-recording vapor detectors. These detectors were described previously in the Instrumentation section. Second, a grid was installed in the spill pad to provide fireball-size measurements. The grid was fabricated of 4 x 1-inch boards marked at two-feet intervals, and arranged in a plane perpendicular to the 75-ft camera position. Third, a grid was installed in the spill tray to measure the temperature distribution within the fireball. The grid was fabricated of 1-inch steel channels and utilized temperature-sensitive paint that changed color with changes in temperature, retaining the color at the highest temperature reached. The paint was placed between two thin aluminum plates. Figure 42 shows both grid arrangements.

Test No. 4

This test was a multiple spill of 500 lb of chlorine trifluoride and 500 lb of anhydrous hydrazine on a dry tray. The propellants were released within a period of 1 second and ignition was immediate upon

Figure 42. Temperature and Fireball-Size Grid Location for a Multiple Propellant Spill Test 4,122 61

propellant contact. Propellant reaction was very rapid and erratic, and lasted about 4 seconds. The blast instrumentation did not sense any overpressures. The flame was white in appearance during the initial reaction (Fig. 43) and changed to an orange color upon disappearance of the fireball. Apparently most of the spilled chlorine trifluoride was burned or thrown out of the spill tray during the initial reaction. The residual hydrazine in the tray burned for about 2 minutes.

The fireball reached a maximum diameter of 30 feet in 2 seconds and disappeared shortly thereafter. This time duration was insufficient to sense steady-state temperatures. As a consequence, a maximum temperature of only 240 F was detected.

Several vapor detectors were positioned downwind during this test. However, all the instruments malfunctioned and no vapor data were recorded. Post-test examination of the spill area showed no damage.

Test No. 5

The test consisted of a singular spillage of 750 lb of chlorine trifluoride on a dry tray. Propellant expulsion was completed in less than 1 second. The initial vapor cloud was green-yellow and turned to brown after 2 to 3 seconds. Complete propellant evaporation was attained in about 9 minutes.

Some of the propellant in the tray escaped through the drain opening, setting the tar joints in the concrete pad afire. This reaction produced several weak overpressure shocks.

The propellant reduced the spill tray surfaces but no fires or overpressures were detected from this reaction. No damage was sustained by the test equipment as a result of the spillage.

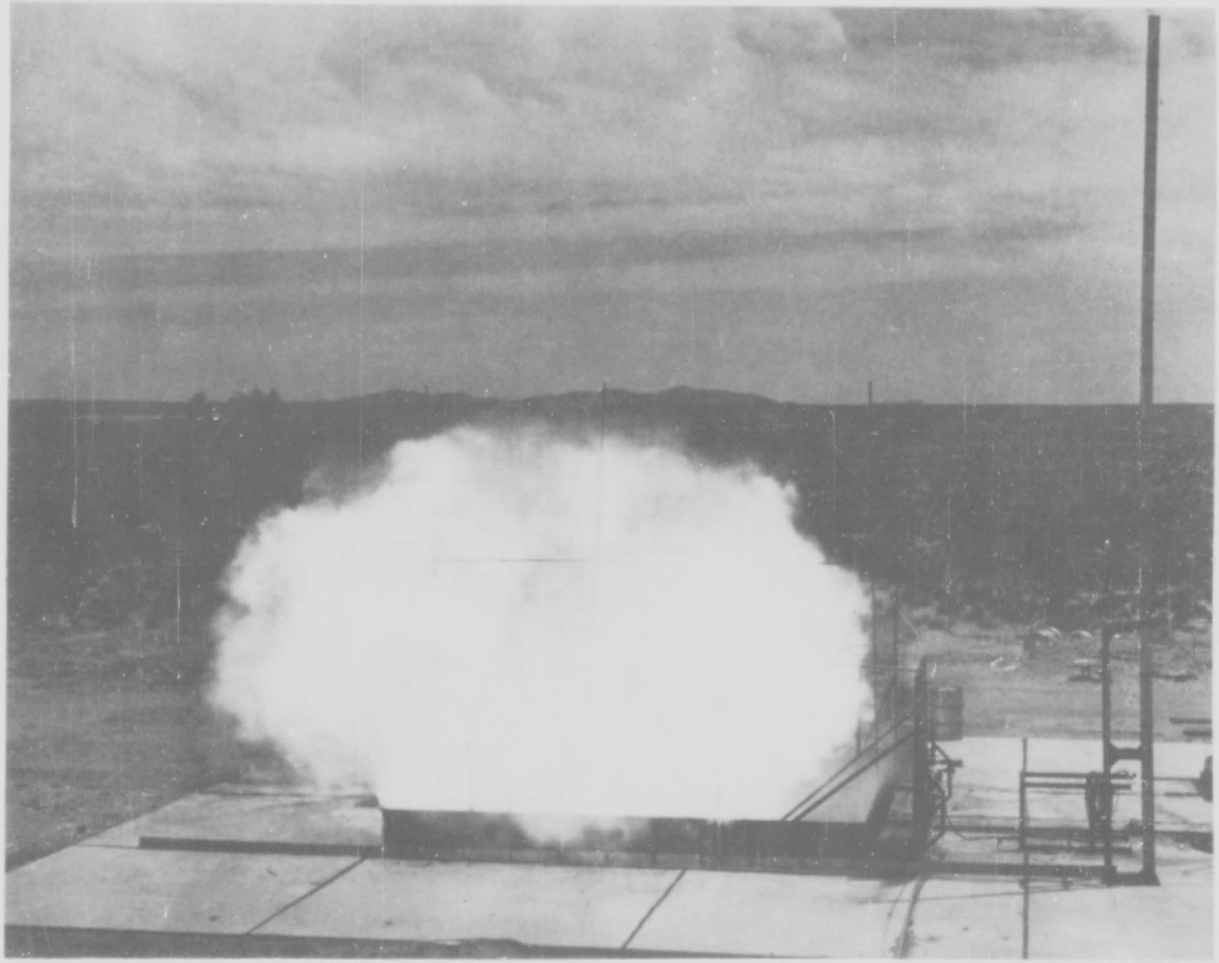


Figure 43. Multiple Spill of 500 Pounds Chlorine Trifluoride and 500 Pounds Hydrazine in a Dry Spill Tray (Test No. 4)

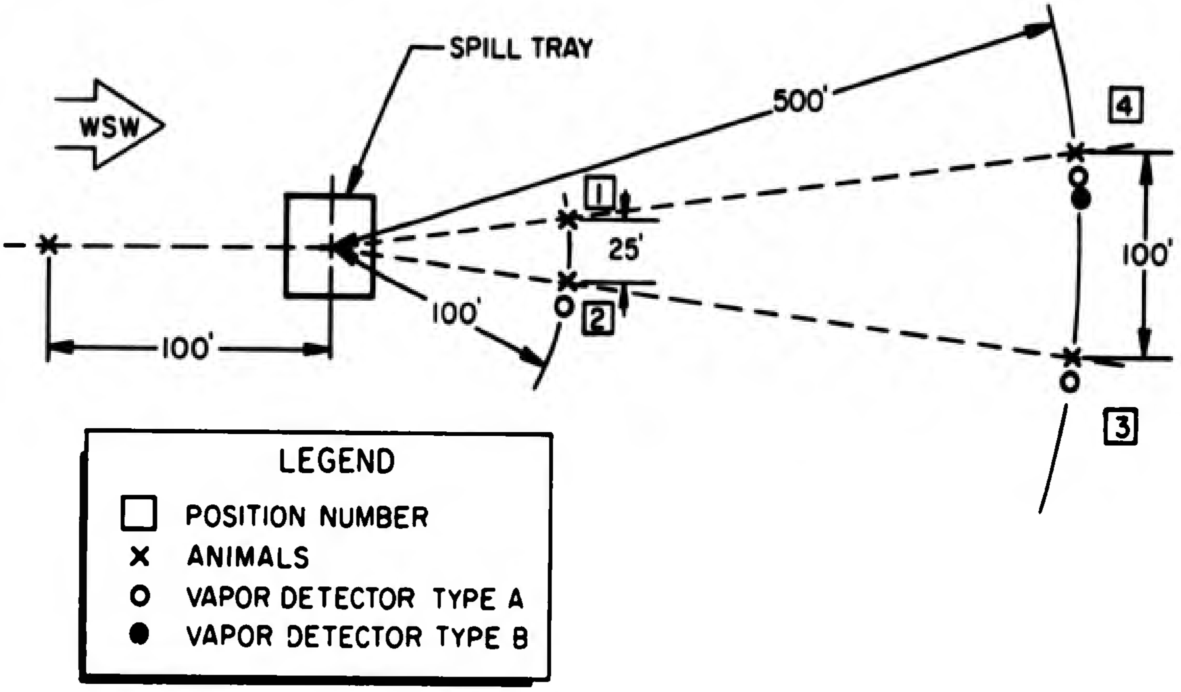
The weather conditions at the time of the spillage were as follows:

Air Temperature, 85 F

Relative Humidity, 23 percent

Wind Velocity, 10 knots WSW (gust to 20)

Vapor detectors and test animals were positioned for the spill as shown below.



The type A detectors operated satisfactorily with very good response and recovery times; the type-B detector did not respond to the presence of the propellant vapor at any time during the test.

During the propellant loading operations, the spill tank vent valve was maintained opened, thus releasing about 3.5 lb/min of gaseous chlorine trifluoride. The record obtained from the type A detector at position 2 during this operation is shown in Fig. 44. A maximum vapor concentration

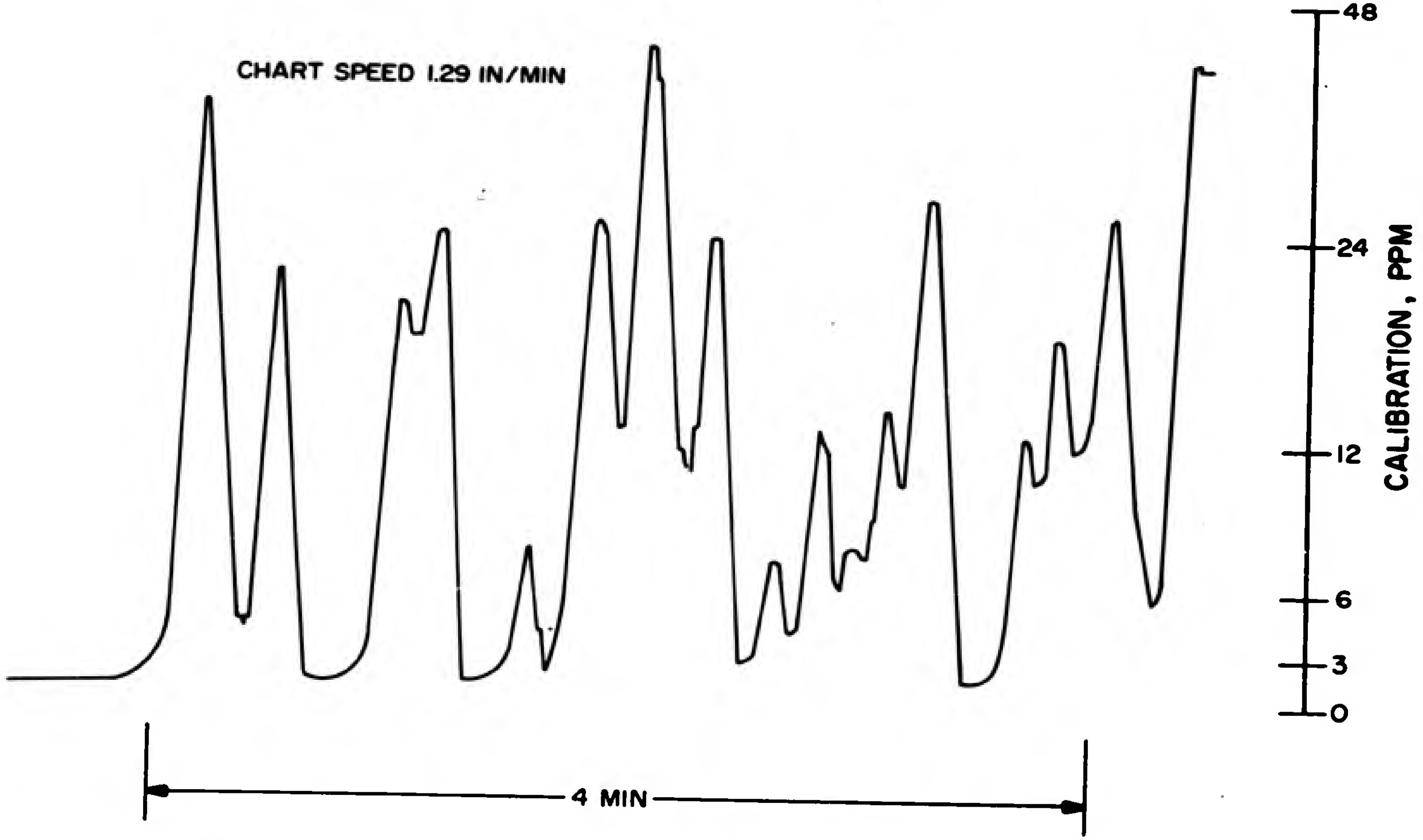


Figure 44. Response of the Type A Vapor Detector (Position 2) to Chlorine Trifluoride Vapors Released During Loading Operations

of 15 ppm was detected at position 4. The response of the instruments demonstrated that the process of vapor diffusion in air is extremely erratic. In some cases, the vapor diffused very slowly and flowed in channels or rivers at very high concentrations. This phenomenon makes it difficult to measure average vapor concentrations in an open area.

The records produced by the type A detectors during the spill test are shown in Fig. 45, 46, and 47. Although these instruments responded adequately, their calibration range was insufficient to record maximum concentrations.

As mentioned previously, test animals (hamsters) were also exposed to the effluent propellant vapor. A hospital report on these animals is presented in Appendix C.

Test No. 6

This test was a singular spill of 750 lb of chlorine trifluoride with a simultaneous water deluge. Propellant expulsion was again completed in less than 1 second. The vapor cloud initially was yellow-green in color but turned brown in about 2 to 3 seconds. The propellant boiloff appeared to be faster than that experienced in Test No. 5. This was probably caused by the exothermic reaction of the propellant with water. In addition, the heat generated by the reaction caused the effluent propellant vapors to stack approximately 25 feet before traveling downwind, with the majority of the vapors passing over the detectors. Small overpressure shocks were detected about 15 to 30 seconds after propellant spillage. These overpressures apparently originated in the corners of the spill tray from the reaction of the propellant with water and/or contaminants, but were not of sufficient magnitude to be detected by the blast instrumentation. The propellant in the tray was completely vaporized or reacted within four minutes. No damage was sustained by the spill system.

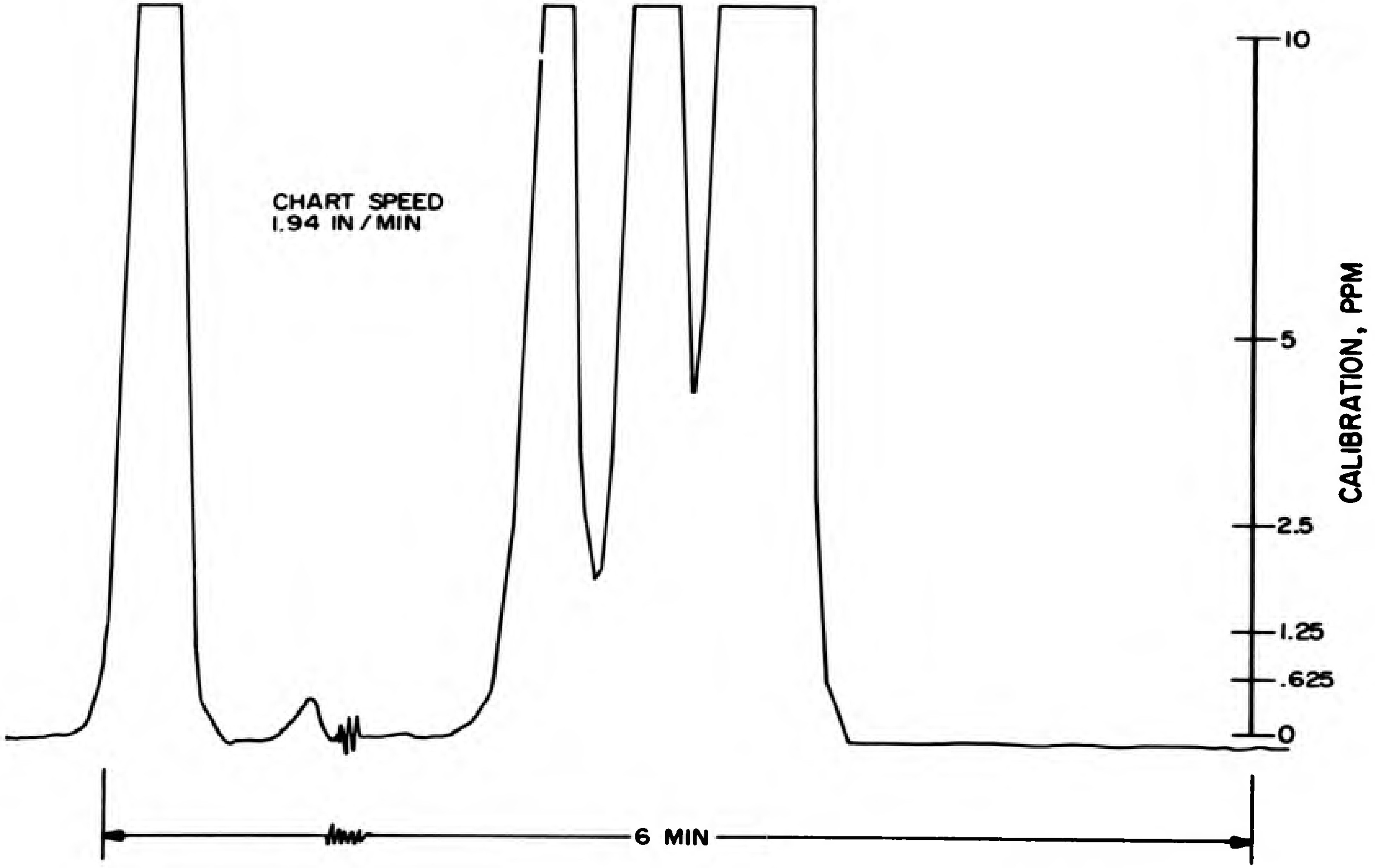


Figure 45. Record Produced by Vapor Detector A at Position 4 During a Spill of Chlorine Trifluoride

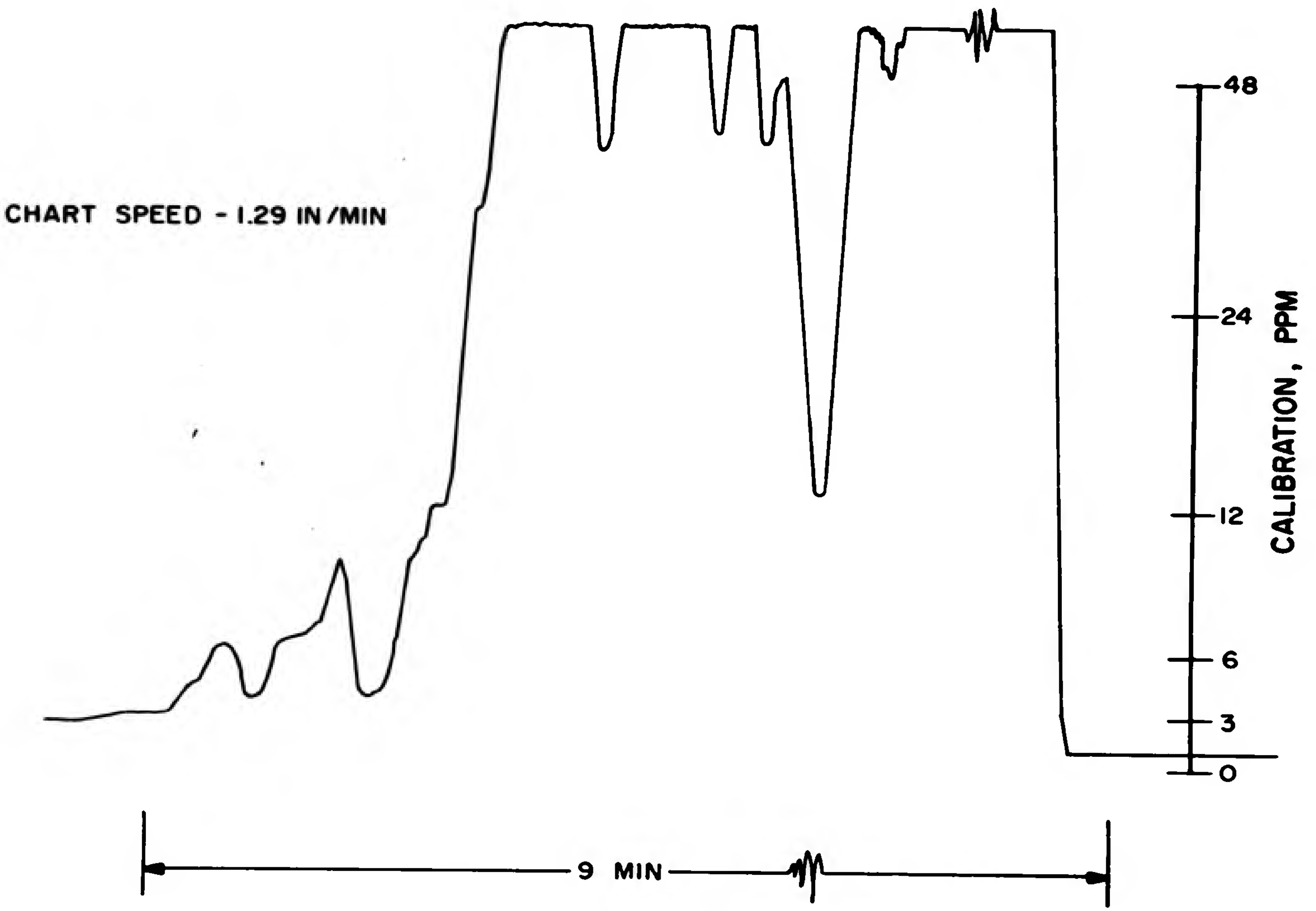


Figure 46. Record Produced by Vapor Detector A at Position 2 During a Spill of Chlorine Trifluoride

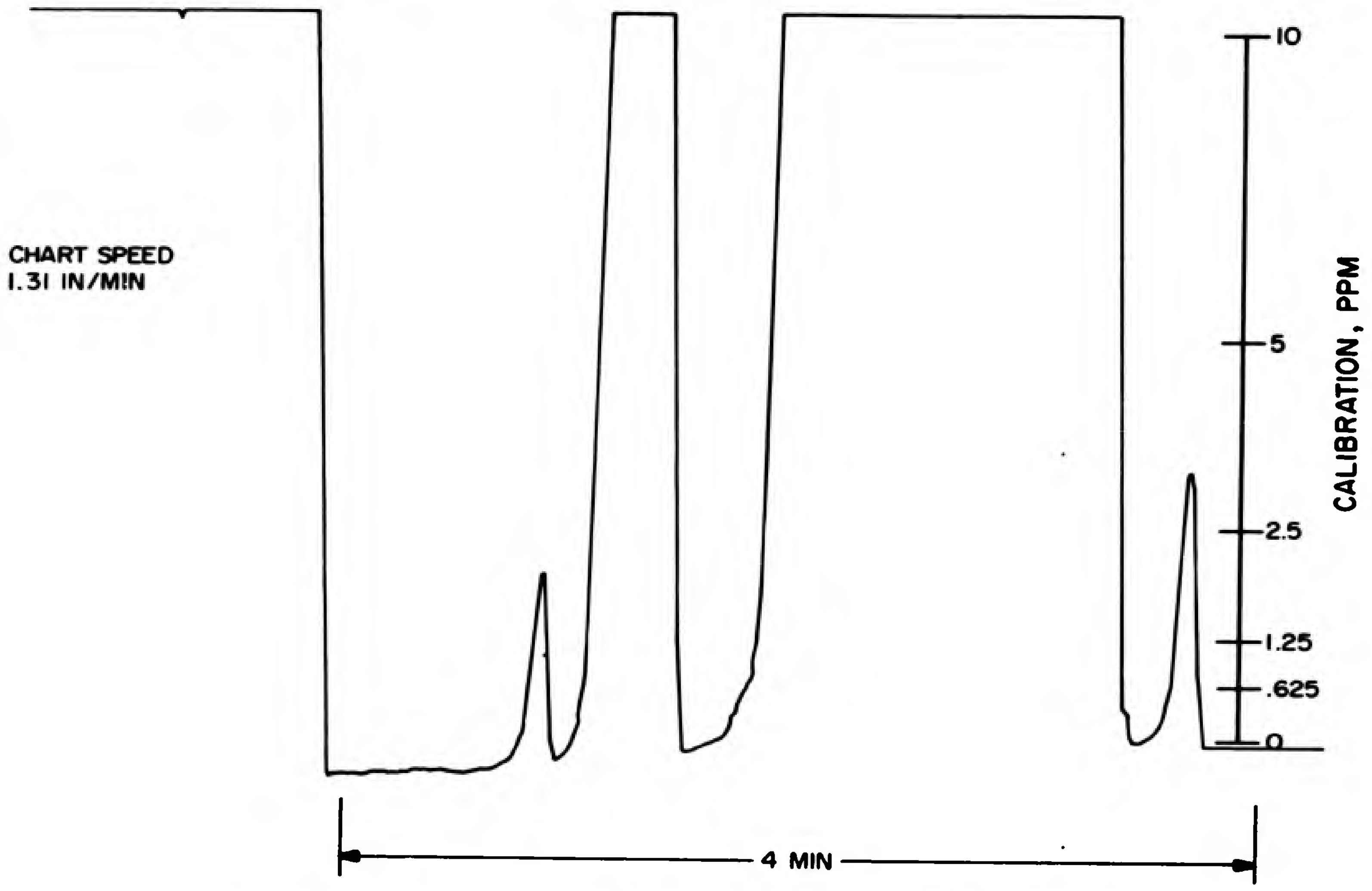
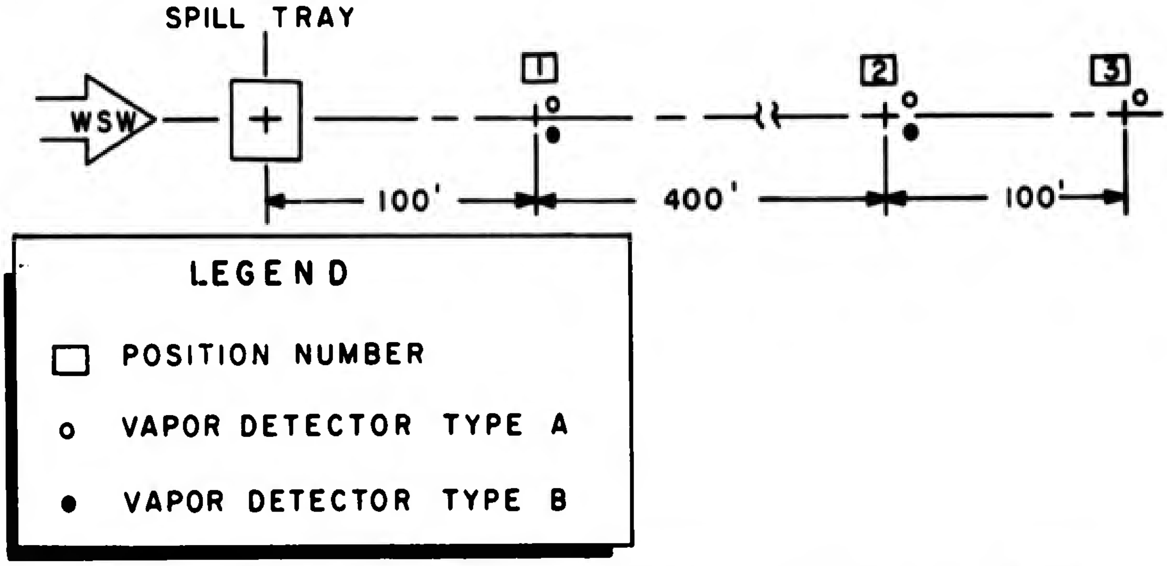


Figure 47. Record Produced by Vapor Detector A at Position 3 During a Spill of Chlorine Trifluoride

The weather conditions at the time of the spill were as follows:

Air Temperature, 108.8 F
Relative Humidity, 16 percent
Wind Velocity, 5 to 6 knots WSW

The vapor detectors were positioned for the test as shown below:



Vapor detectors type A operated again satisfactorily with good response and recovery times. Type B was operational during the test but with very poor sensitivity. Figure 48 shows the response of the two types of detectors placed at position 2. The records obtained from the type A detectors at positions 1 and 3 during the spill test are shown in Fig. 49 and 50, respectively.

Test No. 7

This test was a singular spill of 500 lb of pentaborane on a dry spill tray. The test was originally scheduled as a multiple spill of hydrazine and pentaborane, but difficulties with the test system prevented loading and spillage of the hydrazine.

Propellant ignition was experienced immediately following rupture of the burst diaphragm, and complete expulsion was attained in less than 2 seconds. The rapid release rate of the propellant resulted in violent burning over the entire surface of the spill tray as shown in Fig. 51. The fireball reached a maximum diameter of 40 feet within 3 seconds.

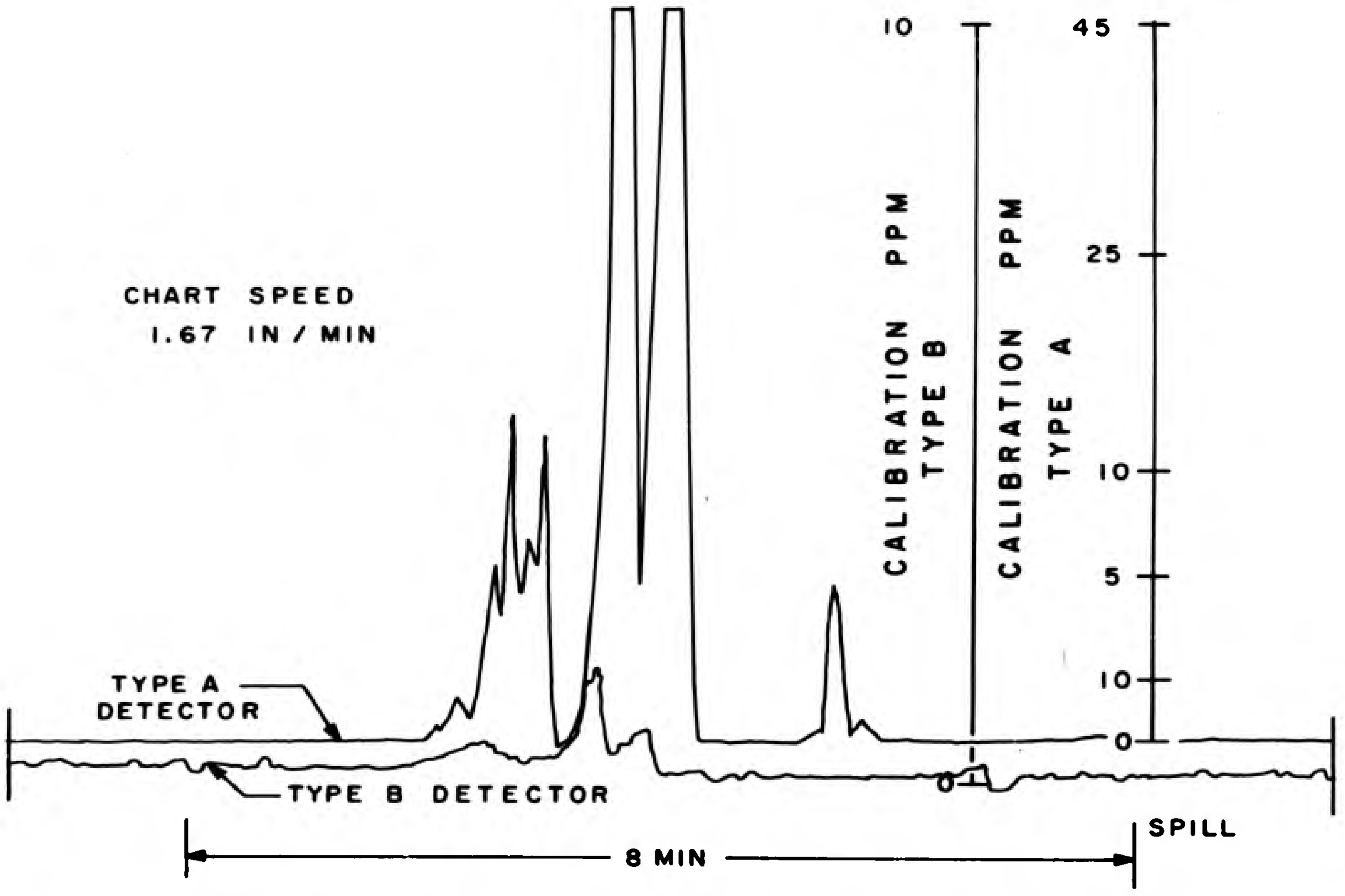


Figure 48. Response of Types A and B Vapor Detectors (Position 2) to Gaseous Chlorine Trifluoride During Spill Test No. 6

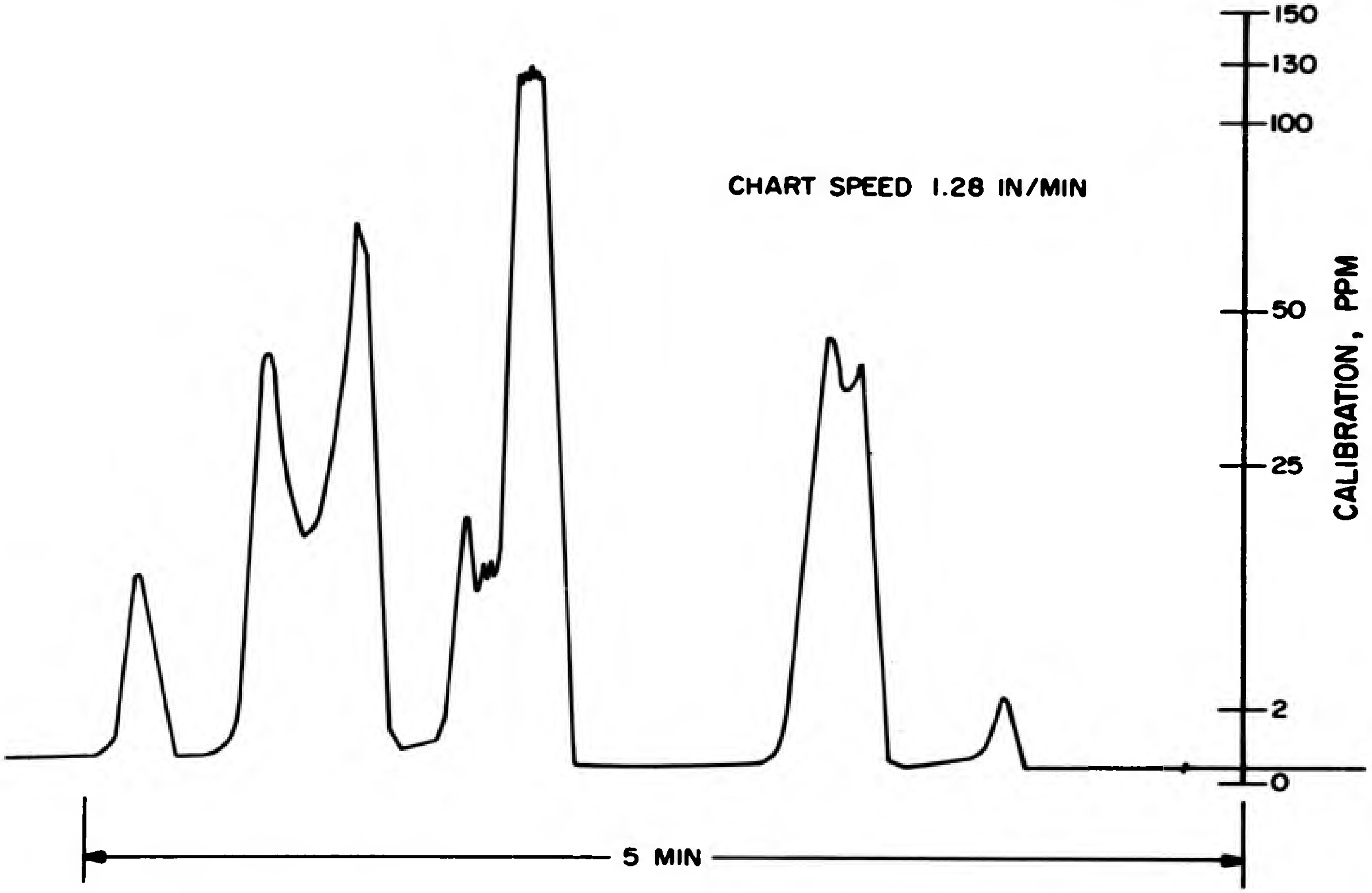


Figure 49. Record Produced by Vapor Detector A at Position 1 During a Spill of Chlorine Trifluoride

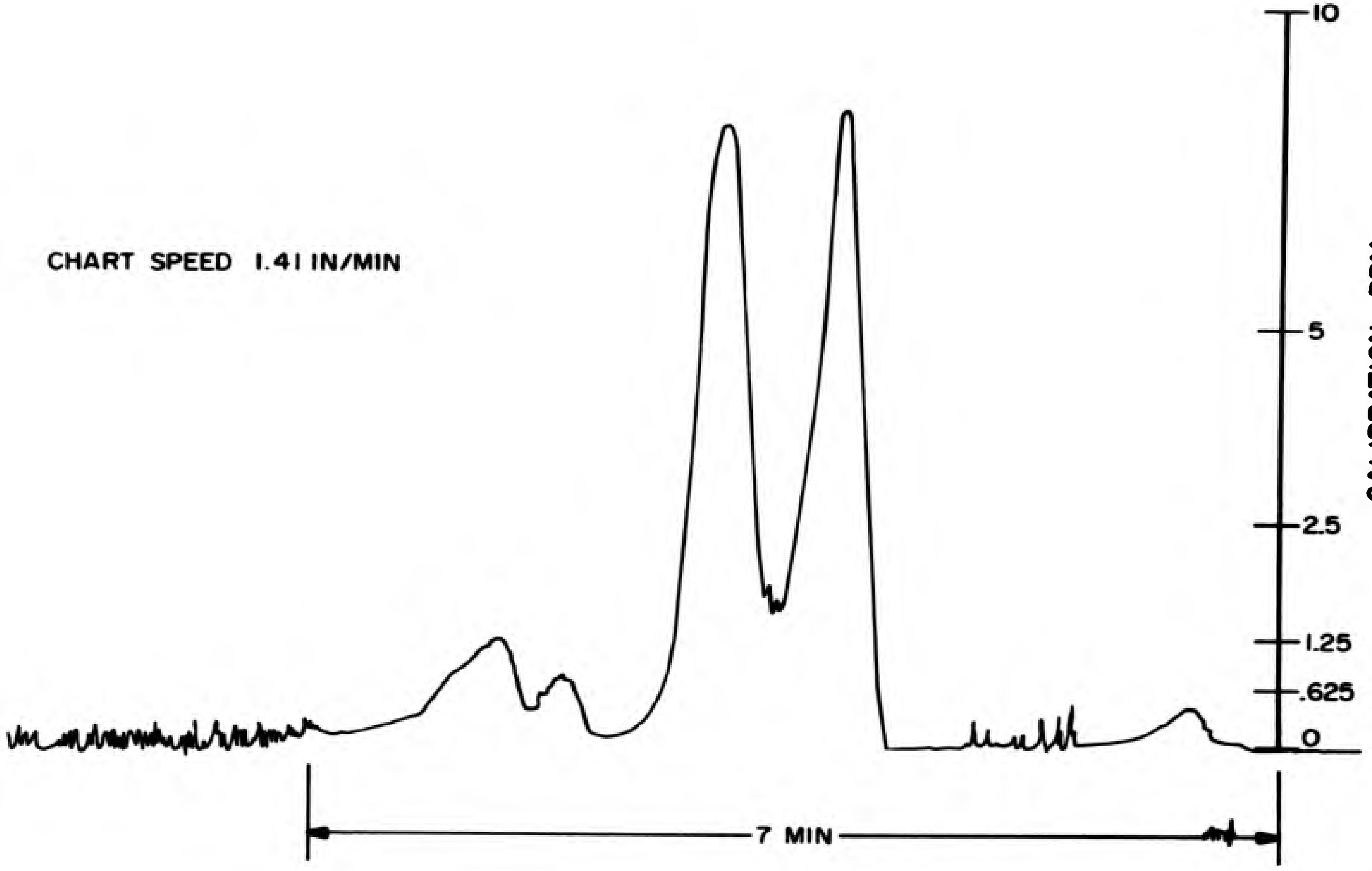


Figure 50. Record Produced by Vapor Detector A at Position 3 During a Spill of Chlorine Trifluoride

Figure 51. Singular Spill of 500 Pounds of Pentaborane on a Dry Spill Tray (Test No. 7)

A very large, white-gray cloud was formed which stacked to a height of over 1000 ft (Fig. 52). The cloud consisted mainly of boric oxide particles and retained its shape for a distance of over 5 miles. After about 90 percent of the propellant had burned, the cloud traveled downwind close to the ground, passing through the air-sampling instrumentation. Small droplets of pentaborane were released from the reaction zone during the entire burning period. These droplets burned very slowly in air. The propellant was completely consumed in about 5 minutes.

The pentaborane spill tank, upon rupture of the burst diaphragm, moved about 10 feet, giving off a sound similar to the release of high-pressure gas. This movement caused some spillage of pentaborane outside the tray. The tank finally rested on the edge of the tray as shown in Fig. 53.

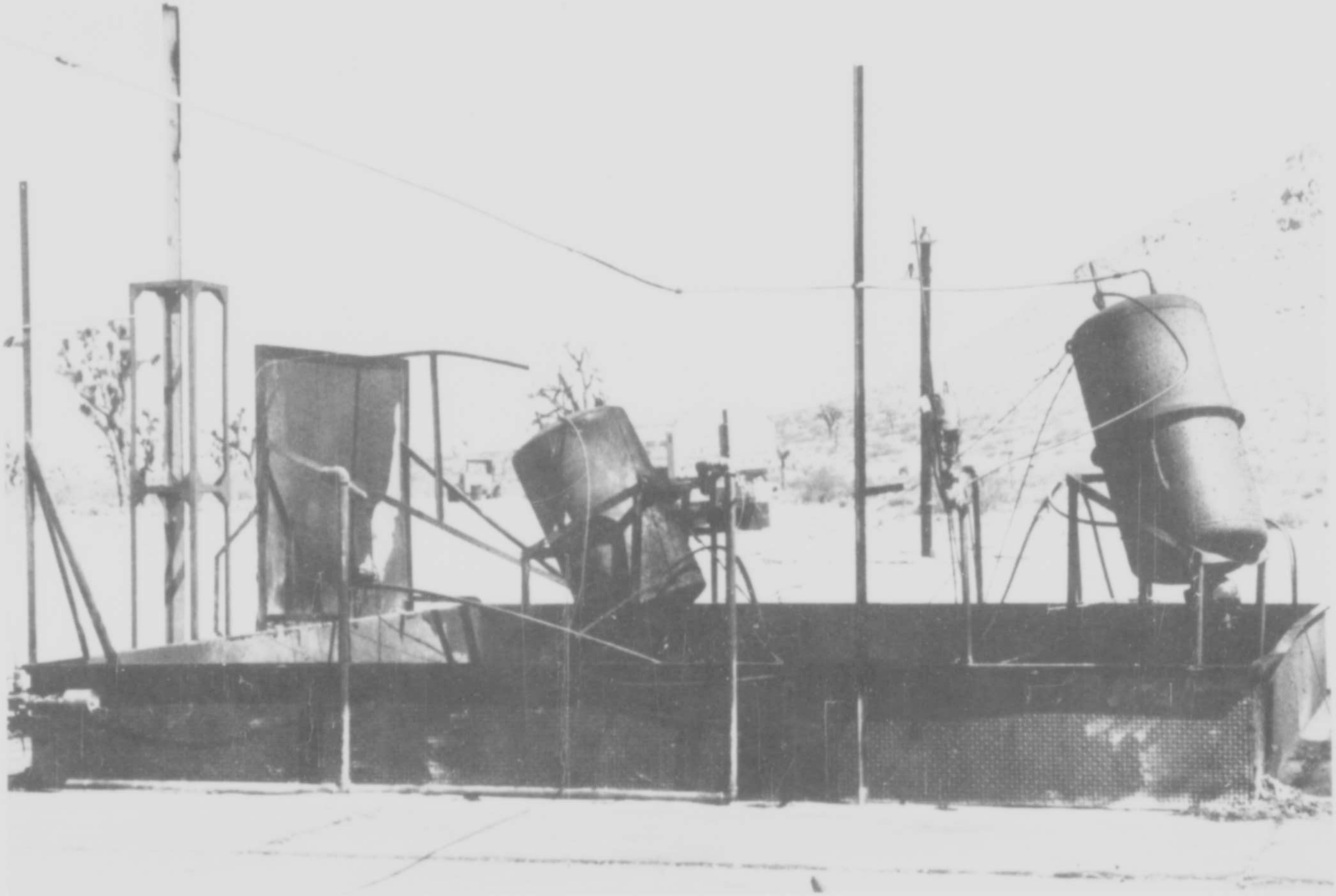
The blast instrumentation did not detect any overpressure shocks.

Post-test examination of the spill system revealed considerable fire damage. All aluminum lines and components located within a radius of 12 feet from the propellant impingement point were melted. Several stainless-steel lines within the 12-foot radius were also damaged. All metal frames and supports within the tray showed some degree of distortion, and internal components of valves and fittings within a radius of 15 feet were rendered unusable. The minimum temperature detected within the tray exceeded 2000 F.

The spill tray was covered with a layer of black, solid combustion products varying from 1/16 to 1 inch in thickness. The main constituents of the deposits were identified as boron nitride, boron oxide, and boric acid, using X-ray diffraction techniques. Spectrographic analysis showed also trace quantities of boron, silicon, aluminum and calcium.

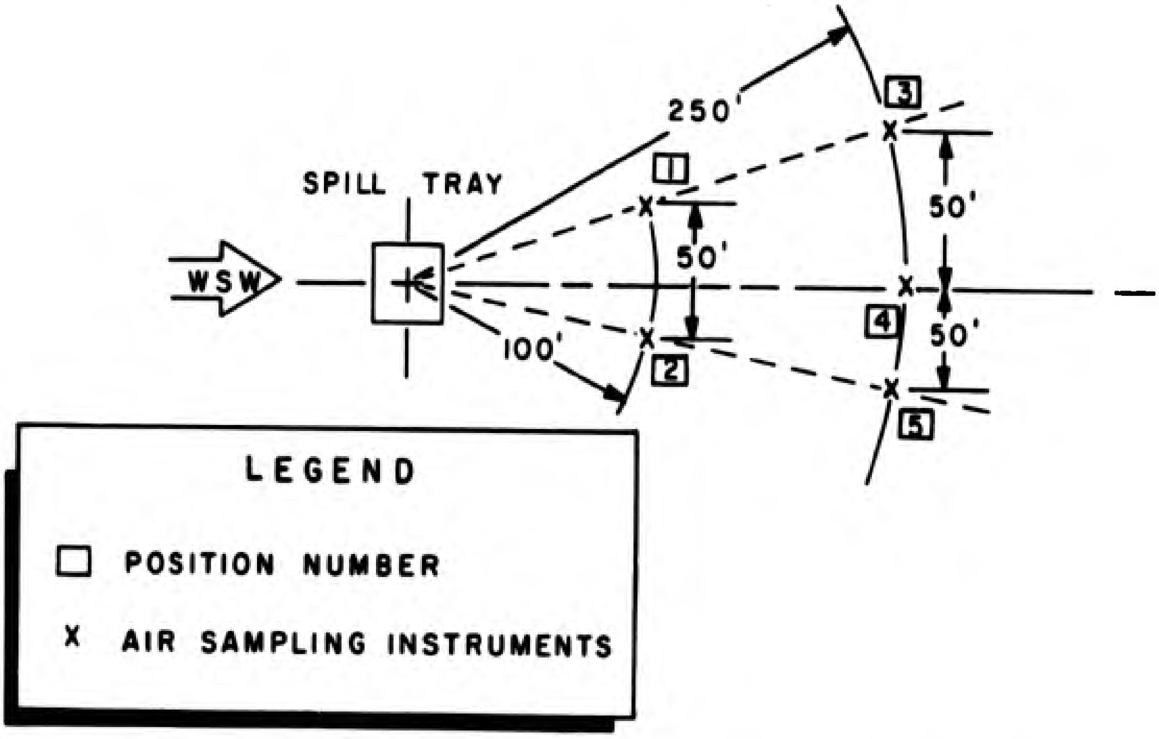
Air-sampling instruments were positioned for the test as shown on the following diagram.

Figure 52. Vapor Cloud Resulting From a Singular Spill of 500 lb of Pentaborane on a Dry Spill Basin



4,695 61

Figure 53. Position of Test Equipment Following a Spill of 500 Pounds of Pentaborane



The analysis of the air samples collected during the test are presented in Table 6. The pentaborane concentrations shown are average values over a sampling period of 2 minutes.

TABLE 6

DOWNWIND VAPOR CONCENTRATION OF PENTABORANE

Position of Sample	Quantity of Pentaborane, milligram	Vapor Concentration, ppm
1	0.026	0.44
2	0.023	0.37
3	0.017	0.28
4	0.020	0.32
5	0.030	0.48

The weather conditions at the time of the spill were as follows:

Air Temperature, 89 F

Relative Humidity, 26 percent

Wind Velocity, 3 knots WSW

Test No. 8

The test consisted of a multiple spill of 275 lb of pentaborane and 100 lb of anhydrous hydrazine. Ignition of the pentaborane was immediate upon rupture of the burst diaphragm. The hydrazine ignited a few milliseconds later upon contact with the burning pentaborane on the surface of the tray. Both propellants were spilled simultaneously at very high release rates. The burning propellants spread over the surface of the tray and a fireball was formed which reached a maximum diameter of 50 feet within a second. The fireball lasted several seconds with the resulting white-gray cloud elevating to a height of over 1000 feet before traveling downwind. The cloud retained its shape for a distance of over 5 miles, with its lower portion passing through the position of the air-sampling instruments. The propellants were completely burned in one minute, except for the residual pentaborane trapped in the spill tank.

Three relatively large explosions were detected following initial propellant reaction. The shock waves raised dust to a height of about 10 ft for a radial distance of over 160 ft from the spill tray, as shown in Fig. 54. This reaction also moved both spill tanks about 10 feet to the edges of the tray (Fig. 55), spilling some of the propellants over opposite sides of the tray.

Complete expulsion of pentaborane from the spill tank was not attained during the test. As a consequence, the tank outlet sustained a fire until the next day when decontaminating liquids were added to neutralize the residual propellant. It was estimated that about one-third of the original 275 lb of pentaborane remained in the tank after the test. Figure 56 shows the final position of the tank and the heavy buildup of boron oxide at the tank opening.

Post-test examination of the test system revealed minor heat and blast damage. The fire damage was limited to the melting of aluminum lines and fittings in the pentaborane spill system. Blast damage consisted of

Figure 54 Vapor Cloud and Dust Trail Following a Large Pentaborane-Hydrazine Explosion

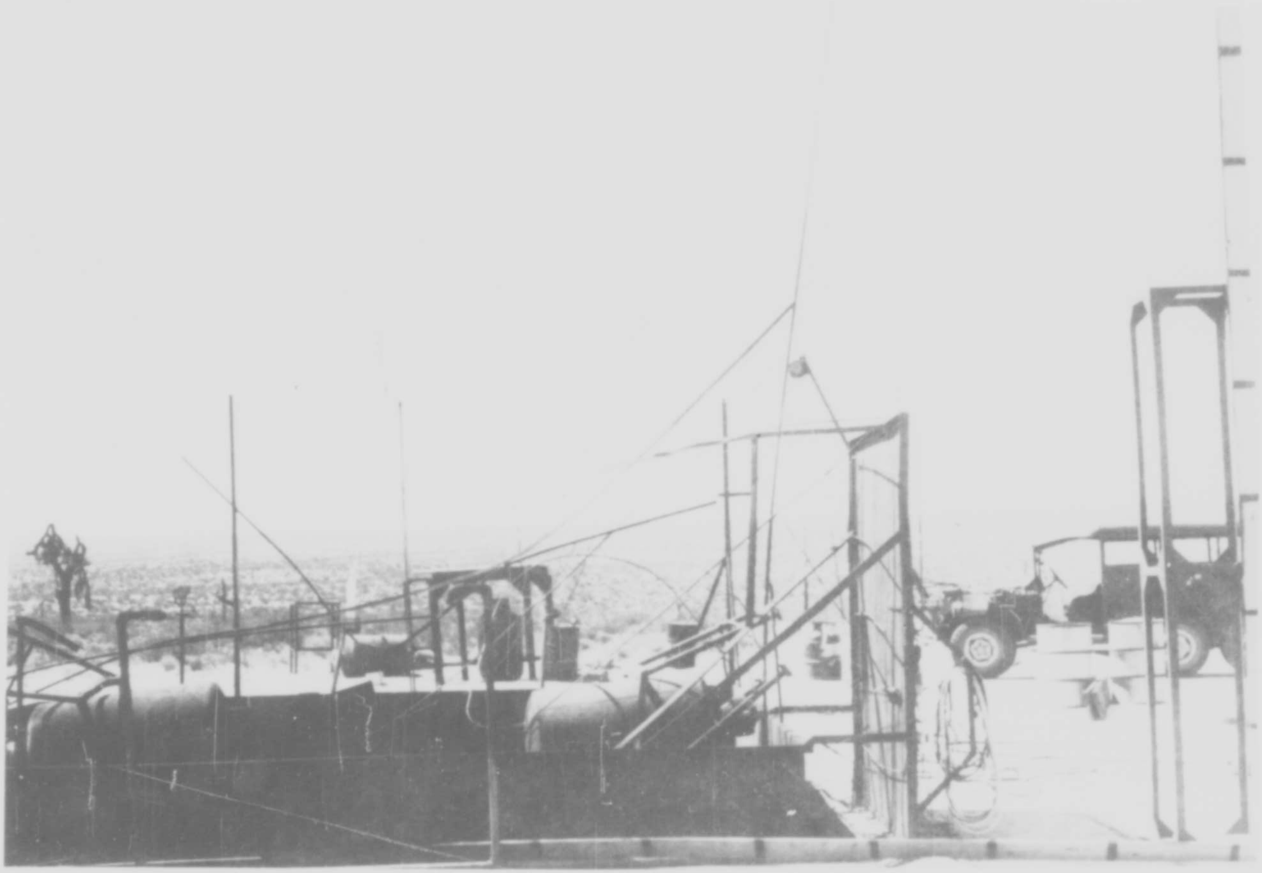


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Figure 55. Position of Hydrazine and Pentaborane Spill Tanks Following an Explosion

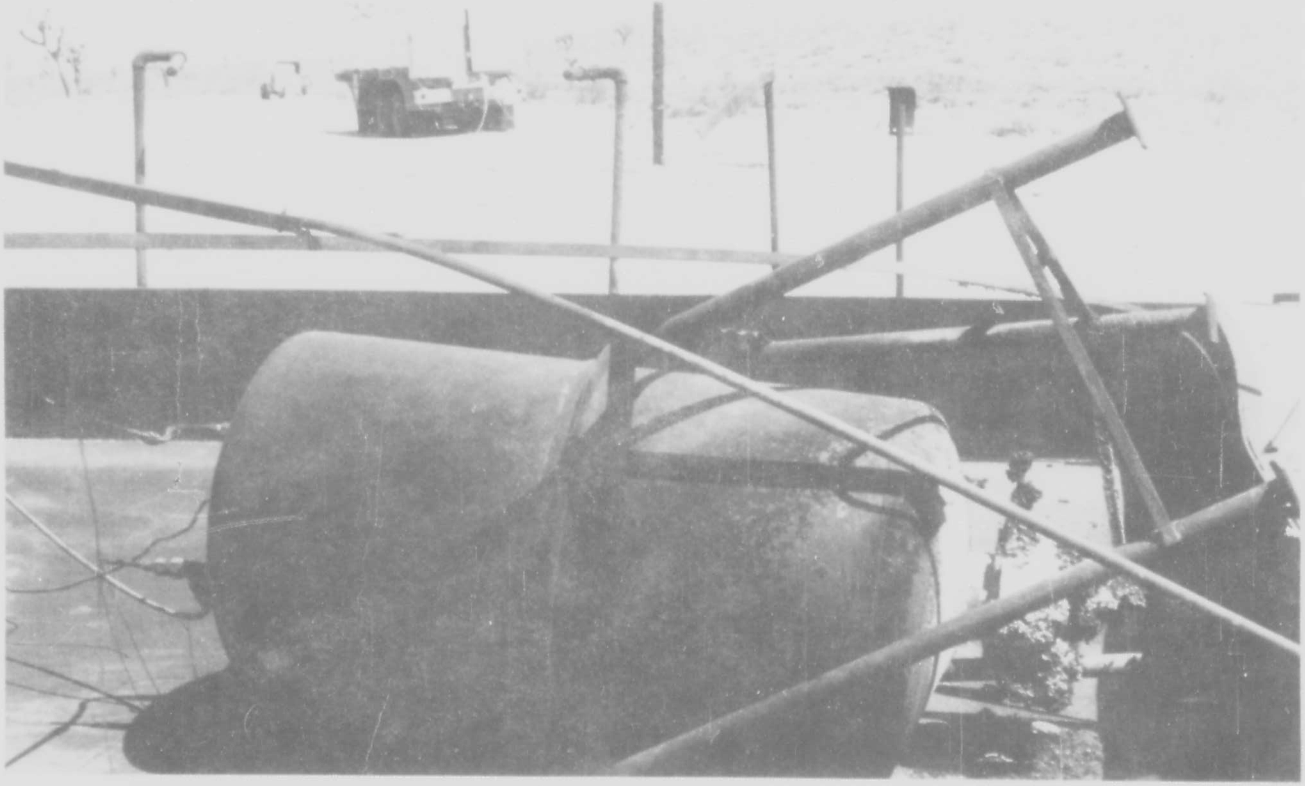


Figure 56. Close View of Pentaborane Spill Tank After Test No. 8
(Note formation of boron oxide on tank opening)

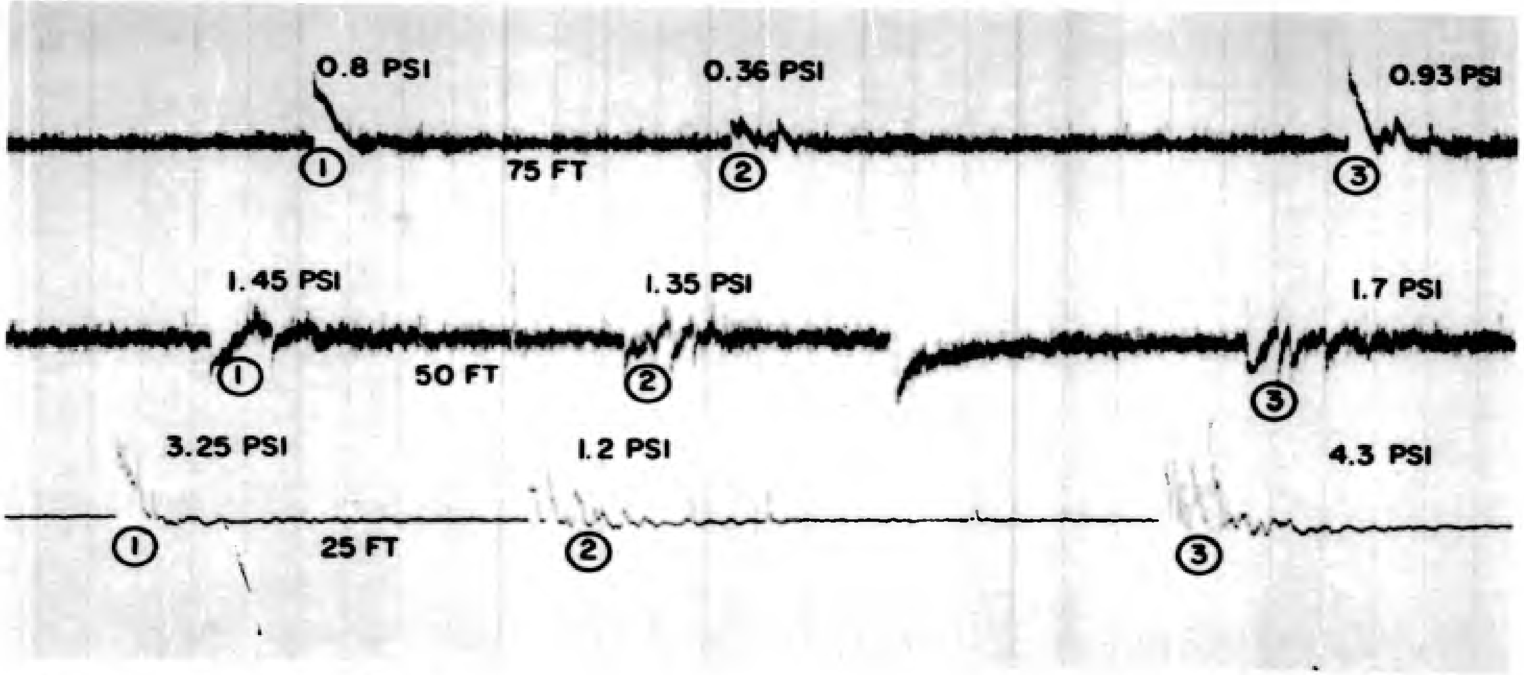
bowing the 5/8-inch-thick pneumatic panel and sides of the spill tray, and the dishing of the bottom surface of the tray. Maximum deformation was 3 inches at the center of the tray.

The spill tray was covered with a thin layer of black, solid combustion products. Examination of these deposits indicated the same constituents reported on test No. 7.

A series of three overpressure shocks were detected by the blast instrumentation during the test, as shown in Fig. 57. Comparison of these overpressure values with those obtained during standard TNT calibration tests (Fig. 58), indicated that the energy released during the spill-test explosions were equivalent to 4, 0.5, and 7 lb of TNT, in order of occurrence. Based on the 300 lb of propellants spilled, the resulting TNT equivalent yields were 1.4, 0.17, and 2.4 percent, respectively. The origin of the explosions (liquid or vapor phase) could not be determined. However, previous test experience with pentaborane and hydrazine had indicated that both liquid- and vapor-phase explosions can occur.

The temperature distribution within the fireball as sensed by the temperature grid, was as shown below (Fig. 59). The temperature-sensing tabs that indicated 900 F were located over the displaced position of the pentaborane spill tank. The temperature of equipment surrounding the spill tray was less than 240 F, as evidenced by the lack of color changes in the temperature-sensitive paint.

Test animals and air-sampling instrumentation were positioned during the test as shown on the following page.



PAPER SPEED: 25 in./Sec
TIME LINES: 0.01 Sec

Figure 57. Oscillographic Record of Overpressure Shocks Sensed During Spill Test No. 8

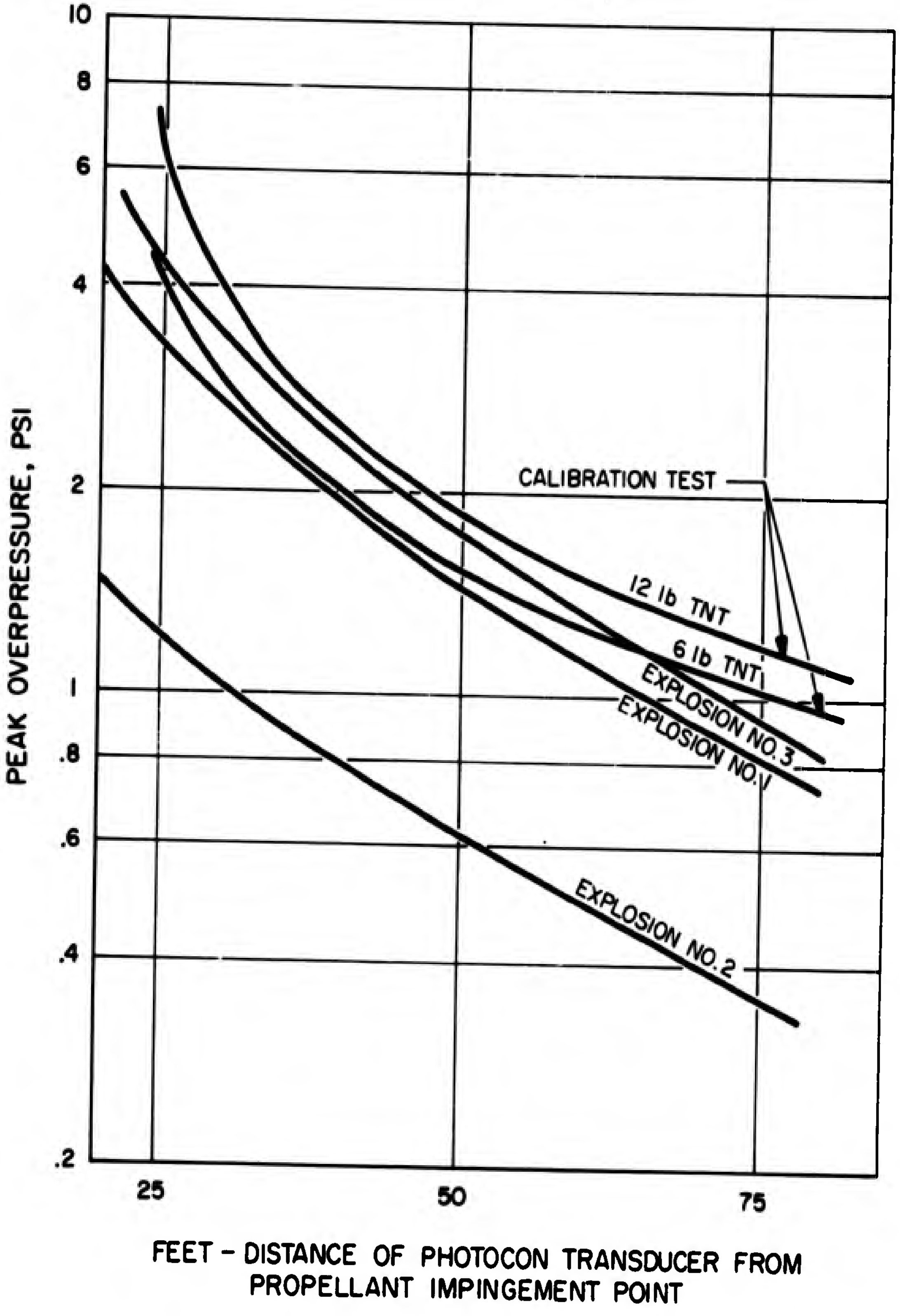
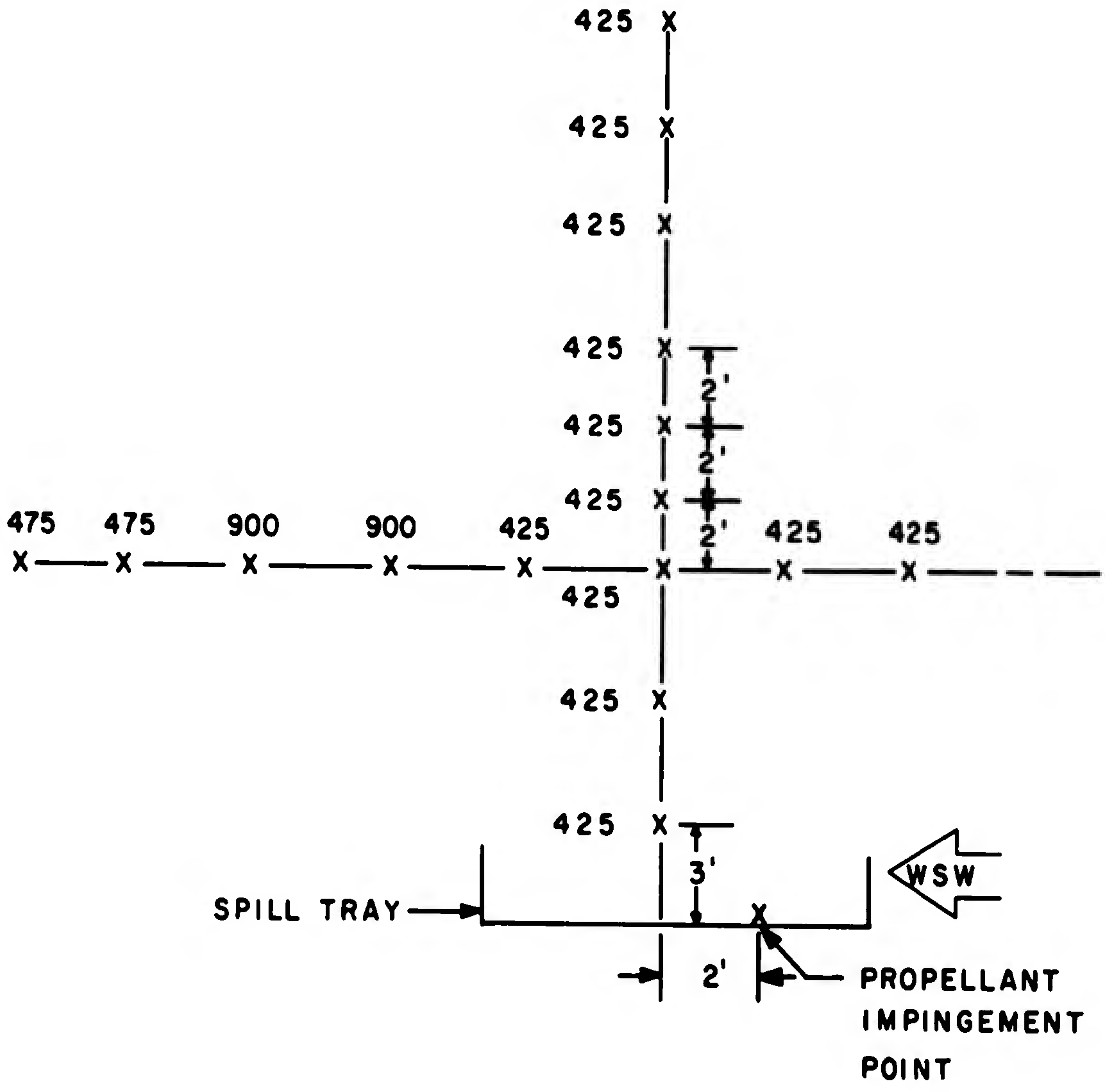


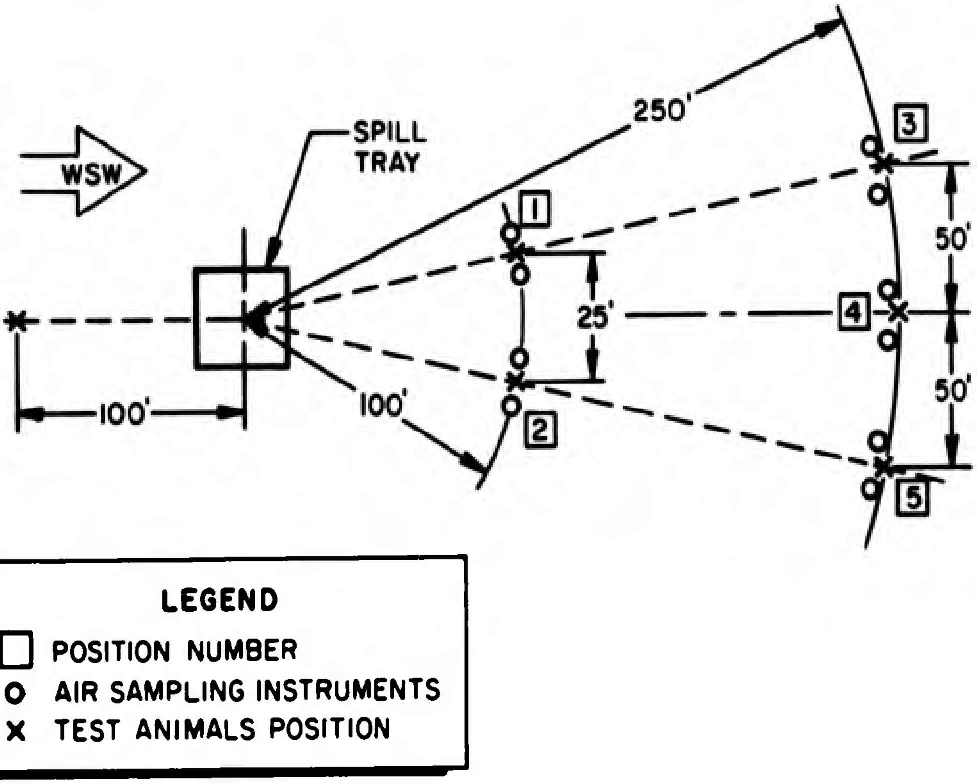
Figure 58. Plot of Overpressure Values Recorded During Test No. 8 and Standard TNT Calibration Tests



NOTE: Distances between adjacent taps is 4 feet unless otherwise indicated.

All temperatures are expressed in degrees Fahrenheit.

Figure 59. Temperature Distribution Within the Fireball



The pentaborane vapor concentration values determined from the trapped air samples during the test are shown in Table 7. These values are average vapor concentrations over a sampling period of two minutes.

TABLE 7

DOWNWIND VAPOR CONCENTRATION OF PENTABORANE

Position of Sample	Quantity of Pentaborane, milligram	Vapor Concentration, ppm
1	0.0015	0.049
	0.003	0.099
2	0.012	0.039
	0.0015	0.049
3	0.0077	0.012
	0.004	0.066
4	0.004	0.066
	0.0077	0.012
5	0.0065	0.010
	0.003	0.099

All the hamsters were found dead after the test. The hospital report (Appendix C) attributed their death to heat exhaustion.

The weather conditions at the time of the test were as follows:

Air Temperature, 103 F

Relative Humidity, 16 percent

Wind Velocity, 5 knots WSW

Test No. 9

This test consisted of externally heating a partially loaded hydrazine storage tank until failure. The test equipment utilized is schematically shown in Fig. 60. A 165-gallon stainless-steel tank, rated at 100 psi, was used for the storage of 16.5 gal of hydrazine. This arrangement provided for a 90-percent ullage volume in the storage tank. Tank heating was effected by burning kerosene in a 4 x 4 x 1/2-ft-deep tray located underneath the test tank. The instrumentation system consisted of two transducers which continuously sensed the temperature and pressure of the stored hydrazine. Flame deflectors were mounted to direct the heating flame toward the bottom of the tank and to protect the instrumentation sensing lines. A 3/4-inch pressure relief valve, rated at 100 psi, was mounted on the tank to permit the simulation of a typical propellant storage system.

The test was initiated (t = 0 min) by igniting the kerosene in the heating tray. Approximately 2 minutes thereafter, a small explosion was sustained within the tank with no apparent consequences. At t = 2.5 min, a larger explosion was experienced which blew the relief valve off the tank, thus allowing ignition of the hydrazine vapors.within the tank. The hydrazine vapor reaction melted the instrumentation sensing lines. A temperature and pressure of 170 F and 0 psia, respectively, were recorded prior to the failure. The hydrazine vapor burned continuously for about 2.5 minutes and provided a 5-to 10-foot flame extending from the opened relief-valve fitting.

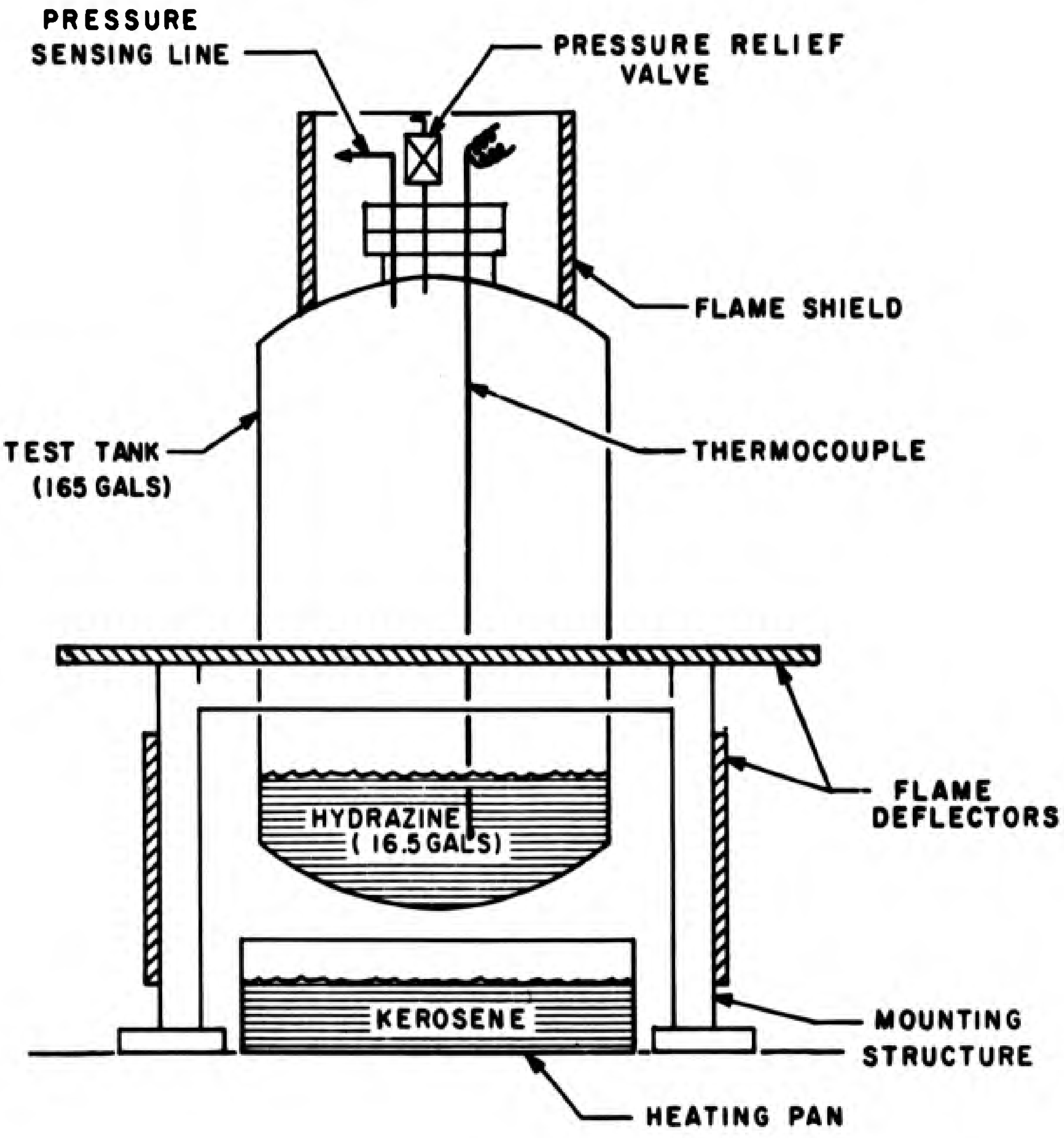


Figure 60. Test Equipment Used for the Hydrazine Heating Test

At t = 5 min, a very large explosion was experienced which fragmented the storage tank and formed a fireball of about 35 ft in diameter. Pieces of the test equipment were scattered over a radius of 1100 ft. The piece found at the 1100-ft point weighed 1/4 pound. The condition of the test equipment following the test is shown in Fig. 61. (Note the hole in the 5/8-inch-thick pneumatic panel caused by a 5-pound piece of the test tank.)

Analysis of the fragmentation distribution, using the techniques presented later in the report, indicated a TNT equivalent yield for the reaction of about 1.0 percent.

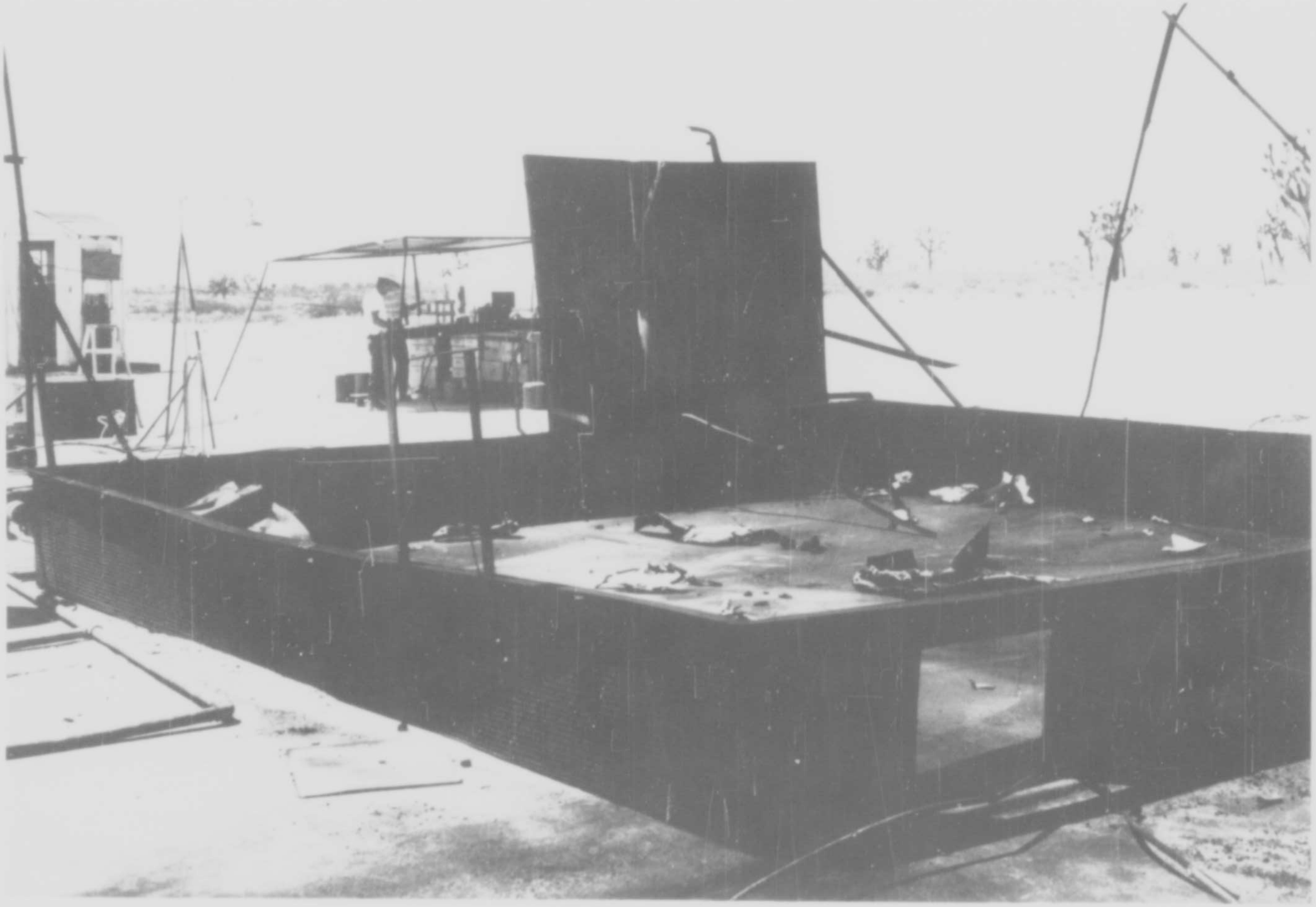


Figure 61. Condition of Test Equipment After the Hydrazine Heating Test

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MEDICAL STUDY

The biological studies performed on three large-scale tests of this program were conducted by the Institute of Medical Research, Huntington Memorial Hospital. The animals to be exposed were placed in downwind positions on a grid layout designed to utilize the available vapor detectors and provide short-term, high-concentration exposures. The cages were elevated approximately five feet above ground level as shown in Fig. 39. Control animals were placed 100 feet upwind of the spill tray. On test 1, the nitrogen tetroxide spill, three animals per position were exposed as shown in Fig. C-1, while on the two biological studies conducted in conjunction with the chlorine trifluoride spill, test 5, and the pentaborane-hydrazine spill, test 8, nine animals per position were exposed (Fig. C-2 and C-3, respectively). After exposure, the animals were collected and returned to the Institute of Medical Research where autopsies were performed to study the physiological effects of the short-term,, high-concentration exposure. Appendix C includes the reports received from the Institute of Medical Research, presenting the results of these three biological studies with hamsters.

PROPELLANT SAFE HANDLING PRACTICES

The establishment of safe handling practices for high-energy propellants is an essential milepost for the successful application of these propellants. In fact, a propellant cannot be conscientiously selected for a specific application in the absence of reliable handling information.

Safe handling practices for hydrazine, nitrogen tetroxide, chlorine trifluoride, and pentaborane were developed and verified in this study program. System failures were simulated in both large and small-scale models, and invaluable information was collected on the extent of the resulting hazards. Techniques for the safe control of these hazards were also derived, and verified whenever possible. In all instances, the postulated and verified criteria agreed without exception.

Propellant handling operations include a variety of tasks such as loading and unloading of storage tanks, disposal of propellant, depressurization of tanks, and handling of shipping containers. Other related tasks are the handling of accidental propellant spills and the neutralization of an area following a spill. The techniques employed on these operations are dependent upon several factors such as previling weather conditions, design of facility, training of operating personnel, and the properties of the propellant.

The prevention of propellant spills is probably the most important single consideration in the safe handling of high-energy propellants. Spills of these propellants present serious toxicity, fire, and blast hazards. It should be noted also that once a spill is experienced, the actions of the attending personnel are limited to the reduction of the prevailing hazards. Therefore, complete freedom from these hazards can be attained only by the prevention of spills.

The prevention of propellant contamination is also of considerable importance. Propellant contamination can result in failures ranging from plugging of critical system components to the explosive destruction of the system. Moreover, contamination reduces the thermal efficiency of the propellant. Techniques for preventing this undesirable situation includes: (1) utilization of compatible materials and components, (2) use of inert and dry gases for pressurization, purging, and padding, (3) prevention of air entrance and entrapment in the system, and (4) use of adequate cleaning and drying procedures. These techniques can be applied successfully with very little effort, especially when considered in the original design of the system.

Weather conditions play an important role in the safe handling of propellants. As shown previously, the hazards resulting from a propellant spill under poor weather conditions are significantly greater than those resulting from a similar spill under neutral or lapse conditions. Consequently, propellant handling operations should be performed during satisfactory weather conditions because the possibility of a spill is greater during these operations.

Successful handling of high-energy propellants for an extended period of time depends largely upon the procedures established for these operations and the degree of personnel adherence to the procedures. The procedures should be established during the system planning and design phases, and presented in written form as an operational order. It should be noted that this criteria does not infer that it is unnecessary for operating personnel to become familiar with the propellant system, it states only that successful handling operations are best attained consistently when a set of well-thought procedures are faithfully followed. A thorough understanding of the propellant system is mandatory to handle properly any emergency situation that may arise.

As mentioned previously, propellant safe handling practices are also dependent upon the specific properties of the propellant. A discussion of specific criteria for each of the propellants studied in the program follows.

HYDRAZINE

The properties of hydrazine affecting safe handling practices are its chemical reactivity, flammability, thermal instability, and toxicity. Although each of these properties requires consideration in the design of a system for hydrazine, it should be noted that hydrazine has been successfully handled and stored for several years.

A detail discussion of safe handling practices for hydrazine is presented in the Hydrazine Handling Manual (AF/SSD-TR-61-7), which was prepared during this program. The material covered in the manual was evolved both from actual experience and a thorough evaluation of the pertinent literature. Much of the experience was gained during this study program.

The prevention of hydrazine contamination during handling and storage is extremely important. Hydrazine is readily oxidized by air at ambient temperatures and is hygroscopic, thus requiring a dry, inert atmosphere at all times. Moreover, hydrazine can be catalytically decomposed when in contact with several common materials of construction. Therefore, the selection of materials for use with the propellant should be limited to those materials proven to be compatible under all expected conditions.

Spillage of hydrazine during this program resulted only in a toxic hazard, which is to be expected when the propellant is spilled in a clean, inert basin. However, if the propellant is allowed to contact an oxidized material or a flame, the potential hazards can be quite serious. Common rust ignites hydrazine in most cases.

Hydrazine handling operations can be performed either locally or remotely. Although local operations are preferred for economical reasons, it should be noted that personnel performing these operations should be fully protected.

NITROGEN TETROXIDE

The properties of nitrogen tetroxide which must be considered in the establishment of safe handling operations are toxicity, chemical reactivity, and low boiling point. These properties need present no serious problems provided they are adequately considered in the design and operation of a propellant system, as evidenced by past experience.

A detailed discussion of safe handling practices for nitrogen tetroxide is presented in AF/SSD-TR-61-8 (Nitrogen Tetroxide Handling Manual), which was prepared during this study program. The material covered in the manual is that considered essential for the safe handling of the propellant, and was evolved both from actual experience, and a thorough evaluation of the pertinent literature.

Nitrogen tetroxide systems must be maintained dry at all times. The absorption of even trace quantities of water can result in a serious corrosion problem due to the formation of nitric acid.

Handling operations involving nitrogen tetroxide can be performed either remotely or locally. Personnel performing local handling operations should be fully protected.

CHLORINE TRIFLUORIDE

The chemical reactivity, toxicity, and low boiling of chlorine trifluoride dictate the establishment of safe handling practices for this propellant. Its reactivity is surpassed only by elemental fluorine, which is the most reactive substance known. The toxicity of this propellant, coupled with its low boiling point, constitutes a very serious hazard in case of propellant spillage.

Safe handling practices for chlorine trifluoride have been developed and are discussed in detail in the Chlorine Trifluoride Handling Manual (AF/SSD-TR-61-9), which was prepared during this program. This manual covers all handling operations expected for the propellant.

The reactivity of chlorine trifluoride dictates no compromises in system design, fabrication, cleaning, and passivation. The materials and components selected for use with the propellant should be limited to those that have been proven compatible. Prior to the admission of the propellant, the system should be thoroughly cleaned and passivated. The passivation of the system should be performed using gaseous fluorine, which forms a passive metal - fluoride film that protects the parent metal from further attack.

Chlorine trifluoride handling operations should be performed remotely. This is necessary because of the extreme reactivity of the propellant and the lack of adequate personal protective equipment.

PENTABORANE

Pentaborane is one of the most hazardous high-energy propellants available at the present time. It is pyrophoric, thermally unstable, chemically reactive, and extremely toxic. However, the propellant can be handled successfully.

Safe handling practices for pentaborane have been developed and are discussed in detail in the Pentaborane Handling Manual (AF/SSD-TR-61-10), which was prepared during this study program. The material covered in the manual was evolved both from actual experience with the propellant, and a thorough evaluation of the pertinent literature.

The toxicity hazard of pentaborane is very serious and several cases of personnel intoxication have been reported. Therefore, respiratory protective equipment should be worn by all personnel involved in any pentaborane handling operation.

A pentaborane spill presents definite fire and blast hazards; therefore, all handling operations must be performed remotely.

PROPELLANT STORAGE DESIGN CRITERIA

Successful propellant-handling operations are the byproduct of properly designed facilities, manned by thoroughly trained personnel. If propellants systems were properly designed, fabricated, operated, and maintained, there would be no need for personnel and equipment protection. Unfortunately, system failures and personnel accidents can be traced to human errors in almost all cases.

The design of reliable facilities for high-energy propellants is an extremely serious and difficult task. In addition to the usual design practices, consideration must be given to weather conditions, safety precautions, and hazardous properties of the propellant. It is felt that if a professional designer understands the properties of a propellant and its safety requirements, his design of a propellant system would be completely adequate for the usual propellant handling operations.

Site selection for the storage of high-energy propellants is dictated mainly by the hazardous properties of the propellants and the prevailing weather conditions. These two factors usually establish the location of the storage area with respect to inhabited buildings, roads, railroads, and other facilities in the general surroundings. The location and orientation of systems and buildings within the storage area are also dictated by the properties of the propellants and the weather conditions. Therefore, the designer of a propellant system must not only be familiar with the propellant, but also have available a detailed weather analysis of the general area. The weather analysis should be prepared by a competent meteorologist.

The selection of materials of construction and equipment for use with high-energy propellants must be carefully considered. In all cases, the designer should limit his selection to materials and equipment proven to be compatible with the propellant. It should always be recorded that a particular material or component would be superior to others for a specific application.

A dike or revetment should be provided for each propellant storage tank in an area. The dike should be fabricated of compatible materials and maintained clean at all times. The capacity of the dike should be sufficient to receive 1-1/2 times the contents of the storage tank.

A water-spray cooling system should be provided for fire protecting each propellant storage tank. The water requirements for this application are dictated by the radiative and convective heat transfer resulting from an adjacent propellant fire. The effects of these fires on adjacent equipment and facilities must be considered also.

The storage area should be laid out so that vehicles receiving or discharging propellants can leave the area in case of emergency. In addition, all loading and unloading points should be paved with concrete or other relatively inert material. The entire area should be adequately fenced, and appropriate warning signs should be posted to keep out unauthorized personnel.

Design criteria for the storage of hydrazine, nitrogen tetroxide, chlorine trifluoride, and pentaborane was established in this program. A detailed discussion of these criteria is presented in the following manuals: (1) AF/SSD-TR-61-6 (Mechanical Systems Design-Criteria Manual for Hydrazine, (2) AF/SSD-TR-61-5 (Mechanical System Design-Criteria Manual for Nitrogen Tetroxide, (3) AF/SSD-TR-61-4 (Mechanical System Design-Criteria Manual for Chlorine Trifluoride), and (4) AF/SSD-TR-61-3 (Mechanical System Design-Criteria Manual for Pentaborane). The material presented in these manuals was evolved both from actual experience and a thorough evaluation of the pertinent literature.

The use of vapor sensors for triggering alarm systems in case of propellant spillage was evaluated in this program. Based upon the results obtained from the spill tests, it appears that in an open area the response of the sensors is significant only when they are located in the path of the resulting vapor plume. Because the direction of the vapor plume is dependent upon wind direction, which can rotate continuously, it would be necessary to locate a large number of sensors to adequately detect propellant spills on a continuous basis. As a consequence, a significant effort would be required also to maintain these instruments in operating order. Therefore, it appears that the use of vapor sensors for detecting spills is impractical. However, the use of sensors for detecting leaks in a propellant system, or for detecting vapor concentrations in a confined area, is very practical. For these applications, a portable sensor is preferred.

THE DETERMINATION OF SAFE DISTANCES FOR THE STORAGE OF HIGH-ENERGY LIQUID PROPELLANTS

The establishment of reliable safe distances for the storage of hydrazine, nitrogen tetroxide, chlorine trifluoride and pentaborane was investigated in this program. This study resulted in a clear definition of the problem areas involved in the determination of safe-distance values and generated a logical approach for the solution to these problems.

The determination of safe distances for the storage of high-energy propellants is a formidable task. This difficulty is the result of (1) the variety of hazardous properties of these propellants, (2) the large number of variables involved in the determination of safe-distance values, and (3) the lack of fundamental data and criteria.

Safe-distance values for the storage of high-energy propellants must be based on three distinct hazards: toxicity, blast, and fire. For most propellants, each hazard will be predominant for specific storage distances. For example, fire may be the controlling hazard in separating storage tanks, whereas blast may indicate the location of support facilities. For large storage distances, about 1500 feet or over, toxicity will probably be the prevailing hazard.

A discussion on the determination of safe-distance values for each specific propellant hazard follows. This discussion is followed by a summary of conclusions, and recommendations. In addition, two distinct sample calculations are presented in the Appendix for the determination of safe-distance values based on toxicity.

TOXICITY

The primary hazard affecting general site selection for the storage of high-energy propellants is toxicity. This hazard is also predominant for storage distances greater than 1500 feet for almost all propellants. In addition, toxicity can be considered the only hazard inherent in the storage of some propellants, such as nitrogen tetroxide.

The downwind pollution problem resulting from an accidental spill of propellants resolves itself into two entities:

1. The initial cloud constituting the vapors that flash immediately.
2. The long, less concentrated plume resulting from the steady boil-off of the standing liquid.

In the case of propellants spilled at temperatures above their normal boiling points, the instantaneous cloud is by far the most important consideration in establishing downwind pollution. In fact, if there exists near the storage area a properly constructed, diked basin leading to a catch tank of small exposed surface area, the steady boil-off problem is of little consequence. However, if a propellant is spilled at temperatures below its normal boiling point, then the steady vaporization problem would constitute the main pollution hazard.

The task of determining safe-distance values based on toxicity can be subdivided into three distinct problems:

1. The rates at which the propellant vapors are released into the atmosphere.
2. The diffusion and transport phenomena of the vapor in air.
3. The maximum permissible vapor concentration to which personnel can be exposed for a given period of time without suffering adverse effects.

The three problems listed above can be thought of as being the source, path, and receiver in a pollution hazard. A detailed discussion of each problem follows.

Propellant Vaporization Rates

In analyzing the source of a pollution hazard, it is more important to determine the rates at which the pollutant is released than the total amount of propellant that will eventually be diffused. In the case of a propellant spilled at a temperature above its boiling point, we are interested primarily in the flash-off rate and secondarily in the boil-off rate. Conversely, if a propellant is spilled at a temperature below its boiling point, we are interested only in the vaporization rate.

The flash-off of propellants such as nitrogen tetroxide and chlorine trifluoride constitutes the main mechanism for estimating safe-distance values for these propellants. However, the flash-off process is neither a steady process nor an instantaneous one, and has not been evaluated experimentally. Thus, this process becomes the first major difficulty in attempting to calculate safe-distance values for nitrogen tetroxide and chlorine trifluoride.

To present a procedure for the solution of a typical safe-distance problem which is applicable to the storage of nitrogen tetroxide and chlorine trifluoride, it is assumed that propellant flash-off occurs in a period of time ranging from 1 to 30 sec. Then the flash-off rates can be estimated as follows:

$$\dot{w}_f = \frac{W_f}{t} \tag{1}$$

where:

$\dot{w}_f$ = average propellant flash-off rate, lb/sec

W_f = total amount of flashed propellant, lb

t = time of significant propellant flashing, sec

The total amount of flashed propellant (W_f, Eq. 1) can be determined accurately using an energy balance:

$$W_t \, C(T_2 - T_1) = W_f \, h_v \tag{2}$$

where:

W_t = total amount of spilled propellant, lb

C = specific heat capacity of liquid propellant at boiling point, Btu/lb-F

T_2 = temperature of spilled propellant, F

T_1 = boiling point of propellant, F

W_f = total amount of flashed propellant, lb

h_v = latent heat of vaporization of spilled propellant, Btu/lb

For propellants such as hydrazine and pentaborane, which are expected to be spilled at temperatures below their boiling points, the steady vaporization rates constitute the main pollution hazard. In the case of pentaborane, however, autoignition is experienced at ambient temperatures of over 77 F, which reduces the toxic hazards above this temperature. The toxic hazards of hydrazine, on the other hand, increase with increased ambient temperatures.

A theoretical solution to the steady boil-off and evaporation problem can be performed using the empirical mass-transfer equation developed by Colburn (Ref. 3). This equation is applicable to the evaporation of liquids from plane surfaces parallel to wind, and is expressed as follows:

$$\frac{K_g'}{G_m} \left(\frac{\mu}{\rho D}\right)_f^{2/3} = 0.036 \left(\frac{LG}{\mu}\right)^{-0.2} \qquad (3)$$

for $\frac{LG}{\mu}$ greater than 20,000

where:

K_g' = mass-transfer coefficient of gas film, lb-mol/sec-ft^2

G_m = molar mass velocity of wind, lb-mol/sec-ft^2

μ = viscosity of gas, lb/ft-sec

ρ = density of gas, lb/ft^3

D = average diffusivity of vapor into air, ft^2/sec

$\left(\frac{\mu}{\rho D}\right)_f$ = Schmidt number of air-vapor film

L = length of plane surface parallel to the direction of wind flow, ft

G = mass velocity of wind, lb/sec-ft^2

The average diffusivity of the propellant vapor into air (D, Eq. 3) can in turn be determined by the empirical relation developed by Gilliland (Ref. 4) for the interdiffusion of two gases. This relation is as follows:

$$D = 0.0043 \frac{T^{2/3}}{P(v_a^{1/3} + v_b^{1/3})^2} \sqrt{\frac{1}{M_a} + \frac{1}{M_b}} \qquad (4)$$

where:

D = average diffusivity of vapor into air, cm^2/sec

T = temperature, K

P = pressure, atm

v_a, b = molecular volumes of gases a, b at their normal boiling points, cm^3/gram-mol

M_a, b = molecular weight of gases a, b

The solution to the mass-transfer equation permits the determination of the steady vaporization rates of liquid propellants. For such a solution, however, several basic assumptions are required which render the solution subject to experimental verification. Thus, the information presented below can be considered to be tentative in nature. It is worth mentioning also that a single experiment was performed utilizing water as the evaporating liquid for comparison purposes. The experimental evaporation rate and that theoretically predicted agreed to within 15 percent, the theoretical value being higher.

The steady vaporization rates of spilled hydrazine as a function of wind speed and at ambient temperatures of 77, 85, and 110 F are presented in Fig. 62. It is interesting to note the marked effect of air temperature on the vaporization rates, and also the near-linear dependency of vaporization rates on wind speed. The vaporization rates shown in the figure are expressed in terms of $AL^{-0.2}$. This is necessary in order to express the vaporization rates independently of the configuration of the diked basin. The symbol A represents the exposed surface area of the propellant, in square feet, and L is the length of the propellant surface parallel to the direction of the wind, in feet.

A spill of pentaborane will provide steady vaporization rates at temperatures of up to 77 F. Above this temperature, the propellant will autoignite resulting in a reduction of the toxic hazards. Therefore, the evaporation

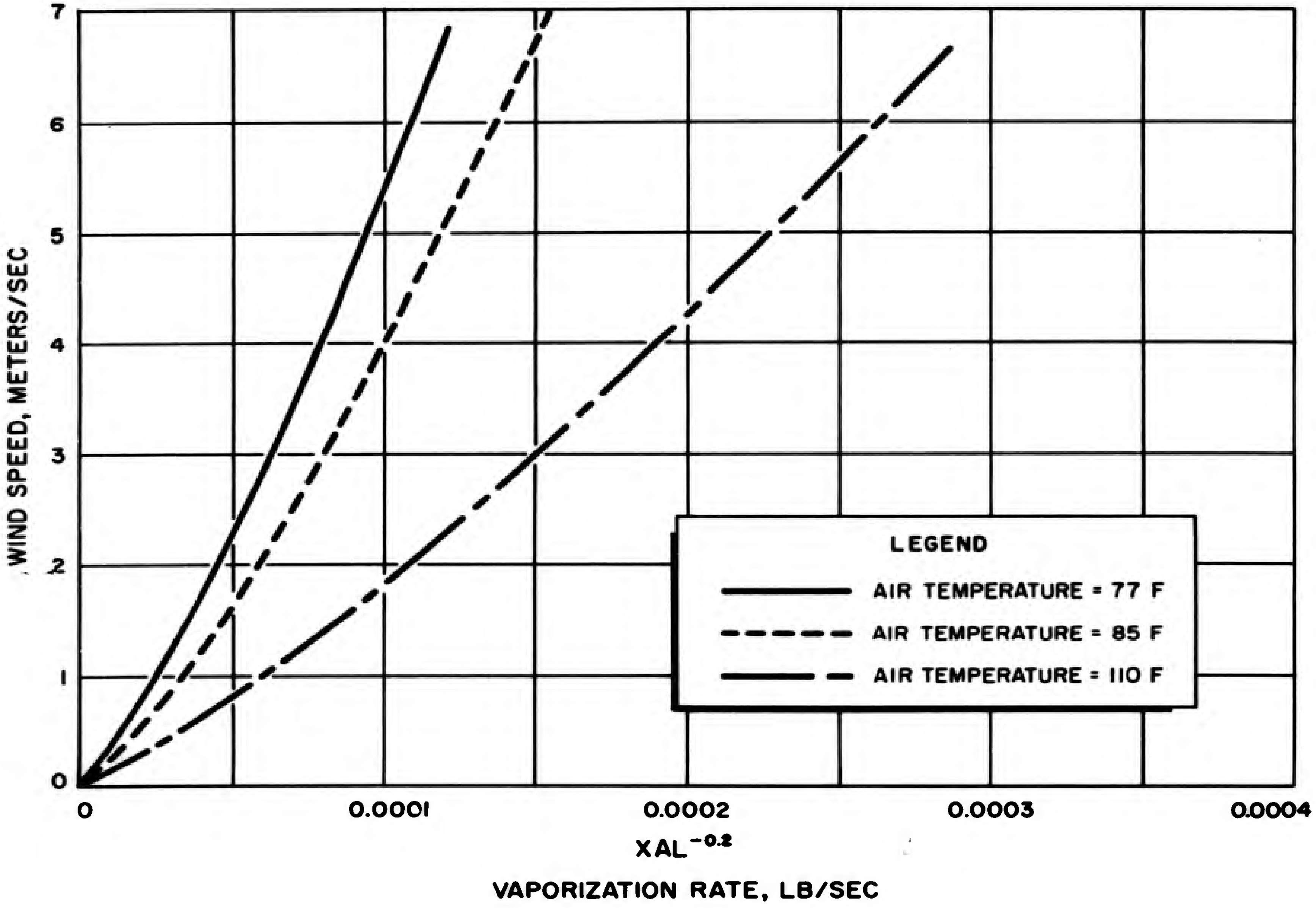

Figure 62. Vaporization Rate Values of Hydrazine

rates of pentaborane at an air temperature of 77 F can be considered the maximum toxic source values for design purposes. These values are shown in Fig. 63 as a function of wind speed. The near-linear dependency of vaporization rate on wind speed is again noted.

The steady boil-off rates of spilled nitrogen tetroxide and chlorine trifluoride are of little significance for estimating safe-distance values for these propellants. However, for the sake of completeness, these rates are presented in Fig. 64 as a function of wind speed. It is noted that in the case of nitrogen tetroxide, the boil-off rates are nearly independent of the air temperature. Since the same phenomenon is expected to prevail in the case of chlorine trifluoride, the vaporization rates for this propellant were calculated only at an air temperature of 85 F.

Atmospheric Diffusion

The diffusion of a gas in the atmosphere is a direct function of the degree of atmospheric turbulence. The nature of the turbulence is primarily governed by such meteorological parameters as: (1) change of temperature with height (lapse rate), (2) horizontal wind speed, and (3) change of wind with height.

Downwind concentrations of a gas are dependent not only on the rate of diffusion but, necessarily, by the nature of the release. Vapor sources commonly are classified as continuous point, instantaneous point, continuous line or instantaneous volume. A detailed discussion on the descriptions of vapor sources as well as meteorological aspects of the diffusion problem can be found in Ref. 5 .

Calculations of downwind concentrations of the propellants in question are derived from applicable formulae and are based upon the following assumptions:

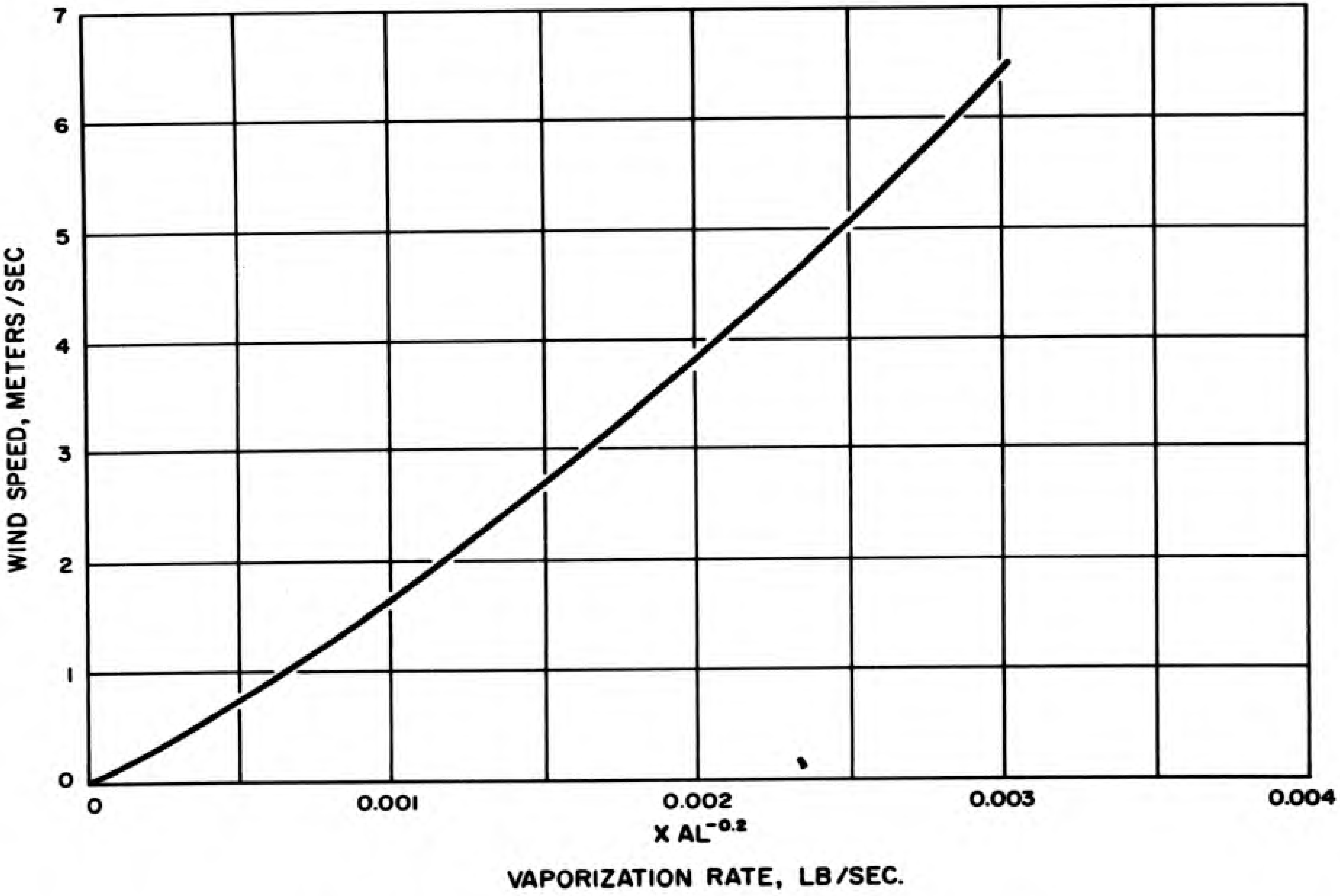

Figure 63. Vaporization Rate Values of Pentaborane at 77 F

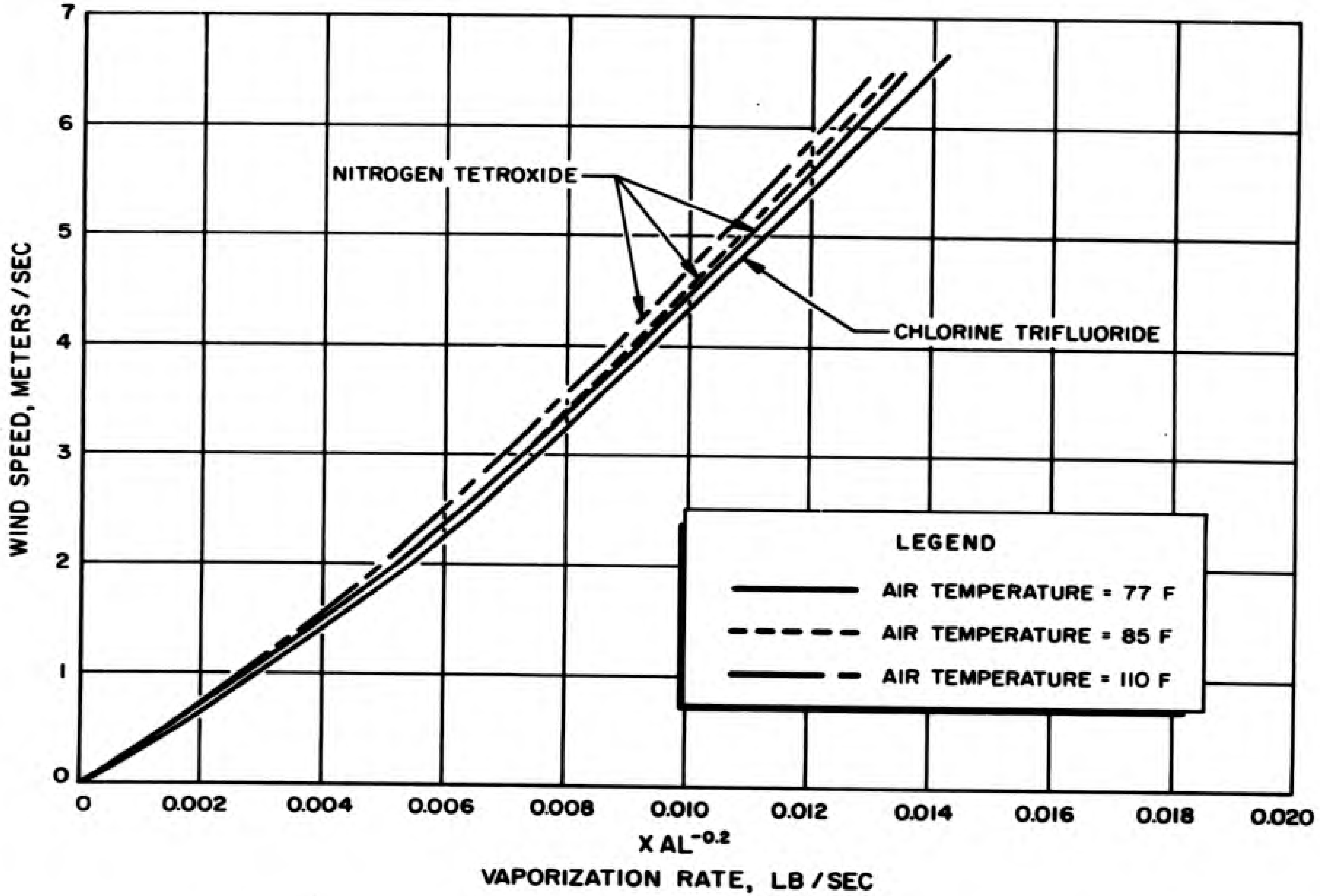

Figure 64. Steady-State Boiloff Values of Nitrogen Tetroxide and Chlorine Trifluoride

1. Propellant vapors are released at ground level
2. Little or no heat is associated with the vapor release
3. Propellant is released gently enough to preclude liquid atomization
4. The cloud trajectory is over level terrain

The cloud center (or axis, if the cloud is plume-shaped) is the point of highest concentrations, and follows a path close to and parallel to the ground. This means that persons downwind can be subjected to the peak concentrations at that distance, the actual value being dependent on the rate of vapor diffusion.

Although many atmospheric diffusion formulae appear in the literature, it is felt that the original Sutton approach seems most valid, and allows for ease of calculation of downwind effects of propellant spills. As mentioned previously, the nature of the release is highly significant, since it governs the aspect of the effluent cloud. In the case of nitrogen tetroxide or chlorine trifluoride, where the release consists of the primary large flash-off cloud, followed by the far less important boil-off plume, calculations of downwind concentrations can be accomplished using Sutton's Instantaneous Point Source Formula on the flash-off and his Continuous Point Source Formula on the boil-off. For pentaborane and hydrazine, where considerations of flash-off are unimportant, only the Continuous Point Source Formula is required.

It should be mentioned that, actually, a flash-off cloud more closely resembles an instantaneous volume rather than a point source due to the rather short period required for creation of a cloud of significant dimensions. However, since concentrations at distances of greater than about 1500 feet show little difference plus the comparative ease afforded by point-source calculations, the volume source consideration is ignored.

The two Sutton Formulae, which express downwind concentrations as functions of a specific type of release and various meteorological parameters, are expressed as follows:

1. Instantaneous Point Source:

$$\chi = \frac{2Q}{\pi^{3/2} C_x C_y C_z (\bar{U}t)^{\frac{3(2-n)}{2}}} \exp\left[-(\bar{U}t)^{n-2} \left(\frac{X^2}{C_x^2} + \frac{Y^2}{C_y^2} + \frac{Z^2}{C_z^2} \right) \right] \tag{5}$$

where:

χ = vapor concentration, g/m^3
Q = source strength, g
C_x, C_y, C_z = diffusion coefficients, m$^{n/2}$, in X, Y and Z planes
$\bar{U}$ = mean wind speed, m/sec
$(\bar{U}t)$ = horizontal distance from source, m
n = nondimensional parameter associated with stability
X, Y, Z = downwind, crosswind and vertical coordinates measured from the center of a moving cloud, m

2. Continuous Point Source:

$$\chi = \frac{2Q}{\pi C_y C_z \bar{U} (X)^{(2-n)}} \exp\left[-X^{(n-2)} \left(\frac{Y^2}{C_y^2} + \frac{Z^2}{C_z^2} \right) \right] \tag{6}$$

where:

χ = vapor concentration, g/m^3
Q = source strength, g/sec
C_y, C_z = diffusion coefficients, m$^{n/2}$, in Y and Z planes

X = horizontal distance from source, m

$\overline{U}$ = mean wind speed, m/sec

n = nondimensional parameter associated with stability

Y, Z = crosswind and vertical coordinates measured from a ground point at source, m

In actual practice the simplest and, perhaps, the most realistic approach is to use only the Continuous Point Source Formula for calculating downwind concentrations, following the assumption that the instantaneous flash-off occurs over a finite period of time. Observations of many nitrogen tetroxide spills suggest that this, in fact, does take place. Unfortunately, no scientific study has been undertaken up to now to give a conclusive idea of how much vapor is flashed over what duration under a given set of conditions.

Equation (6) can be solved once the source strength (vaporization or flash-off rate) is known and the proper meteorological parameters are applied. This equation has the additional virtue of providing values of Total Integrated Dosages (TID) downwind, simply by multiplying the calculated concentrations by the number of seconds of release.

The application of Sutton's Continuous Point Source Formula to the determination of downwind concentrations resulting from both a flash-off cloud and a boil-off plume is shown in detail in the sample calculations presented in the Appendix.

For the purposes of this study, weather conditions were selected which reasonably could be expected to occur with the temperatures under consideration. These conditions provide little atmospheric turbulence (moderate inversion), average turbulence (neutral) and extreme turbulence (large lapse). The various coefficients and wind speeds applicable to these weather conditions were selected from Ref. 5 and 6 and are summarized in Table 8.

TABLE 8

SELECTED WEATHER PARAMETERS

Variable	Moderate Inversion	Neutral	Large Lapse
n	0.33	0.25	0.20
$\overline{U}$, m/sec	2.00	4.00	6.00
C_y, $m^{n/2}$	0.08	0.21	0.64
C_z, $m^{n/2}$	0.05	0.12	0.36

Permissible Propellant Vapor Concentrations

When the propellant vaporization rates are established and the applicable atmospheric diffusion formula is solved, the propellant vapor concentration as functions of downwind distance and weather conditions are obtained. The next logical step in the solution of the safe-distance problem is to determine the maximum propellant vapor concentrations to which personnel can be exposed without suffering adverse effects. These vapor concentrations are dependent upon the toxic hazards of the particular propellant spilled, the nature of the personnel exposed to the vapor, and duration of exposure. Thus, the maximum permissible propellant vapor concentrations are logically the product of medical research and operational policies.

Because maximum permissible propellant-vapor-concentration values have not been established, applicable criteria will be presented herein for the sole purpose of permitting the solution of typical safe-distance problems. The criteria stipulated in these problems are:

1. The location of the storage area is selected so that if an accidental propellant spill occurs, off-site personnel will not be exposed to vapor concentrations higher than the MAC values established by the American Conference of Governmental Industrial Hygienists.
2. The location of inhabited buildings within the site is dictated by the propellant vapor concentration to which personnel can be exposed for 15 minutes without suffering adverse effects. It is stipulated that personnel in these buildings will be evacuated shortly after a propellant spill is reported.
3. The storage distances for the criteria presented in 1 and 2, above, are based upon the worst expected weather conditions.

Maximum allowable concentration values for almost all propellants are readily obtained from Ref. 7. References 8 and 9 present "emergency tolerance values" for nitrogen tetroxide and unsymmetrical dimethylhyzrazine, respectively. Emergency tolerance values for other propellants are expected to become available in the near future. These values can be used to locate inhabited buildings within the site.

Concluding Remarks

Techniques for determining safe-distance values for the storage of high-energy propellants, based on toxicity, were presented above. This information consisted of evaluating the source, path, and receiver of a pollution hazard. Although several assumptions were made where fundamental information was lacking, these assumptions do not change the basic approach to the solution of the problem.

The mechanics of solving typical safe-distance problems based on toxicity are shown in Appendix A and B. These problems consider the case of propellants spilled at temperatures both above and below their normal boiling points. Nitrogen tetroxide and hydrazine were used, respectively, as typical propellants.

The information presented above, coupled with that provided in the sample problems, suggest that two basic experimental programs are required to establish reliable safe-distance values based on toxicity. These programs consist of (1) the verification of steady vaporization and boiloff rates, and (2) the determination of flashoff rates. It appears that both of these programs can be easily performed in a short period of time with very limited financial effort.

BLAST

Blast is the second hazard that must be considered in the establishment of safe-distance values for the storage of high-energy propellants. This hazard can result from the decomposition of a propellant within a storage tank, or by the reaction of a spilled propellant with air or other substances. A discussion of both modes of blast effects follows.

Explosive Reactions

The spillage of high-energy propellants in a storage area can result in explosive reactions. These reactions are usually initiated by the action of air and area contaminants, and cause oxidation, reduction, and/or decomposition of the propellants. Although some of the reactions may be inherently stable, the reaction products formed may be detonative. Specifically, the generation of hydrogen in a semiconfined area, such as a storage tank revetment, can definitely result in a violent hydrogen-air explosion.

The blast hazards resulting from spillages of chlorine trifluoride, nitrogen tetroxide, hydrazine, and pentaborane were investigated in this program. Spills of chlorine trifluoride on water, dirt, and asphalt resulted in either ignition or weak audible reports; no reaction was detected when the propellant was spilled on dry, clean conrete. However, when one considers the reactivity of chlorine trifluoride, coupled with the low probability of having an adequately clean revetment in case of spillage, it becomes apparent that blast hazards must be considered in the storage of chlorine trifluoride.

Spills of nitrogen tetroxide on water, dirt, concrete, and asphalt failed to produce a reaction. Actual field experience have demonstrated also that the probability of having an explosion in case of spillage is extremely low. Therefore, spills of nitrogen tetroxide are not expected to constitute a blast hazard, provided that the storage area is maintained reasonably clean and free of combustibles.

Hydrazine spilled on dirt, asphalt, water, and concrete failed to produce a noticeable reaction. However, actual field experience has demonstrated that spills of hydrazine on dirt, rusted materials, and asphalt can produce a reaction. This reaction can be accompanied by blast effects since hydrogen is usually generated. Consequently, blast hazards must be considered in the storage of hydrazine.

Spills of pentaborane on dirt, asphalt, concrete, and water resulted in spontaneous ignition with air under some of the conditions tested. On dirt and asphalt, reaction between the test surface and fuel ignited the propellant at temperatures below 70 F. (The autoignition temperature of pentaborane in air has been established at about 77 F.) Contrary to expectation, no blast effects were noted on these tests. Actual field experience with the propellant, however, has demonstrated that it is definitely possible to obtain severe blast effects from the accidental spillage of pentaborane. This latter finding results from the fact that pentaborane decomposes at relatively low temperatures and oxidizes readily in air, liberating large quantities of hydrogen. The severity of the blast effects are dependent upon the quantity of hydrogen liberated, which is a function of ignition delay time, and the degree of confinement in the revetment. Thus, it becomes apparent that blast effects must be considered in the storage of pentaborane.

The blast potential of propellants can best be expressed in equivalent TNT yields. This approach, which is at this time controversial, is extremely useful since most professional designers are familiar with the effects of TNT charges. In addition, a substantial amount of information is available for the calculation of loads resulting from this explosive.

The TNT equivalent yields of propellants, i.e., the pounds of TNT needed to produce an explosion equal in magnitude to that produced by a given weight of propellant, are derived both from experiment and field experience. Based upon the experience and information available at this time, a set of tentative TNT yields are presented in Table 9. These are expected to be adequate for the design of storage facilities for these propellants.

TABLE 9

TENTATIVE TNT YIELDS OF PROPELLANTS SPILLED SINGULARLY ON CLEAN BASINS

Propellant	TNT Equivalent Yield,* percent
Hydrazine	2
Nitrogen Tetroxide	0
Chlorine Trifluoride	0.5
Pentaborane	4

*Pounds of TNT per 100 pound of propellant

In a properly designed storage facility, spillage from one propellant tank should have no influence on surrounding tanks. Therefore, the maximum spillage hazard in a storage area would derive from the contents of the largest tank in the area. Based on this quantity of propellant, the equivalent TNT charge can be computed from the yield values shown in Table 9.

The overpressures resulting from the calculated TNT charge, as sensed by a "side-on" transducer, can be obtained from the following empirical relations:

$$P = \frac{4120}{Z^3} - \frac{105}{Z^2} + \frac{39.5}{Z} \qquad (7)$$

and

$$Z = \frac{R}{W^{1/3}} \qquad (8)$$

where

P = side-on pressure, psi
R = radial distance, feet
W = weight of TNT charge, pounds

The solution to the above equations can be simplified by the use of the nomogram shown in Fig. 65.

The overpressure values obtained from Eq 7 and 8, or Fig. 65, can be used directly in most cases for design purposes. When other forms of blast energy are required for a specific design problem, they can be obtained from standard TNT charts and tables, once the total weight of the TNT charge has been computed from Table 9.

Fragmentation Hazards

Additional blast hazards must be considered in the storage of hydrazine and pentaborane. These hazards are derived from the susceptibility of these propellants to: (1) thermal and catalytic decomposition, (2) oxidation by air, and (3) reaction with contaminants. The presence of such reactions within a storage tank can generate sufficient hydrogen to constitute a definite blast potential.

The blast effects resulting from a propellant explosion within a tank are drastically different from those of a spilled propellant. In the

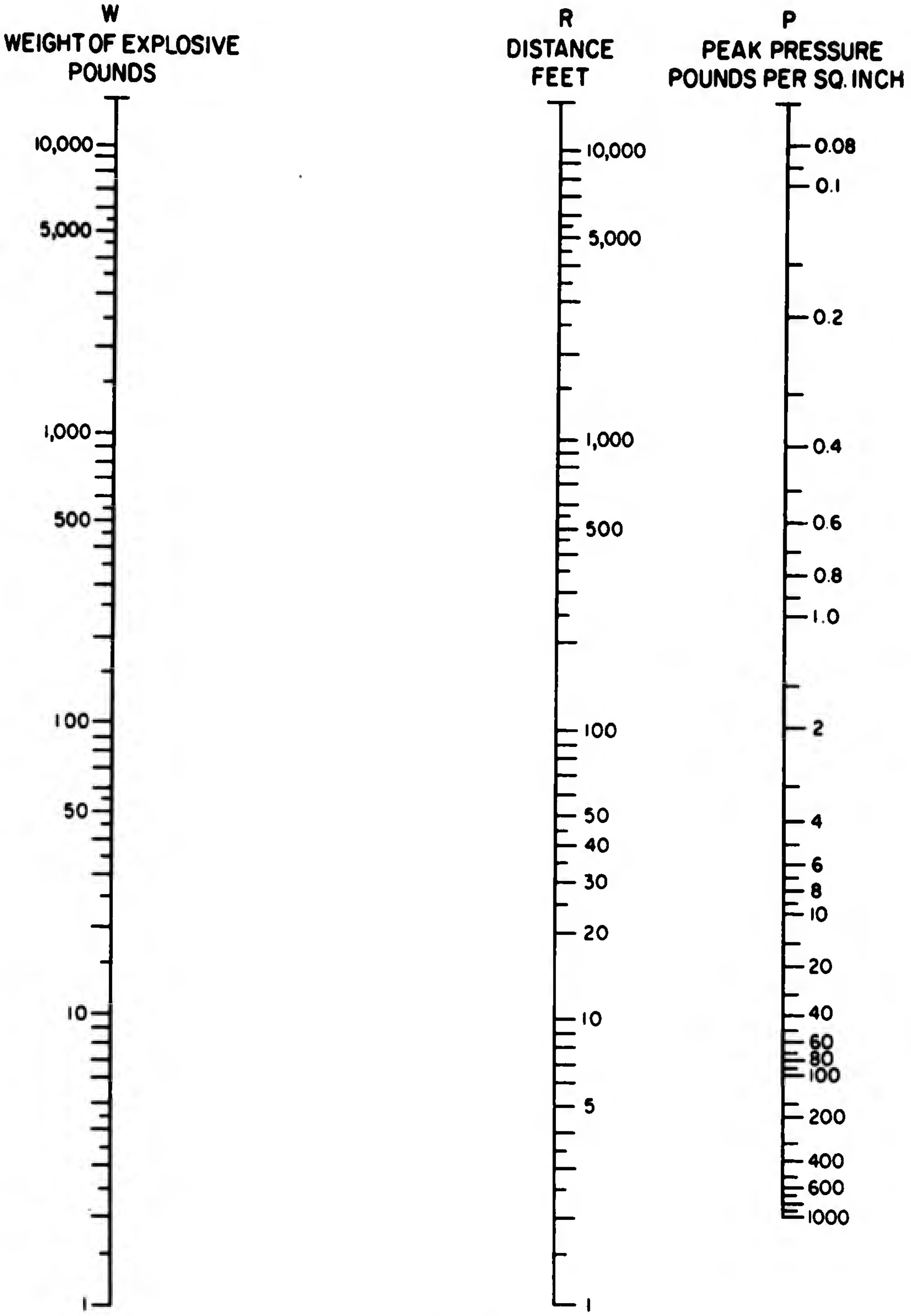

Figure 65. Nomogram of Peak Blast Pressure as a Function of Distance and Weight of Explosive

NOTE: Values are estimated accurate to about 25 percent. Readings taken with gage "side-on" to the blast wave; for "face-on" gage, pressure value should be approximately doubled.

former case, the reaction is completely "confined" and results in a fragmentation hazard. As mentioned in the preceding section, the main hazard resulting from "unconfined" explosions are overpressures or impulses.

The information presently available about the fragmentation hazards resulting from a propellant explosion within a storage tank is rather limited. In this program, a single test was performed to evaluate the thermal stability of hydrazine (see details on Large Scale Test No. 9). The test resulted in an explosion which scattered tank pieces within a radius of 1100 feet. The calculated TNT equivalent yield for this reaction was slightly less than one percent.

The determination of the fragmentation hazards resulting from the improper storage of pentaborane and hydrazine is a formidable task. The magnitude of these hazards is dependent upon the physicochemical properties of the propellants, nature of the reaction, configuration of storage tank, ullage space in the tank, etc. Consequently, it is impossible at this time to establish firm TNT equivalent yields for stored pentaborane and hydrazine based on the available data. However, tentative yield values can be derived by comparing the information available to that generated for propellant spills. Based on this approximate linear relationship, tentative values are presented in Table 10.

TABLE 10

TENTATIVE TNT YIELDS OF CONTAINED PROPELLANTS

Propellant	TNT Equivalent Yield,* percent
Hydrazine	1
Nitrogen Tetroxide	0
Chlorine Trifluoride	0
Pentaborane	2

*Pounds of TNT for 100 pounds of propellant

The equivalent charge of TNT resulting from the storage of the propellants considered herein can be derived from Eq. 9 and Table 10. It is again assumed that the contents of the largest single storage tank in the area would constitute the reference quantity of propellant.

$$W = x \frac{W_T}{100} \tag{9}$$

where

W = weight of TNT charge, pounds

x = TNT equivalent yield, percent

W_T = total weight of propellant in the storage tank, pounds

The magnitude of the fragmentation hazards, expressed as the maximum radial distance traveled by the fragments from the storage tank, can be calculated using the simplified procedure presented below.

The total explosive potential energy available in the storage tank can be expressed as

$$E = WH \tag{10}$$

where

E = total potential energy, foot-pound

W = weight of TNT charge, pounds

H = specific explosive energy of TNT charge, equal to 1,513,000 ft-lb/lb

The total potential energy in the storage tank during a propellant explosion is expended in (1) deforming the propellant tank, (2) compressing the fluid within the tank, and (3) propelling the tank fragments. However, in the determination of fragment hazards we are interested only in that portion of the energy utilized for propelling the fragments. Previous studies (Ref. 10) have demonstrated that in the case of gas explosions in vessels and piping, the energy expended in propelling the resulting fragments was about 10 percent of the total available energy. Thus, in this study we will assume an energy conversion efficiency of 10 percent.

The energy imparted to the fragments is equal to the change in kinetic energy of the fragments. This energy balance can be expressed as follows:

$$E\eta = 1/2\ MV^2 \tag{11}$$

where

E = total potential energy, ft-lb
η = energy conversion efficiency, assumed to be numerically equal to 0.10
M = total mass of dry storage tank, slugs
V = initial velocity of fragments, ft/sec

Equation 11 can be solved for the initial velocity of the fragments, which can subsequently be used to determine the maximum distance (range) expected to be traveled by the fragments, as follows:

$$R = \frac{V^2}{g} \tag{12}$$

where

R = maximum fragmentation range, feet
V = initial fragment velocity, ft/sec
g = gravitational constant, equal to 32.2 ft/sec^2 at sea level

The calculated value R is the solution to the problem. This value is the maximum to be expected since Eq. 12 neglects air resistance and assumes a maximum angle of launching.

Concluding Remarks

The blast hazards that must be considered in the storage of chlorine trifluoride, nitrogen tetroxide, hydrazine, and pentaborane were discussed. It was concluded that: (1) both fragmentation and overpressure hazards must be considered in the storage of pentaborane and hydrazine, (2) only overpressure hazards must be considered in the storage of chlorine trifluoride, and (3) nitrogen tetroxide can be stored without consideration of blast effects.

The techniques for establishing overpressure and fragmentation hazards were discussed in detail. It was found that although these techniques are relatively straightforward, their application to an actual situation is rather difficult. This difficulty arises from the fact that TNT equivalent yields for the propellants are not firmly established. To mitigate this deficiency, a set of tentative TNT yields were derived based on the limited information available, and were presented in Tables 9 and 10.

The need of reliable TNT-equivalent-yield values for establishing safe distances for the storage of the propellants is obvious. It is strongly recommended that an applied research program be implemented to verify and/or correct the estimates presented herein.

FIRE

The third hazard that must be considered in the establishment of safe distances for the storage of high-energy liquid propellants is fire. This hazard is limited to flammable propellants and can be particularly serious in the case of fuels having monopropellant tendencies. As a consequence, fire hazards must be considered in the storage of hydrazine and pentaborane, but can be neglected in the storage of chlorine trifluoride and nitrogen tetroxide. In general, fire hazards are expected to influence the design of storage tanks and support facilities, the separation between storage tanks, the location of control equipment, and the design of fire protection systems.

The hazards resulting from a propellant fire are derived primarily from the size of the propellant flame, the flame temperature, and the radiation intensity. Each propellant and the quantity of propellant stored in a tank have an effect on these parameters, which will vary the storage area design criteria. This criteria is based upon the energy released per unit time from the burning fuel and the fraction of this energy radiated to surrounding surfaces.

Factors that influence the release, transmittance, and absorption of energy from burning fuels are discussed below.

Burning Rates

The burning rate of a liquid fuel in an open revetment is dependent upon the dimensions of the revetment, the amount of heat transferred from the flame to the liquid, the presence of convective currents, and the heat associated with vaporization and combustion of the fuel.

Revetment Dimensions. Some work has been done in recent years to determine the effects of container dimensions upon the burning rate of liquid fuels. Most of this research (Ref. 11, 12, and 13) has utilized circular trays of less than 40 inches in diameter. As determined from this work, the radiation from the flame per unit area of liquid can be expressed as

$$\frac{q}{A} = \sigma F(T_F^4 - T_B^4)(1 - e^{-kd}) \qquad (13)$$

where

q = rate of heat flow, Btu/hr
A = area of exposed liquid surface, ft^2
σ = Stefan-Boltzmann constant, 0.1713×10^{-8} Btu/ft^2-hr-R^4

F = geometrical factor

T_F = absolute flame temperature, R

T_B = absolute saturation temperature of liquid fuel, R

k = opacity coefficient, ft^{-1}

d = tray diameter, ft

The variation of fuel burning rate with tray diameter is determined primarily by the term $(1 - e^{-kd})$. A limiting value of burning rate is attained when e^{-kd} becomes effectively zero. For hydrocarbon flames, the value of k has been found to be in the order of 0.6 - 0.9 ft^{-1}; consequently, the function e^{-kd} approaches zero when the tray diameter is about 4 feet. Since storage tank revetments are expected to be much larger than 4 feet in diameter, it is reasonable to assume that the fuel burning rate will be independent of the revetment dimensions. In addition, the test data has indicated also that the burning rates of fuels are not influenced appreciably by the depth of the standing liquid.

Liquid Regression Rate. Experimental studies have been performed to determine the fuel regression rate (a measure of burning rate) resulting from the transfer of heat from the flame to the liquid in large shallow trays. The rate of fuel consumption, expressed as a linear regression rate, is given by the equation

$$V = V_{\infty} \left[1 - e^{-kd}\right] \qquad (14)$$

where

V = liquid regression rate for tray under consideration, cm/sec

V_∞ = liquid regression rate for trays of large diameters, cm/sec

k = a constant, approximately equal to one, ft^{-1}

d = tray diameter, ft

With fuels such as unsymmetrical dimethylhydrazine, methanol, and benzene, the value of V_∞ in Eq. (14) is related to the fraction of heat of combustion that is fed back to the liquid to support vaporization. This relationship can be expressed as follows

$$V_\infty = 0.0077 \left(\frac{\Delta H_c}{\Delta H_v}\right) \tag{15}$$

where

V_∞ = liquid regression rate for trays of large diameters, cm/sec

ΔH_c = net heat of combustion of fuel, Btu/lb

ΔH_v = effective latent heat of vaporization of liquid fuel, Btu/lb

Equation (15) is expected to apply to all pure fuels, but not to any of the fuels that exhibit monopropellant tendencies which can develop heat of decomposition in the liquid and vapor phases without the necessity of radiant heat transfer.

Experiments have demonstrated that in the case of large fires, such as those expected from the spillage of the contents of a propellant tank into a diked basin, the heat transfer from the flame to the liquid by radiation is by far more significant than that by convection and conduction. Under most favorable burning conditions for convection (fuel such as methanol), radiation accounts for as much as three times the heat transfer by convection.

Effects of Wind Conditions. The primary effect of moderate winds (10 to 15 mph) on the burning of fuels in open pools is to increase the burning rate to the limiting (large diameter) value. Since the spillage of flammable propellants into diked basins is expected to result in large fires, it is reasonable to state that the effect of moderate winds on such fires is negligible for all practical purposes. In the case of strong winds, however, the flame may be completely blown off, or burning rates in excess of the limiting value may be obtained.

Radiation From Fuel Flames

The radiant energy interchange between a propellant fire and surrounding objects can basically be estimated using the same factors presented in Eq. (13). This equation is based upon the assumption that bodies emitting or absorbing the radiant energy are gray bodies. A gray body absorbs all wavelength of radiation with the same absorptivity, and since its total absorptivity is independent of the energy distribution in the incident radiation, the emissivity may be used as the absorptivity.

The assumption of gray-body conditions for luminous gases generally does not introduce appreciable errors, but in the treatment of radiation from non-luminous gases, it is necessary to consider the dependence of the emissivity or absorptivity on wavelength.

The direct net interchange of radiant energy between two non-black bodies (Ref. 14) can be expressed as

$$
\begin{aligned}
q &= \epsilon_h \alpha_c \; F_{h \rightarrow c} \; A_h \sigma \left(T_h^4 - T_c^4\right) \\
&= \epsilon_c \alpha_h \; F_{c \rightarrow h} \; A_c \sigma \left(T_h^4 - T_c^4\right)
\end{aligned}
\tag{16}
$$

where

q = net rate of heat flow, Btu/hr

ϵ = emissivity

α = absorptivity

A = projected surface area, ft^2

σ = Stefan-Boltzmann constant, 0.1713×10^{-8} Btu/ft^2-hr-R^4

F = geometrical factor

T = absolute surface temperature, R

subscripts

h = hot body

c = cold body

Equation (16) is relatively simple since only one shape factor, one absorptivity, and one emissivity are required for its solution. Its main limitation is the assumption of direct energy interchange, which is only a portion of the total radiative energy since it disregards the reflected radiant energy component.

The actual energy radiated from a propellant fire to surrounding objects is only a fraction of the total energy generated by the combustion of the propellant. As discussed previously, a portion of the total energy (20 to 40 percent) is radiated back to the liquid surface to effect propellant vaporization and thus support the fire. In addition, the radiant energy transmitted by the fire to surrounding objects is severly attenuated before striking the object surfaces. This attenuation is caused by the absorption of energy by water vapor and other nonsymmetrical constituents in air.

Considering all the possible energy losses from a propellant fire, it appears possible to relate the effective radiant heat transfer to nearby objects to the total energy liberated from the propellant fire. This relationship can be expressed as

$$q = \eta \frac{I}{I_o} q_c \qquad (17)$$

where

q = effective rate of heat flow, Btu/hr

η = fraction of energy radiated to surrounding objects

I = effective intensity of radiated energy, Btu/hr - ft^2

I_o = total intensity of radiated energy, Btu/hr - ft^2

q_c = total energy liberated by propellant fire, Btu/hr

The effective and total intensity of the radiated energy can be expressed as

$$\frac{I}{I_o} = e^{-kr} \qquad (18)$$

where

I = effective intensity of radiated energy, Btu/hr - ft^2

I_o = total intensity of radiated energy, Btu/hr - ft^2

k = absorption coefficient, ft^{-1}

r = distance from object to flame, ft

Experiments performed by the Bureau of Mines (Ref. 13) with liquid hydrogen yielded an absorption coefficient (k, Eq. 18) value of 0.015w, where the term "w" is the percentage of water vapor present in the atmosphere under consideration.

Surrounding Objects

The heat transfer phenomenom from propellant fires to surrounding objects was discussed in the preceding paragraphs. Consideration was given to the heat flow resulting from such fires and the effects on surface temperatures of nearby objects. The actual effect of external surface temperature on a propellant stored within a tank is dependent upon:

1. The heat flow from the hot surface to the propellant
2. Duration of fire
3. Thermal stability of stored propellant
4. Heat capacity and conductivity of propellant and storage-tank material
5. Thickness and size of storage tank
6. Quantity of stored propellant.

However, once the external surface temperature of a storage tank is known, the temperature distribution within the tank can be established using conduction and convection energy transfer techniques.

Safe Distances

As mentioned previously, several variables influence the determination of the burning rates of fuels, emissivity of fuel flames, and the absorption of radiant energy by surrounding surfaces. All of these variables affect to some degree the establishment of safe-distance values for the storage of pentaborane and hydrazine based on fire hazards. Actual determination of these variables has been limited to just a few pure fuels. This work was further limited to shallow small trays and was primarily directed toward the determination of burning rates.

The determination of safe distance values based on fire hazards for the storage of fuels such as pentaborane and hydrazine is further complicated by the fact that these fuels have inherent monopropellant tendencies. This not only influences the fuel burning rates, but also the amount of energy a tank containing these fuels can absorb before rapid decomposition or an explosion occurs.

Concluding Remarks

Safe-distance values based on fire hazards for the storage of hydrazine and pentaborane are not available. In addition, these values are of such nature that they cannot even be grossly approximated analytically.

An applied research program should be instituted to establish firm quantity-distance values based on fire hazards for the storage of pentaborane and hydrazine. This program should determine the burning rates of these propellants in open pools, the energy distribution of such fires, radiation intensity patterns, and the effect of such fires on adjacent equipment. The conduction of the program is expected to be straightforward; however, a considerable amount of instrumentation and data analysis would be required.

CONCLUDING REMARKS ON SAFE DISTANCES

A logical approach for the establishment of safe distances for the storage of hydrazine, pentaborane, nitrogen tetroxide, and chlorine trifluoride has been presented. The effects of all hazards influencing safe distances were discussed in reasonable detail. A concerted effort was made in each case to utilize all pertinent information available and to generate the maximum data and criteria possible within the scope of the program. However, the information evolved from this effort is far from sufficient to establish firm safe distances for the storage of the propellants. To overcome this limitation, a special effort was made to provide a general but detailed analysis of the problem in terms of simple mathematical relations. This approach was selected to provide an understanding of all variables involved in the problem and should prove useful in motivating further work to solve the problem reliably. Recommendations were made at the end of the discussion on each hazard to perform limited applied research programs to obtain the required information.

The hazards that must be considered in the storage of high-energy propellants are toxicity, blast, and fire. Consideration must be given also to the two possible blast effects: fragmentation and overpressures. Fragmentation hazards are the result of propellant explosions within confined systems; whereas, overpressures can be generated by propellant explosions within revetments. The hazards that must be considered in the storage of the propellants studied here are summarized in Table 11.

TABLE 11

CONSIDERATION OF HAZARDS FOR PROPELLANT STORAGE

Propellant	Hazards			
		Blast		
	Toxicity	Overpressure	Fragmentation	Fire
Hydrazine	X	X	X	X
Pentaborane	X	X	X	X
Chlorine Trifluoride	X	X		
Nitrogen Tetroxide	X			

The establishment of safe distances for the storage of each propellant requires that (1) all the potential hazards of the propellant are defined, and (2) the specific effects of each hazard are established. With this information, the location of a storage facility can be reliably selected. The safe distance from the propellant storage tank to support facilities, roads, railroads, inhabited buildings, etc. would be the maximum distance indicated by any of the potential hazards for that specific item under consideration.

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APPENDIX A

SAMPLE CALCULATION OF SAFE-DISTANCE VALUES, BASED ON TOXICITY, FOR A POTENTIAL PROPELLANT SPILLAGE AT TEMPERATURES BELOW THE PROPELLANT BOILING POINT

The mechanics employed in the sample problem that follows is applicable to any propellant spilled at temperatures below its boiling point, provided that (1) there is no heat or chemical reaction associated with the spillage, (2) the propellant is spilled gently without atomization, and (3) the temperature of the propellant is approximately equal to the ambient air temperature. In this sample problem, hydrazine was selected as the typical propellant. Air temperatures of 77, 85, and 110 F were considered at moderate inversion, neutral, and large-lapse weather conditions. This selection of propellant and conditions permits the establishment of safe-distance values over a sufficient spectrum to provide a clear understanding of the variables involved in the problem.

The contents of a hydrazine storage tank is assumed to be spilled gently into an inert, diked basin. The basin is 25-feet long, 15-feet wide, and of sufficient depth to accommodate the spilled propellant. It is assumed also that sufficient fuel is spilled to cover the floor of the basin.

VAPORIZATION RATES

The determination of the propellant vaporization rates for each assumed air temperature is presented below. These rates will be established for each type of assumed weather condition.

Air Temperature of 77 F

The solution to the mass-transfer formula (Eq. 3) will be attempted by parts. This equation is repeated below for convenience.

$$\frac{K'_g}{G_m}\left(\frac{\mu}{\rho D}\right)_f^{2/3} = 0.036\left(\frac{LG}{\mu}\right)^{-0.2} \qquad \text{(3) repeated}$$

The properties of hydrazine and air required for the solution of Eq. (3), at a temperature of 77 F, are presented in Table A-1. These properties were obtained from the available literature whenever possible. When this was not possible, their values were derived from idealized physicochemical relationships.

TABLE A-1

PROPERTIES OF AIR AND HYDRAZINE AT 77 F

	Air	Hydrazine
Gas viscosity, lb/ft-sec	1.18×10^{-5}	0.589×10^{-5}
Gas density, lb/cu ft	0.0739	0.0817
Gas pressure, psia	14.7	0.285
Molecular weight	29.0	32.2
Molecular volume, cc/g-mol	29.9	34.4

The interdiffusion of the hydrazine vapor and air (D, Eq. 3) can be obtained from Eq. (4), which is repeated below.

$$D = 0.0043 \frac{T^{3/2}}{P(v_a^{1/3} + v_b^{1/3})^2} \sqrt{\frac{1}{M_a} + \frac{1}{M_b}} \qquad (4) \text{ repeated}$$

Substituting in Eq. (4) the applicable properties of air and hydrazine in the proper units, we obtain,

$$D = 0.0043 \frac{(298)^{3/2}}{1\left[(29.9)^{1/3} + (34.4)^{1/3}\right]^2} \sqrt{\frac{1}{29} + \frac{1}{32}}$$

$$= \frac{0.0043 \times 5150 \times 0.256}{40.3}$$

$$= 0.1405 \text{ cm}^2/\text{sec}$$

$$= 1.511 \times 10^{-4} \text{ ft}^2/\text{sec}$$

The evaluation of the Schmidt number, $\left(\frac{\mu}{\rho D}\right)_f$, for the air-vapor film requires the values of viscosity and density in the film. These properties can be evaluated by assuming that the composition of the gas mixtures is dictated solely by the pressure (partial pressure) of the constituents.

The volumetric fraction of a component in a gas mixture can be expressed as,

$$B_x = \frac{P_x}{P_m} \tag{A-1}$$

where,

B_x = volumetric mole fraction of component x

P_x = partial pressure of component x, psia

P_m = total pressure of gas mixture, psia

Solving Eq. (A-1) for the conditions of this problems,

$$B_{air} \approx \frac{14.7}{15.0} \approx 0.98$$

and,

$$B_{N_2H_4} \approx \frac{0.3}{15.0} \approx 0.02$$

which indicates that the gas film consists of 98 percent air and 2 percent hydrazine, by volume. This analysis can be converted into gravimetric form using Eq. (A-2).

$$G_x = \frac{B_x M_x}{B_x M_x + B_y M_y} \tag{A-2}$$

where:

G_x = gravimetric fraction of component x

$B_{x,y}$ = volumetric fraction of components, x, y

$M_{x,y}$ = molecular weight of components, x, y

Substituting the appropriate values in Eq. (A-2),

$$G_{air} = \frac{0.98 \times 29}{0.98 \times 29 + 0.02 \times 32}$$

and,

$$G_{N_2H_4} = \frac{0.02 \times 32}{0.02 \times 32 + 0.98 \times 29}$$

which reduces to,

$$G_{air} = 0.978$$

and,

$$G_{N_2H_4} = 0.022$$

With the gravimetric analysis values obtained above, the viscosity of the air-vapor film can be approximated using Eq. (A-3).

$$\mu_f = \mu_x G_x + \mu_y G_y \qquad \text{(A-3)}$$

The substitution of the proper values in Eq. (A-3) gives,

$$\mu_f = 1.18 \times 10^{-5} \times 0.978 + 0.589 \times 10^{-5} \times 0.022$$

$$= 1.168 \times 10^{-5} \text{ lb/ft-sec}$$

Similarly, the density of the film can be obtained using Eq. (A-4).

$$\rho_f = \rho_x G_x + \rho_y G_y \qquad \text{(A-4)}$$

Substituting the proper values in the equation we obtain,

$$\rho_f = 0.0739 \times 0.978 + 0.0817 \times 0.022$$

$$= 0.0741 \text{ lb/cu ft}$$

Solving for the Schmidt number of the air-vapor film,

$$\left(\frac{\mu}{\rho D}\right)_f = \frac{1.168 \times 10^{-5}}{0.0741 \times 1.511 \times 10^{-4}}$$

$$= 1.04$$

The molar mass velocity of wind (G_m, Eq. 3) for the three assumed weather conditions (Table 8) can be determined using the following equation,

$$G_m = \frac{\rho \bar{U}}{M} \tag{A-5}$$

where,

G_m = molar mass velocity of wind, lb-mol/sec-ft^2

ρ = density of air, lb/cu ft

$\bar{U}$ = average wind speed, ft/sec

M = molecular weight of air

The molar mass velocity of wind for each assumed weather condition is,

(a) Moderate Inversion

$$G_m = \frac{0.0739 \times 6.56}{29}$$

$$= 0.0167 \text{ lb-mol/sec-ft}^2$$

(b) Neutral

$$G_m = \frac{0.0739 \times 13.12}{29}$$

$$= 0.0334 \text{ lb-mol/sec-ft}^2$$

(c) Large Lapse

$$G_m = \frac{0.0739 \times 19.68}{29}$$

$$= 0.0501 \text{ lb-mol/sec-ft}^2$$

Similarly, the mass velocity of wind (G, Eq. 3) can be expressed as,

$$G = \rho \bar{U} \tag{A-6}$$

where,

G = mass velocity of wind, $lb/sec\text{-}ft^2$

ρ = density of air, lb/cu ft

$\bar{U}$ = average wind speed, ft/sec

For the following weather conditions, the value of G is:

(a) Moderate Inversion

$$G = 0.0739 \times 6.56$$
$$= 0.485 \ lb/sec\text{-}ft^2$$

(b) Neutral

$$G = 0.739 \times 13.12$$
$$= 0.970 \ lb/sec\text{-}ft^2$$

(c) Large Lapse

$$G = 0.0739 \times 19.68$$
$$= 1.455 \ lb/sec\text{-}ft^2$$

The Reynolds number ($\frac{LG}{\mu}$, Eq. 3) for each weather condition selected, and assuming that the wind direction is along the longitudinal axis of the dike, is:

(a) Moderate Inversion

$$\frac{LG}{\mu} = \frac{25 \times 0.485}{1.18 \times 10^{-5}}$$
$$= 1.028 \times 10^{6}$$

(b) Neutral

$$\frac{LG}{\mu} = \frac{25 \times 0.970}{1.18 \times 10^{-5}}$$

$$= 2.055 \times 10^{6}$$

(c) Large Lapse

$$\frac{LG}{\mu} = \frac{25 \times 1.455}{1.18 \times 10^{-5}}$$

$$= 3.08 \times 10^{6}$$

The substitution of the parameters calculated above into the mass-transfer equation results in the determination of the film mass-transfer rate (K'_g, Eq. 3). This rate information can be modified to provide the desired propellant vaporization rates. These operations are performed as follows:

(a) Moderate Inversion

$$\frac{K'_g}{0.0167} \quad (1.04)^{2/3} = 0.036 \, (1.028 \times 10^{6})^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0167} \times 1.026 = 0.036 \times 0.06275$$

rearranging terms,

$$K'_g = \frac{0.0167 \times 0.036 \times 0.06275}{1.026}$$

$$= 0.0000368 \text{ lb-mol/sec-ft}^2$$

The vaporization rate of the propellant can be expressed as,

$$\dot{w}_v = K'_g M_f A G_{N_2H_4} \qquad \text{(A-7)}$$

where, $\dot{w}_v$ = vaporization rate of propellant lb/sec

K'_g = mass-transfer coefficient of gas film, lb-mol/sec-ft^2

M_f = molecular weight of gas film

A = cross-sectional area of diked basin, ft^2

G = gravimetric fraction of propellant in gas film

The molecular weight of the gas film, M_f, can be in turn derived as follows:

$$M_f = B_x M_x + B_y M_y \tag{A-8}$$

substituting the appropriate values,

$$M_f = 0.98 \times 29 + 0.02 \times 32$$
$$= 29.04$$

The cross-sectional area of the diked basin is the product of the length and width of the basin, which, based on our assumed conditions, is 375 sq. feet.

Solving Eq. (A-7) for the propellant vaporization rate, we obtain,

$$\dot{w}_v = 0.0000368 \times 29.04 \times 375 \times 0.022$$
$$= 0.0088 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 77 F for the assumed moderate inversion weather condition.

(b) Neutral

Following the same order of presentation as that employed for moderate inversion, we obtain,

$$\frac{K'_g}{0.0334} (1.04)^{2/3} = 0.036 \, (2.055 \times 10^6)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0334} \times 1.026 = 0.036 \times 0.05463$$

rearranging terms,

$$K'_g = \frac{0.0334 \times 0.036 \times 0.05463}{1.026}$$

$$= 0.000064 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.000064 \times 29.04 \times 375 \times 0.022$$

$$= 0.0153 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 77 F for the assumed neutral weather condition.

(c) **Large Lapse**

Similarly,

$$\frac{K'_g}{0.0501} (1.04)^{2/3} = 0.036 \quad (3.08 \times 10^6)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0501} \times 1.026 = 0.036 \times 0.05038$$

rearranging terms,

$$K'_g = \frac{0.0501 \times 0.036 \times 0.05038}{1.026}$$

$$= 0.0000886 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000886 \times 29.04 \times 375 \times 0.022$$

$$= 0.0212 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 77 F for the assumed large lapse weather condition.

Air Temperature of 85 F

The determination of the vaporization rates resulting from a hydrazine spill at an air temperature of 85 F is presented below. For simplicity, the calculations are presented in the same order as that employed for an air temperature of 77 F.

The properties of hydrazine and air required for the solution of the mass-transfer equation are presented in Table A-2. These properties were obtained from the available literature whenever possible. When this was impossible, the values were derived from idealized physicochemical relationships.

TABLE A-2

PROPERTIES OF AIR AND HYDRAZINE AT 85 F

	Air	Hydrazine
Gas viscosity, lb/ft-sec	1.26×10^{-5}	0.589×10^{-5}
Gas density, lb/cu ft	0.0728	0.0805
Gas pressure, psia	14.7	0.368
Molecular weight	29.0	32.0
Molecular volume, cc/g-mol	29.9	34.4

The interdiffusion coefficient of the hydrazine vapor in air is obtained from the following relation,

$$D = \frac{0.0043\ (302.44)^{3/2}}{1\left[(29.9)^{1/3} + (34.4)^{1/3}\right]^2} \sqrt{\frac{1}{29} + \frac{1}{32}}$$

$$= \frac{0.0043 \times 5260 \times 0.256}{40.3}$$

$$= 0.1435 \text{ cm}^2/\text{sec}$$

$$= 1.544 \times 10^{-4} \text{ ft}^2/\text{sec}$$

The volumetric fraction of air and hydrazine vapor in the film, respectively, is,

$$B_{air} \approx \frac{14.7}{15.1} \approx 0.974$$

and,

$$B_{N_2H_4} \approx \frac{0.4}{15.1} \approx 0.026$$

Solving for the gravimetric fraction of the components in the film,

$$G_{air} = \frac{0.974 \times 29}{0.974 \times 29 + 0.026 \times 32}$$

and,

$$G_{N_2H_4} = \frac{0.026 \times 32}{0.026 \times 32 + 0.974 \times 29}$$

which reduces to,

$$G_{air} = 0.971$$

and,

$$G_{N_2H_4} = 0.029$$

The viscosity of the air-vapor film is,

$$\mu_f = 1.26 \times 10^{-5} \times 0.971 + 0.589 \times 10^{-5} \times 0.029$$

$$= 1.24 \times 10^{-5} \text{ lb/ft-sec}$$

Similarly, the density of the film is,

$$\rho_f = 0.0728 \times 0.971 + 0.0805 \times 0.029$$

$$= 0.0730 \text{ lb/cu ft}$$

Solving for the Schmidt number of the air-vapor film,

$$\left(\frac{\mu}{\rho D}\right)_f = \frac{1.24 \times 10^{-5}}{0.0730 \times 1.544 \times 10^{-4}}$$

$$= 1.10$$

The molar mass velocity of wind for the assumed weather conditions is:

(a) Moderate Inversion

$$G_m = \frac{0.0728 \times 6.56}{29}$$

$$= 0.0165 \text{ lb-mol/sec-ft}^2$$

(b) Neutral

$$G_m = \frac{0.0728 \times 13.12}{29}$$

$$= 0.0330 \text{ lb-mol/sec-ft}^2$$

(c) Large Lapse

$$G_m = \frac{0.0728 \times 19.68}{29}$$

$$= 0.0494 \text{ lb-mol/sec-ft}^2$$

Similarly, the mass velocity of wind is:

(a) Moderate Inversion

$$G = 0.0728 \times 6.56$$

$$= 0.4775 \text{ lb/sec-ft}^2$$

(b) Neutral

$$G = 0.0728 \times 13.12$$

$$= 0.956 \text{ lb/sec-ft}^2$$

(c) Large Lapse

$$G = 0.0728 \times 19.68$$

$$= 1.432 \text{ lb/sec-ft}^2$$

The Reynolds number for each weather condition selected, and assuming that the wind direction is again along the longitudinal axis of the dike, is:

(a) Moderate Inversion

$$\frac{LG}{\mu} = \frac{25 \times 0.4775}{1.26 \times 10^{-5}}$$

$$= 0.948 \times 10^6$$

(b) Neutral

$$\frac{LG}{\mu} = \frac{25 \times 0.956}{1.26 \times 10^{-5}}$$

$$= 1.897 \times 10^6$$

(c) Large Lapse

$$\frac{LG}{\mu} = \frac{25 \times 1.432}{1.26 \times 10^{-5}}$$

$$= 2.84 \times 10^6$$

The molecular weight of the air-vapor film is,

$$M_f = 0.974 \times 29 + 0.026 \times 32$$

$$= 29.05$$

The vaporization rate of hydrazine for each selected weather condition can be obtained as follows:

(a) Moderate Inversion

$$\frac{K'_g}{0.0165} (1.10)^{2/3} = 0.036 \, (0.948 \times 10^6)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0165} \times 1.066 = 0.036 \times 0.06377$$

rearranging terms,

$$K'_g = \frac{0.0165 \times 0.036 \times 0.06377}{1.066}$$

$$= 0.0000356 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000356 \times 29.05 \times 375 \times 0.029$$

$$= 0.01125 \text{ lb/sec}$$

which is the vaporization rate of the propellant at an air temperature of 85 F for the assumed moderate inversion weather condition.

(b) Neutral

$$\frac{K'_g}{0.0330} (1.10)^{2/3} = 0.036 \left(1.897 \times 10^6\right)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0330} \times 1.066 = 0.036 \times 0.05551$$

rearranging terms,

$$K'_g = \frac{0.0330 \times 0.036 \times 0.05551}{1.066}$$

$$= 0.0000618 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000618 \times 29.05 \times 375 \times 0.029$$

$$= 0.01953 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 85 F for the assumed neutral weather condition.

(c) Large Lapse

$$\frac{K'_g}{0.0494} (1.10)^{2/3} = 0.036 (2.84 \times 10^6)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0494} \times 1.066 = 0.036 \times 0.05121$$

rearranging terms,

$$K'_g = \frac{0.0494 \times 0.036 \times 0.05121}{1.066}$$

$$= 0.0000854 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000854 \times 29.05 \times 375 \times 0.029$$

$$= 0.0270 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 85 F for the large lapse weather condition selected.

Air Temperature of 110 F

The determination of the vaporization rates of hydrazine at an air temperature of 110 F follows. For consistency and simplicity, these calculations are presented in the same order as that employed for an air temperature of 77 F.

The properties of air and hydrazine required for the solution of this problem are presented in Table A-3. These properties were obtained from the available literature wherever possible. When this was impossible, they were calculated using idealized physicochemical formulae.

TABLE A-3

PROPERTIES OF AIR AND HYDRAZINE AT 110 F

	Air	Hydrazine
Gas viscosity, lb/ft-sec	1.3×10^{-5}	0.589×10^{-5}
Gas density, lb/cu ft	0.0696	0.077
Gas pressure, psia	14.7	0.785
Molecular weight	29.0	32.0
Molecular volume, cc/g-mol	29.9	34.4

The interdiffusion coefficient of the hydrazine vapor in air (Eq. 4) is expressed as follows,

$$D = \frac{0.0043\ (316)^{3/2}}{1\left[(29.9)^{1/3} + (34.4)^{1/3}\right]^2} \sqrt{\frac{1}{29} + \frac{1}{32}}$$

$$= \frac{0.0043 \times 5617 \times 0.256}{40.3}$$

$$= 0.1532\ \text{cm}^2/\text{sec}$$

$$= 1.65 \times 10^{-4}\ \text{ft}^2/\text{sec}$$

The volumetric fraction of the air and hydrazine vapor in the film, respectively, can be obtained as follows,

$$B_{air} \approx \frac{14.7}{15.5} \approx 0.948$$

and,

$$B_{N_2H_4} \approx \frac{0.8}{15.5} \approx 0.052$$

Solving for the gravimetric fraction of the components in the film,

$$G_{air} = \frac{0.948 \times 29}{0.948 \times 29 + 0.052 \times 32}$$

and,

$$G_{N_2H_4} = \frac{0.052 \times 32}{0.948 \times 29 + 0.052 \times 32}$$

which reduces to,

$$G_{air} = 0.943$$

and,

$$G_{N_2H_4} = 0.057$$

The viscosity of the air-vapor film is,

$$\mu_f = 1.3 \times 10^{-5} \times 0.943 + 0.589 \times 10^{-5} \times 0.057$$

$$= 1.26 \times 10^{-5} \text{ lb/ft-sec}$$

Similarly, the density of the film is,

$$\rho_f = 0.0696 \times 0.943 + 0.077 \times 0.057$$

$$= 0.0701 \text{ lb/cu ft}$$

Solving for the Schmidt number of the air-vapor film,

$$\left(\frac{\mu}{\rho D}\right)_f = \frac{1.26 \times 10^{-5}}{0.0701 \times 1.65 \times 10^{-4}}$$

$$= 1.088$$

The molar mass velocity of wind for the assumed weather conditions is:

(a) Moderate Inversion

$$G_m = \frac{0.0696 \times 6.56}{29}$$

$$= 0.01577 \text{ lb-mol/sec-ft}^2$$

(b) Neutral

$$G_m = \frac{0.0696 \times 13.12}{29}$$

$$= 0.0315 \text{ lb-mol/sec-ft}^2$$

(c) Large Lapse

$$G_m = \frac{0.0696 \times 19.68}{29}$$

$$= 0.0472 \text{ lb-mol/sec-ft}^2$$

Similarly, the mass velocity of wind is:

(a) Moderate Inversion

$$G = 0.0696 \times 6.56$$

$$= 0.456 \text{ lb/sec-ft}^2$$

(b) Neutral

$$G = 0.0696 \times 13.12$$

$$= 0.914 \text{ lb/sec-ft}^2$$

(c) Large Lapse

$$G = 0.0696 \times 19.68$$

$$= 1.369 \text{ lb/sec-ft}^2$$

The Reynolds number for each weather condition selected, and assuming that the wind direction is again along the longitudinal axis of the dike, is:

(a) Moderate Inversion

$$\frac{LG}{\mu} = \frac{25 \times 0.456}{1.3 \times 10^{-5}}$$

$$= 0.877 \times 10^6$$

(b) Neutral

$$\frac{LG}{\mu} = \frac{25 \times 0.914}{1.3 \times 10^{-5}}$$

$$= 1.754 \times 10^{6}$$

(c) Large Lapse

$$\frac{LG}{\mu} = \frac{25 \times 1.369}{1.3 \times 10^{-5}}$$

$$= 2.63 \times 10^{6}$$

The molecular weight of the air-vapor film is,

$$M_f = 0.948 \times 29 + 0.052 \times 32$$

$$= 29.16$$

The vaporization rate of hydrazine for each selected weather condition can be obtained as follows:

(a) Moderate Inversion

$$\frac{K'_g}{0.01577} (1.088)^{2/3} = 0.036 (0.877 \times 10^{6})^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.01577} \times 1.058 = 0.036 \times 0.06477$$

rearranging terms,

$$K'_g = \frac{0.01577 \times 0.036 \times 0.06477}{1.058}$$

$$= 0.0000348 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000348 \times 29.16 \times 375 \times 0.057$$

$$= 0.02168 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 110 F for the assumed moderate inversion weather condition.

(b) Neutral

$$\frac{K'_g}{0.0315}(1.088)^{2/3} = 0.036\,(1.754 \times 10^6)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0315} \times 1.058 = 0.036 \times 0.05639$$

rearranging terms,

$$K'_g = \frac{0.0315 \times 0.036 \times 0.05639}{1.058}$$

$$= 0.0000605 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000605 \times 29.16 \times 375 \times 0.057$$

$$= 0.0377 \text{ lb/sec}$$

which is the vaporization rate of hydrazine at an air temperature of 110 F for the neutral weather condition assumed.

(c) Large Lapse

$$\frac{K'_g}{0.0472}(1.088)^{2/3} = 0.036\,(2.63 \times 10^6)^{-0.2}$$

which reduces to,

$$\frac{K'_g}{0.0472} \times 1.058 = 0.036 \times 0.052$$

rearranging terms,

$$K'_g = \frac{0.0472 \times 0.036 \times 0.052}{1.058}$$

$$= 0.0000835 \text{ lb-mol/sec-ft}^2$$

and,

$$\dot{w}_v = 0.0000835 \times 29.16 \times 375 \times 0.057$$

$$= 0.052 \text{ lb/sec}$$

which is the vaporization rate of hydrazine for the large lapse weather condition assumed, at an air temperature of 110 F.

Remarks on Vaporization Rates

The vaporization rate values of hydrazine calculated above are plotted in Fig. A-1 as functions of wind speed and air temperature. It should be noted that these values are valid only for the conditions stipulated in the problem.

Of significant importance is the fact that the vaporization rate of hydrazine is independent of the quantity of propellant spilled. The only assumption made in this respect was that sufficient propellant was spilled to cover the floor of the basin. In this manner, the vaporization rate becomes a function of the diked basin configuration.

ATMOSPHERIC DIFFUSION

The propellant vapor concentration as functions of source strength (vaporization rate), source distance, and weather conditions can be estimated using Sutton's Continuous Point Source Formula. This equation is repeated below for convenience.

$$\chi = \frac{2Q}{\pi C_y C_z \bar{U} X^{2-n}} \exp\left[-X^{n-2}\left(\frac{Y^2}{C_y^2} + \frac{Z^2}{C_z^2}\right)\right] \qquad \text{(6) repeated}$$

The maximum concentration in a vapor cloud, which is of primary interest, exists along the axis of the cloud. Therefore, we can modify Eq. (6) by placing $Y = 0$ and $Z = 0$, thus obtaining,

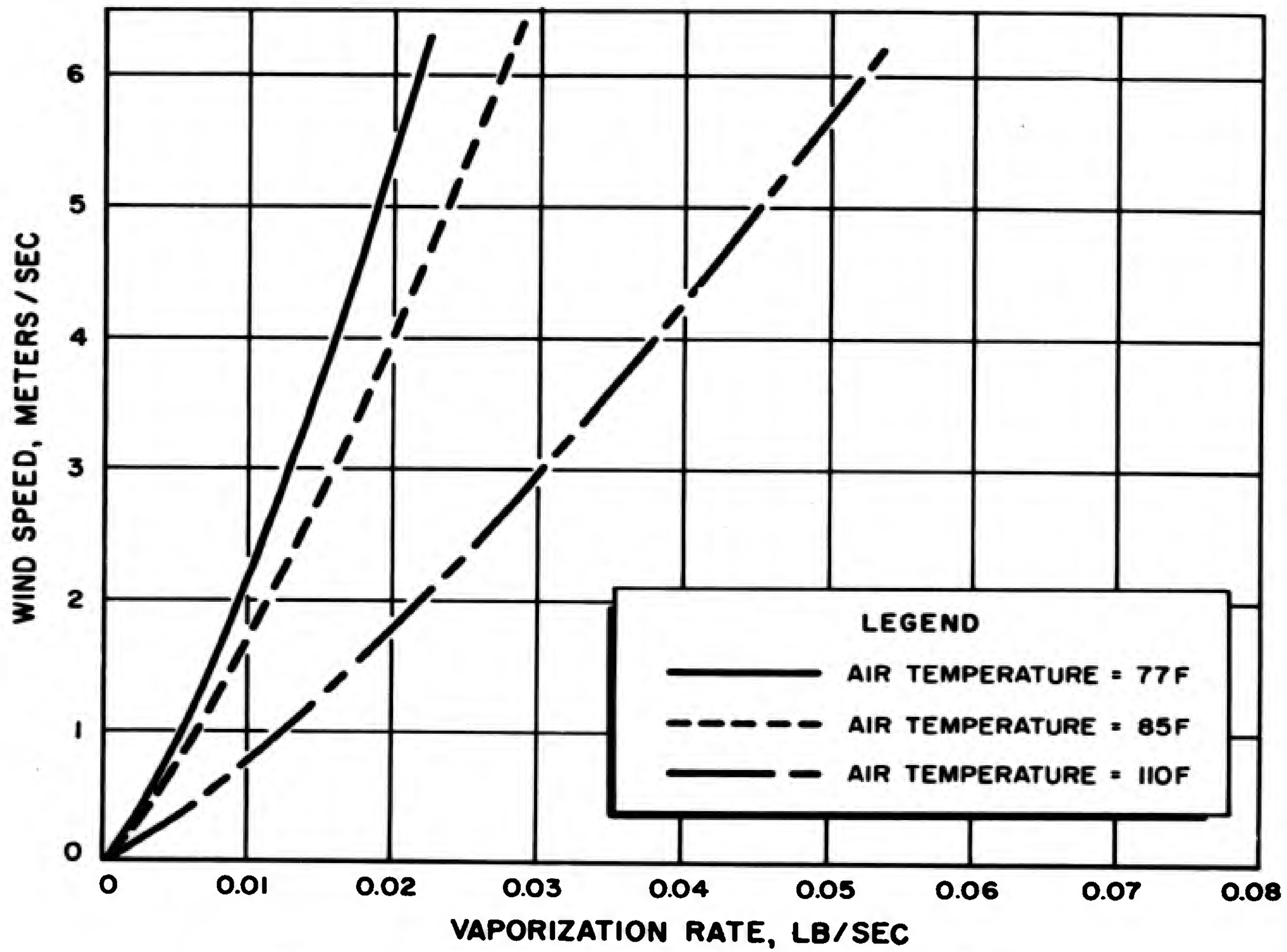

Fig. A-1 Vaporization Rate Values of Hydrazine (Conditions of large lapse and wind blowing over 15 ft x 25 ft revetment)

$$\chi = \frac{2Q}{\pi C_y \; C_z \; \bar{U} \; X^{2-n}} \qquad \text{(A-9)}$$

which simplifies our numerical computations.

As in the case of estimating vaporization rates, the solution of Eq. (A-9) will be performed for each assumed weather condition at each selected air temperature. Typical source distances of 500, 1000, 2000, and 5000 ft will be evaluated.

The values of C_y, C_z, $\bar{U}$, and n in Eq. (A-9) are obtained from Table 8 for each assumed weather condition. The source strength, Q, is the vaporization rate values calculated previously.

The vapor concentration values obtained from Eq. (A-9) are expressed in grams per cubic meter. These values can be converted into parts per million (ppm) as follows,

$$\chi_o = \frac{62.43\chi}{\rho} \qquad \text{(A-10)}$$

where,

χ_o = propellant vapor concentration, ppm

χ = propellant vapor concentration, g/m^3

ρ = density of propellant vapor at the temperature under consideration, lb/ft^3

Air Temperature of 77 F

The hydrazine vapor concentration at the instantaneous center of the travelling vapor cloud for the assumed weather conditions is determined as follows:

(a) Moderate Inversion

$Q = \dot{w}_v = 0.0088$ lb/sec

$= 3.99$ g/sec

(1) $X = 500$ ft $= 152.5$ m

Solving Eq. (A-9),

$$\chi = \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times (152.5)^{2-0.33}}$$

$$= \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times 4427}$$

$$= 0.0718 \text{ g/m}^3$$

Converting to ppm using Eq. (A-10),

$$\chi_o = \frac{0.0718 \times 62.43}{0.0817}$$

$$= 54.9 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

Solving Eq. (A-9)

$$\chi = \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times (304.8)^{2-0.33}}$$

$$= \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times 14070}$$

$$= 0.02258 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.02258 \times 62.43}{0.0817}$$

$$= 17.25 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

Solving Eq.(A-9),

$$\chi = \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times (609.6)^{2-0.33}}$$

$$= \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times 44770}$$

$$= 0.00708 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.00708 \times 62.43}{0.0817}$$

$$= 5.4 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times (1524.0)^{2-0.33}}$$

$$= \frac{2 \times 3.99}{3.142 \times 0.08 \times 0.05 \times 2 \times 206800}$$

$$= 0.001535 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.001535 \times 62.43}{0.0817}$$

$$= 1.172 \text{ ppm}$$

(b) Neutral

$$Q = \dot{w}_v = 0.0153 \text{ lb/sec}$$

$$= 6.95 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5\text{m}$

Solving Eq.(A-9),

$$\chi = \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times (152.5)^{2-0.25}}$$

$$= \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times 6618}$$

$$= 0.00663 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.00663 \times 62.43}{0.0817}$$

$$= 5.07 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times (304.8)^{2-0.25}}$$

$$= \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times 22230}$$

$$= 0.001978 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.001978 \times 62.43}{0.0817}$$

$$= 1.51 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times (609.6)^{2-0.25}}$$

$$= \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times 74790}$$

$$= 0.000587 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.000587 \times 62.43}{0.0817}$$

$$= 0.45 \text{ ppm}$$

$$(4)\ X = 5000 \text{ ft} = 1524.0 \text{ m}$$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times (1524.0)^{2-0.25}}$$

$$= \frac{2 \times 6.95}{3.142 \times 0.21 \times 0.12 \times 4 \times 371700}$$

$$= 0.000118 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.000118 \times 62.43}{0.0817}$$

$$= 0.0901 \text{ ppm}$$

(c) Large Lapse

$$Q = \dot{w}_v = 0.0212 \text{ lb/sec}$$

$$= 9.62 \text{ g/sec}$$

$$(1)\ X = 500 \text{ ft} = 152.5 \text{ m}$$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times (152.5)^{2-0.20}}$$

$$= \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times 8509}$$

$$= 0.000521 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.000521 \times 62.43}{0.0817}$$

$$= 0.398 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times (304.8)^{2-0.20}}$$

$$= \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times 29600}$$

$$= 0.000149 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.000149 \times 62.43}{0.0817}$$

$$= 0.114 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

Solving Eq. (A-9),

$$\chi = \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times (609.6)^{2-0.20}}$$

$$= \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times 103500}$$

$$= 0.0000428 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.0000428 \times 62.43}{0.0817}$$

$$= 0.0327 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

Solving Eq.(A-9),

$$\chi = \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times (1524.0)^{2-0.20}}$$

$$= \frac{2 \times 9.62}{3.142 \times 0.64 \times 0.36 \times 6 \times 537500}$$

$$= 0.0000825 \text{ g/m}^3$$

Converting to ppm,

$$\chi_o = \frac{0.0000825 \times 62.43}{0.0817}$$

$$= 0.0063 \text{ ppm}$$

Air Temperature = 85 F

The calculation of the vapor concentrations that follows will be presented in identical order to that presented at an air temperature of 77 F. For simplicity, the interconnecting details between numerical relations will be omitted herein.

(a) Moderate Inversion

$$Q = \dot{w}_v = 0.01125 \text{ lb/sec}$$

$$= 5.0 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times (152.5)^{2-0.33}}$$

$$= \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times 4427}$$

$$= 0.0898 \text{ g/m}^3$$

$$\chi_o = \frac{0.0898 \times 62.43}{0.0805}$$

$$= 69.5 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$= \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times (304.8)^{2-0.33}}$$

$$= \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times 14070}$$

$$= 0.0283 \text{ g/m}^3$$

$$\chi_o = \frac{0.0283 \times 62.43}{0.0805}$$

$$= 21.9 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times (609.6)^{2-0.33}}$$

$$= \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times 44770}$$

$$= 0.00889 \text{ g/m}^3$$

$$\chi_o = \frac{0.00889 \times 62.43}{0.0805}$$

$$= 6.88 \text{ ppm}$$

(4) $X = 50000 \text{ ft} = 1524.0 \text{ m}$

$$\chi = \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times (1524)^{2-0.33}}$$

$$= \frac{2 \times 5.0}{3.142 \times 0.08 \times 0.05 \times 2 \times 206800}$$

$$= 0.00192 \text{ g/m}^3$$

$$\chi_o = \frac{0.00192 \times 62.43}{0.0805}$$

$$= 1.488 \text{ ppm}$$

(b) Neutral

$$Q = \dot{w}_v = 0.01953 \text{ lb/sec}$$

$$= 8.86 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times (152.5)^{2-0.25}}$$

$$= \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times 6618}$$

$$= 0.00845 \text{ g/m}^3$$

$$\chi_o = \frac{0.00845 \times 62.43}{0.0805}$$

$$= 6.55 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$= \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times (304.8)^{2-0.25}}$$

$$= \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times 22230}$$

$$= 0.002515 \text{ g/m}^3$$

$$\chi_o = \frac{0.002515 \times 62.43}{0.0805}$$

$$= 1.95 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times (609.6)^{2-0.25}}$$

$$= \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times 74790}$$

$$= 0.000748 \text{ g/m}^3$$

$$\chi_o = \frac{0.000748 \times 62.43}{0.0805}$$

$$= 0.58 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

$$= \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times (1524)^{2-0.25}}$$

$$\chi = \frac{2 \times 8.86}{3.142 \times 0.21 \times 0.12 \times 4 \times 371700}$$

$$= 0.0001505 \text{ g/m}^3$$

$$\chi_o = \frac{0.0001505 \times 62.43}{0.0805}$$

$$= 0.117 \text{ ppm}$$

(c) Large Lapse

$$Q = \dot{w}_v = 0.0270 \text{ lb/sec}$$

$$= 12.24 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times (152.5)^{2-0.20}}$$

$$= \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times 8509}$$

$$= 0.000662 \text{ g/m}^3$$

$$\chi_o = \frac{0.000662 \times 62.43}{0.0805}$$

$$= 0.513 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$\chi = \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times (304.8)^{2-0.20}}$$

$$= \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times 29600}$$

$$= 0.0001905 \text{ g/m}^3$$

$$\chi_o = \frac{0.0001905 \times 62.43}{0.0805}$$

$$= 0.148 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times (609.6)^{2-0.20}}$$

$$= \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times 103500}$$

$$= 0.0000544 \text{ g/m}^3$$

$$\chi_o = \frac{0.0000544 \times 62.43}{0.0805}$$

$$= 0.042 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

$$\chi = \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times (1524)^{2-0.20}}$$

$$= \frac{2 \times 12.24}{3.142 \times 0.64 \times 0.36 \times 6 \times 537500}$$

$$= 0.0000105 \text{ g/m}^3$$

$$\chi_o = \frac{0.0000105 \times 62.43}{0.0805}$$

$$= 0.00815 \text{ ppm}$$

Air Temperature = 110 F

The hydrazine vapor concentrations at this air temperature will be presented in identical order to that presented at an air temperature of 77 F. For simplicity, the interconnecting details will be omitted herein.

(a) Moderate Inversion

$$Q = \dot{w}_v = 0.02168 \text{ lb/sec}$$

$$= 9.85 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times (152.5)^{2-0.33}}$$

$$= \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times 4427}$$

$$= 0.177 \text{ g/m}^3$$

$$\chi_o = \frac{0.177 \times 62.43}{0.077}$$

$$= 143.4 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$\chi = \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times (304.8)^{2-0.33}}$$

$$= \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times 14070}$$

$$= 0.0557 \text{ g/m}^3$$

$$\chi_o = \frac{0.0557 \times 62.43}{0.077}$$

$$= 45.1 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times (609.6)^{2-0.33}}$$

$$= \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times 44770}$$

$$= 0.01755 \text{ g/m}^3$$

$$\chi_o = \frac{0.01755 \times 62.43}{0.077}$$

$$= 14.22 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

$$\chi = \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times (1524)^{2-0.33}}$$

$$= \frac{2 \times 9.85}{3.142 \times 0.08 \times 0.05 \times 2 \times 206800}$$

$$= 0.00378 \text{ g/m}^3$$

$$\chi_o = \frac{0.00378 \times 62.43}{0.077}$$

$$= 3.31 \text{ ppm}$$

(b) Neutral

$$Q = \dot{w}_v = 0.0377 \text{ lb/sec}$$

$$= 16.72 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times (152.5)^{2-0.25}}$$

$$= \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times 6618}$$

$$= 0.01595 \text{ g/m}^3$$

$$\chi_o = \frac{0.01595 \times 62.43}{0.077}$$

$$= 12.95 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$\chi = \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times (304.8)^{2-0.25}}$$

$$= \frac{2 \times 16.72}{3142 \times 0.21 \times 0.12 \times 4 \times 22230}$$

$$= 0.00475 \text{ g/m}^3$$

$$\chi_o = \frac{0.00475 \times 62.43}{0.077}$$

$$= 3.85 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times (609.6)^{2-0.25}}$$

$$= \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times 74790}$$

$$= 0.00141 \text{ g/m}^3$$

$$\chi_o = \frac{0.00141 \times 62.43}{0.077}$$

$$= 1.141 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

$$\chi = \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times (1524)^{2-0.25}}$$

$$= \frac{2 \times 16.72}{3.142 \times 0.21 \times 0.12 \times 4 \times 371700}$$

$$= 0.000284 \text{ g/m}^3$$

$$\chi_o = \frac{0.000284 \times 62.43}{0.077}$$

$$= 0.23 \text{ ppm}$$

(c) Large Lapse

$$Q = \dot{w}_v = 0.052 \text{ lb/sec}$$

$$= 23.6 \text{ g/sec}$$

(1) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times (152.5)^{2-0.20}}$$

$$= \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times 8509}$$

$$= 0.00128 \text{ g/m}^3$$

$$\chi_o = \frac{0.00128 \times 62.43}{0.077}$$

$$= 1.037 \text{ ppm}$$

(2) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$\chi = \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times (304.8)^{2-0.20}}$$

$$= \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times 29600}$$

$$= 0.0003675 \text{ g/m}^3$$

$$\chi_o = \frac{0.0003675 \times 62.43}{0.077}$$

$$= 0.298 \text{ ppm}$$

(3) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times (609.6)^{2-0.20}}$$

$$= \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times 103500}$$

$$= 0.000105 \text{ g/m}^3$$

$$\chi_o = \frac{0.000105 \times 62.43}{0.077}$$

$$= 0.085 \text{ ppm}$$

(4) $X = 5000 \text{ ft} = 1524.0 \text{ m}$

$$\chi = \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times (1524)^{2-0.20}}$$

$$= \frac{2 \times 23.6}{3.142 \times 0.64 \times 0.36 \times 6 \times 537500}$$

$$= 0.00002024 \text{ g/m}^3$$

$$\chi_o = \frac{0.00002024 \times 62.43}{0.077}$$

$$= 0.0164 \text{ ppm}$$

Concluding Remarks

The calculation of hydrazine vapor concentration as functions of distance from spill and weather conditions has been shown. It should be noted that these calculated vapor concentrations are the maximum to be expected under the conditions stipulated in the problem.

A plot of the calculated vapor concentrations versus distance for the three assumed weather conditions is shown in Fig. A-2. The effect of air temperature and weather condition on the vapor concentration at a given distance from the spillage area is clearly noted. This derived fact serves as the basis for recommending that propellant handling operations be performed only during satisfactory weather conditions. It should be noted also that the values shown in the Figure are independent of the quantity of hydrazine spilled, but are dependent upon the configuration of the diked basin. The quantity of propellant however would influence the duration of a vapor concentration at a given downwind location.

STORAGE DISTANCES

Once the vapor concentrations as a function of spillage distances are established, the next logical step is to establish the vapor concentration to which personnel can be exposed without suffering adverse effects. In this problem, we are stipulating that off-site personnel will not be exposed to a vapor concentration higher than the MAC value, which for hydrazine is 1 ppm. In the case of inhabited buildings within the site, we are assuming that personnel in those buildings will evacuate the area within 15 minutes after a propellant spillage is experienced. Consequently, we are interested in the hydrazine vapor concentration to which personnel can be exposed for 15 minutes without suffering adverse effects. This vapor concentration value is not available for hydrazine, but is given for unsymmetrical dimethylhydrazine in Ref. 9. Thus, if we assume the toxic hazards of these two propellants to be similar, we can use a value of 35 ppm given in the reference for a 15 minute exposure.

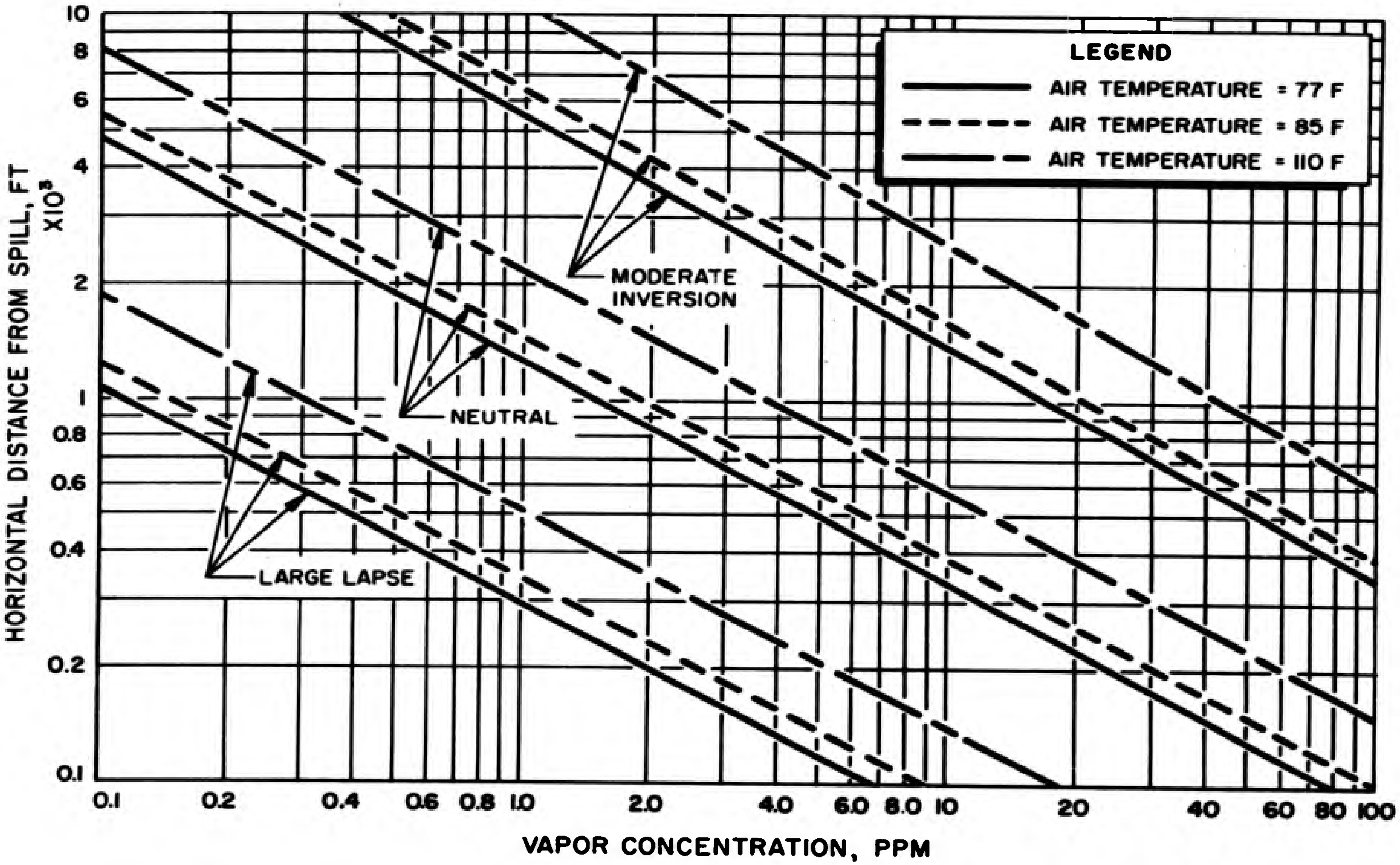

Figure A-2. Concentration of Hydrazine Vapor as a Function of Distance from Spillage for General Weather Conditions

The storage distances, based on the vapor concentration criteria stipulated above, can be obtained directly from Fig. A-2 for the assumed conditions. These distances are given in Table A-4 as functions of air temperatures and weather conditions.

TABLE A-4

HYDRAZINE STORAGE DISTANCES BASED ON TOXICITY

Storage Distances in Feet To:	Moderate Inversion			Neutral			Large Lapse		
	110F	85F	77F	110F	85F	77F	110F	85F	77F
Off-site Population	10100	6400	5600	2200	1490	1270	520	350	300
In-site Inhabited Buildings	1185	760	660	280	190	165	<100	<100	<100

The criteria for site selection of storage areas for high-energy propellants must be based on the possibility of propellant spillage. Although this possibility depends upon numerous factors such as system design and fabrication, and training and quality of operating personnel, it appears that complete freedom from propellant spillage cannot be realized in practice. Once this spillage possibility is accepted as real, it is important to determine the weather conditions under which a propellant spillage is expected to occur. Because it is impossible to predict an actual spillage, it is prudent to assume that propellant spillage might occur under the worst possible weather conditions.

The selection of the worst expected weather condition is a basic meteorological problem. In general, inversion conditions provide very poor diffusion and transport of propellant vapors. However, the air temperatures accompanying those conditions can effect the rate of propellant release into the atmosphere and therefore must be considered.

Strong inversion conditions are characterized by cold surface temperatures;therefore, the vaporization rates of hydrazine would be reduced considerably. In the case of moderate inversion conditions, the air temperature can be as high as 77 F, which as shown in the preceding calculations, produces significant vaporization rates. Consequently, moderate inversion is selected as the worst condition for the storage of hydrazine.

The final solution to this sample problem is that hydrazine storage areas should be located not less than 5600 ft from off-site populated areas, and a minimum of 660 ft from in-site inhabited buildings. It should be noted that this solution is based only on toxicity hazards and is valid only for the conditions stipulated in the problem.

APPENDIX B

SAMPLE CALCULATION OF SAFE-DISTANCE VALUES, BASED ON TOXICITY, FOR A POTENTIAL PROPELLANT SPILLAGE AT TEMPERATURES ABOVE THE PROPELLANT BOILING POINT

The sample calculation presented herein considers the spillage of nitrogen tetroxide under the worst expected weather conditions. This information is presented in a manner that requires a thorough understanding of the material covered in the text and Appendix A.

A 10,000-gallon load of nitrogen tetroxide is assumed to have spilled into an inert, diked basin of sufficient capacity to accommodate the propellant. The spillage was effected without liquid atomization. In addition, a moderate inversion weather condition prevailed at an air temperature of 77 F. (Although a strong inversion is a worse situation, this condition could not be expected to occur with a surface temperature of 77 F.)

The amount of propellant that flashes can be computed from Eq. 2 which is repeated below,

$$W_t \, C \, (T_2 - T_1) = W_f \, h_v \qquad \text{(Eq. 2, repeated)}$$

Substituting the applicable physicochemical properties of the propellant and assumed conditions, we obtain:

$$\frac{10{,}000 \times 1.43 \times 62.4}{7.481} \times 0.368 \; (77\text{-}70) = W_f \times 178$$

which reduces to,

$$W_f = \frac{119{,}700 \times 0.368 \times 7}{178} = 1731 \text{ lb}$$

The propellant flash-off rate can be determined using Eq. 1 which is repeated below, provided that the time of propellant flashing is known. Since this time increment is not known, we will assume a value of 30 seconds. It is extremely important to note that there is no technical reasoning behind this assumption and that it is presented only to show the techniques involved in solving this type of problem.

$$\dot{w}_f = \frac{W_f}{t} \qquad \text{(Eq. 1, repeated)}$$

Solving for the flash-off rate,

$$\dot{w}_f = \frac{1731}{30} = 57.8 \text{ lb/sec} .$$

The maximum concentration of the nitrogen tetroxide vapor as a function of distance from the spill for the assumed conditions can be obtained from Eq. A-9 which is repeated below.

$$\chi = \frac{2Q}{\pi Cy\ Cz\ \overline{U}\ X^{2-n}} \qquad \text{(Eq. A-9, repeated)}$$

The source strength (Q, Eq. A-9) in this case is equal to the propellant flash-off rate, rather than the vaporization rate used in Appendix A. Thus,

$$Q = \dot{w}_f = 57.8 \text{ lb/sec} = 26{,}240 \text{ g/sec}$$

Solving Eq. A-9 for the following spillage distances:

(a) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 26{,}240}{3.142 \times 0.08 \times 0.05 \times 2 \times (152.5)^{2-0.33}}$$

$$= \frac{2 \times 26{,}240}{3.142 \times 0.08 \times 0.05 \times 2 \times 4427}$$

$$= 472.0 \text{ g/m}^3$$

or,

$$\chi_0 = 138{,}900 \text{ ppm}$$

(b) $X = 1000 \text{ ft} = 304.8 \text{ m}$

$$\chi = \frac{2 \times 26{,}240}{3.142 \times 0.08 \times 0.05 \times 2 \times (304.8)^{2-0.33}}$$

$$= \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times 14,070}$$

$$= 148.4 \text{ g/m}^3$$

or,

$$\chi_o = 43,700 \text{ ppm}$$

(c) $X = 2000 \text{ ft} = 609.6 \text{ m}$

$$\chi = \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times (609.6)^{2-0.33}}$$

$$= \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times 44,770}$$

$$= 46.6 \text{ g/m}^3$$

or,

$$\chi_o = 13,720 \text{ ppm}$$

(d) $X = 5000 \text{ ft} = 152.4 \text{ m}$

$$\chi = \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times (1524.0)^{2-0.33}}$$

$$= \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times 206,800}$$

$$= 10.09 \text{ g/m}^3$$

or,

$$\chi_o = 2966 \text{ ppm}$$

(e) $X = 10,000 \text{ ft} = 3048 \text{ m}$

$$\chi = \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times (3048)^{2-0.33}}$$

$$= \frac{2 \times 26,240}{3.142 \times 0.08 \times 0.05 \times 2 \times 658,100}$$

$$= 3.175 \text{ g/m}^3$$

or,

$$\chi_o = 935 \text{ ppm}$$

(f) $X = 20{,}000 \text{ ft} = 6096 \text{ m}$

$$\chi = \frac{2 \times 26{,}240}{3.142 \times 0.08 \times 0.05 \times 2 \times (6096)^{2-0.33}}$$

$$= \frac{2 \times 26{,}240}{3.142 \times 0.08 \times 0.05 \times 2 \times 2{,}094{,}000}$$

$$= 0.977 \text{ g/m}^3$$

or,

$$\chi_o = 293.4 \text{ ppm}$$

The above calculations provide the vapor concentration as a function of distance for a spillage of 10,000 gallons of nitrogen tetroxide. Because we are interested in determining also the quantity of propellant spilled as a function of distance, we will assume in the calculations to follow a nitrogen tetroxide spill of 5000 gallons. All other conditions in the problem remain invariant. The new set of calculations will be presented in identical order to that previously discussed.

The quantity of propellant that flashes is expressed as,

$$\frac{5000 \times 1.43 \times 62.4}{7.481} \times 0.368\ (77 - 70) = W_f \times 178$$

which simplifies to,

$$W_f = \frac{59{,}800 \times 0.368 \times 7}{178}$$

$$= 866 \text{ lb}$$

Assuming again a flashing period of 30 seconds, the flash-off rate is,

$$\dot{w}_f = \frac{866}{30}$$

$$= 28.86 \text{ lb/sec}$$

The source strength (Q, Eq. A-9) is,

$$Q = \dot{w}_f = 28.86 \text{ lb/sec}$$

$$= 13{,}100 \text{ g/sec}$$

Solving the simplified Sutton's equation as a function of spillage distance, we have:

(a) $X = 500 \text{ ft} = 152.5 \text{ m}$

$$\chi = \frac{2 \times 13{,}100}{3.142 \times 0.08 \times 0.05 \times 2 \times (152.5)^{2-0.33}}$$

$$= \frac{2 \times 13{,}100}{3.142 \times 0.08 \times 0.05 \times 2 \times 4427}$$

$$= 235.5 \text{ g/m}^3$$

or,

$$\chi_o = 69{,}450 \text{ ppm}$$

The vapor concentration value obtained above is noted to be equal to one-half the value obtained for a 10,000-gallon spillage at the same distance. Therefore, under identical conditions, the vapor concentration resulting from the spillage is directly proportional to the quantity of propellant spilled. Based on this simple relation, the vapor concentration vs distance for nitrogen tetroxide spillages of 10,000, 5000, and 1000 gallons are plotted in Fig. B-1. In this figure it is noted that even relatively small quantities of nitrogen tetroxide such as 1000 gallons, can give very large vapor concentrations at distances of over four miles under poor weather conditions.

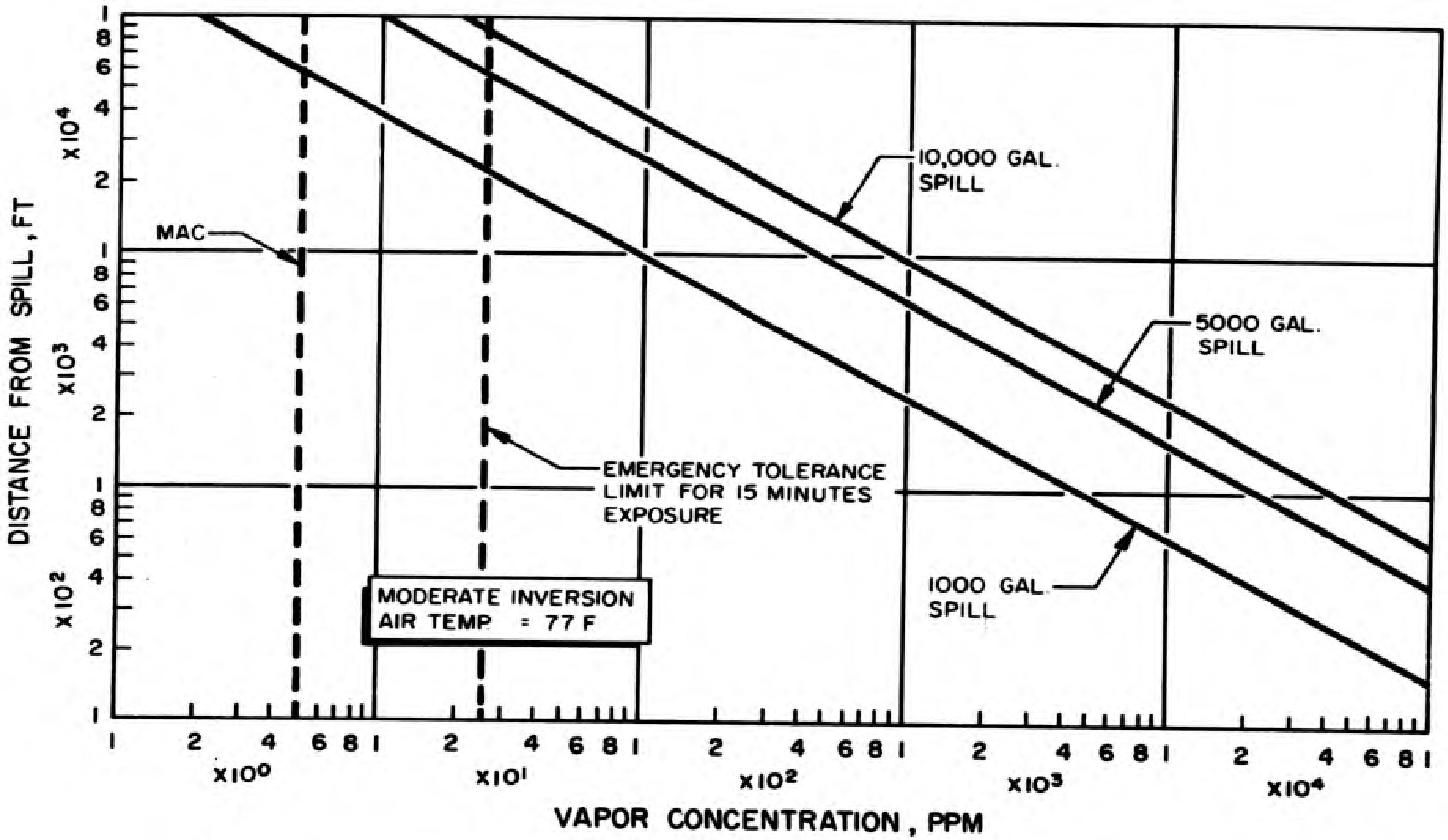

Figure B-1. Downwind Axial Vapor Concentration of Spilled Nitrogen Tetroxide as a Function of Distance from Spillage

The information obtained from the calculations appear to be somewhat doubtful. This finding is not surprising since the derived flash-off rates were based on an increment of time which was "picked from the air." However, the techniques of solving the problem are considered adequate. Thus, it becomes obvious that the experimental determination of flash-off rates for propellants such as nitrogen tetroxide and chlorine trifluoride is mandatory if reliable safe-distance values are desired.

The safe-distance values on this sample problem,which is based on the most unfavorable meteorological conditions anticipated, can be obtained from Fig. B-1 using the criteria established in Appendix A. These values are shown in Table B-1 below.

TABLE B-1

NITROGEN TETROXIDE STORAGE DISTANCES BASED ON TOXICITY

	Storage Distances in Feet to:	
Quantity of Propellant, gallons	Off-Site Population	In-Site Inhabited Buildings
1,000	58,000	24,500
5,000	148,000	57,000
10,000	220,000	87,000

In addition to the limitations imposed on the results derived from this calculation, it should be noted that the Sutton's formula is not expected to be applicable at storage distances greater than 20,000 feet. This additional limitation is based on the fact that the weather parameters are not expected to remain constant over the time and distance of such a cloud trajectory.

APPENDIX C

MEDICAL STUDY

Medical studies were performed by personnel of the Institute of Medical Research, Huntington Memorial Hospital, 734 Fairmount Avenue, Pasadena, California in conjunction with three of the large-scale spills at Haystack Butte. The results of the animal studies are presented below. Each study is identified by the test number on the particular propellant combination spilled.

EXPOSURE TO NITROGEN TETROXIDE, TEST 1

This study was made in conjunction with a singular spill of 1800 lb of nitrogen tetroxide, accomplished 23 August 1960.

Placement of Animals at Test Site

The biological study group from the Institute of Medical Research arrived at Edwards Air Force Base at 9:20 a.m., August 23, 1960 with the hamsters to be exposed in the nitrogen tetroxide spill test. Placement of the hamsters in the cages on the designated downwind grid pattern (shown in Fig. C-1) was begun at 1:30 p.m. and completed by 4:00 p.m. Three animals were placed at each animal position. The animals were placed in the outer rows first, working in toward the spill site; the inner and upwind control rows were completed last. All animals were in good health when put into the exposure cages. At approximately 5:30 p.m. while waiting for personnel to complete their preparations, the animals were again examined. One hamster in the innermost row was dead, and all appeared sick; one was dead and many sick in the next row. Since the animals were shaded from direct sun, the weather was moderate in temperature, and the inner rows were the last completed, heat was probably not a factor in the deaths and apparent sickening of these animals. No definite cause was determined; however, possibly exhaust fumes from a diesel engine located close to and upwind from these animals may have been, in part, responsible. The dead animals were replaced with extra stock taken to the site.

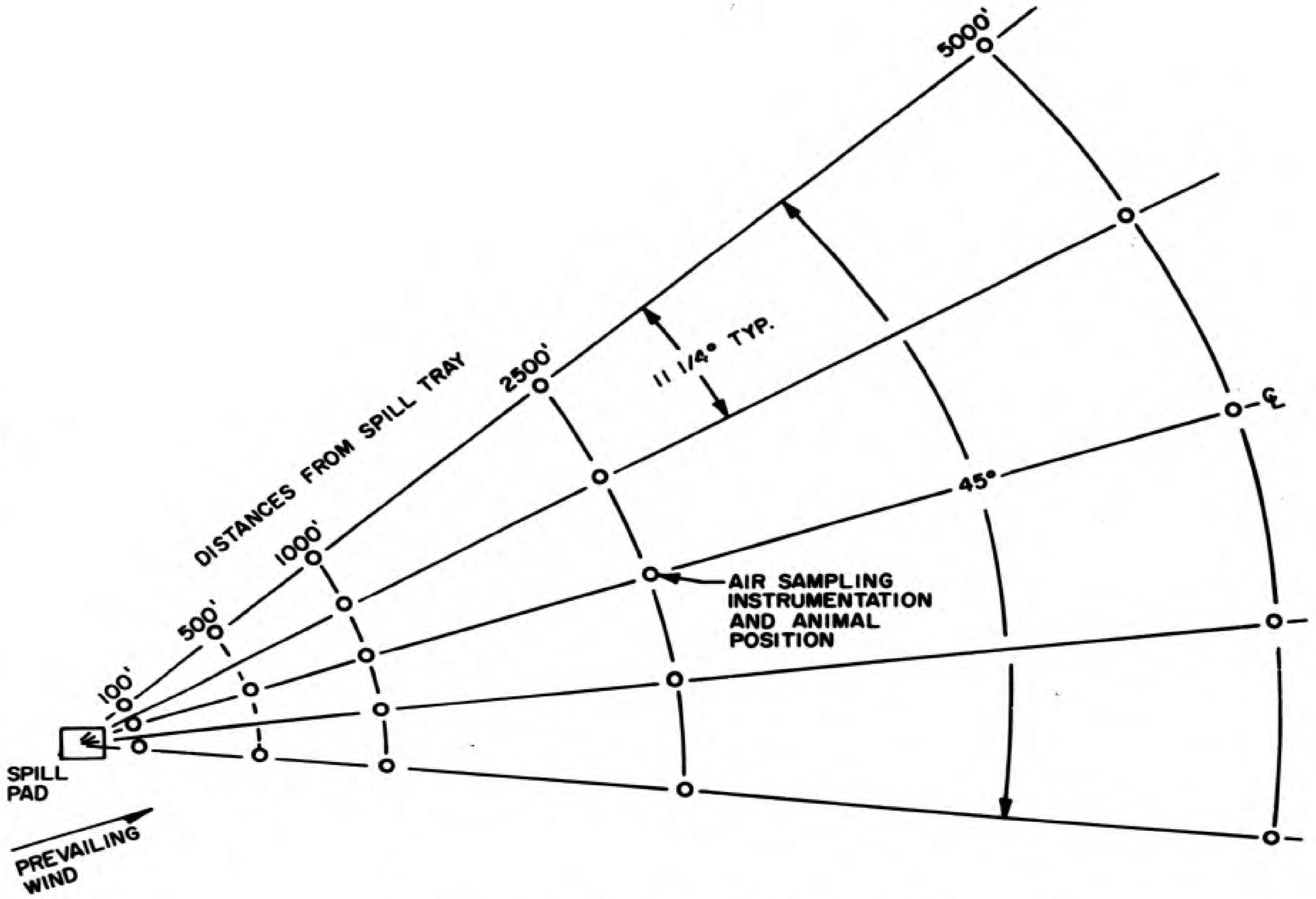

Figure C-1. Animal Exposure and Air-Sampling Positions

The propellant transfer operation exposed the animals in the first row to small amounts of the vapor escaping through a vent. The spill tank was then ruptured at 7:00 p.m.; however, the rupture was incomplete and only a gradual loss occurred.

Collection of the animals began at 8:30 p.m. and was finished at 10:00 p.m. One animal in position 15 (No. 26) was found dead. The biological study group returned to the Institute of Medical Research at about midnight where post-mortem examinations of those animals which had died at the spill site were performed and completed by 1:00 a.m.

Pathological Findings

Gross Pathology. At autopsy, all lungs were brighter red than normal. This was true regardless of position at the spill site or date of sacrifice after the spill. This was also found in the control animals and may be attributed to the pentobarbital used in sacrificing these animals. Other gross changes of the lungs are noted in Table C-1.

TABLE C-1

GROSS LUNG PATHOLOGY OF HAMSTERS USED IN N_2O_4 SPILL OF AUGUST 23, 1960

Animal Number	Date Sacrificed	Position, See Fig.	Observations
19	8-24-60	11	Apex L. lung dark red--hemorrhage
45	8-24-60	9	Lungs pale and yellowish
77	8-24-60	1	Red mottling of lung--hemorrhage
11	8-31-60	20	Large dark areas in R. lung; few smaller ones L. lung--hemorrhage
53	8-31-60	4	Small dark red areas in R.lung; hemorrhage
1	9-7-60	20	Numerous dark spots on lungs--hemorrhage
35	9-7-60	4	Scattered dark red spots in R. lung--hemorrhage

No further gross pathology was noted in any other tissue or any other animal.

Miscroscopic Pathology. Microscopic examination of the lungs showed hyperemia and focal hemorrhage to a greater or lesser degree in both control and test animals regardless of position at the spill site or date of sacrifice. Pentobarbital may be responsible to some extent for this. All other tissues appeared normal.

Conclusions

Considering (1) the paucity of pathological changes in these animals, (2) the position at the test site of those few that did show gross lung pathology, and (3) the fact that such pathology was found in those that were sacrificed two weeks after the spill, as well as in those sacrificed the next day, it seems unlikely that under the conditions of this experiment, nitrogen tetroxide has any demonstrable toxic effects.

EXPOSURE TO CHLORINE TRIFLUORIDE, TEST 5

This study was made in conjunction with a singular spill of 750 lb of chlorine trifluoride, accomplished 6 June 1961.

Placement of Animals at Test Site

The biological study group from the Institute of Medical Research, Huntington Memorial Hospital arrived at Haystack Butte test site at 7:10 a.m., June 6, 1961 with the hamsters to be exposed in the CTF spill. Since the spill was not carried out in the morning as planned, the animals were not placed in their exposure cages until approximately 1:30 p.m. Nine animals were placed at each sampling position. Chlorine trifluoride was spilled at 2:15 p.m. and the animals were collected from the range at 2:30 p.m. All animals were found alive. The hamsters in position No. 2, which presumably received the most intense exposure, were found clinging to the tops of their compartments, eyes closed and showing severe lacrimation. All other hamsters appeared normal. Figure C-2 illustrates the placement of the animals at the test site. When collected from the test sites, three hamsters from each cage were arbitrarily assigned to each of three groups to be scarificed at 24 hours, 7 days, and 14 days following exposure.

Pathological Findings

Gross Pathology--24 Hours. No hamsters died within the first 24 hours after CTF exposure. Therefore, the three animals from each cage to be sacrificed at this time were injected intraperitoneally with an overdose of sodium pentobarbital at 2:15 p.m. on June 7, 1961 and autopsied immediately after death. The pathological findings are summarized in Table C-2.

All lungs were brighter red than normal regardless of position of the animal on the test site. In addition, some degree of pulmonary hemorrhage was a common, although not consistent finding. These changes may be related to the pentobarbital used in sacrificing these animals. Opacities were found in the eyes of some of these animals; these were found to be the result of the formation of a white opaque fluid in the anterior chamber. No such eye changes were noted among the control (position No. C) animals. Kidney and liver changes were noted but these changes, as those in the lung, bore no apparent relation to CTF exposure.

Microscopic Pathology--24 Hours. Some degree of hyperemia, hemorrhage, and increased cellularity was common to the lungs of all animals; unless these changes were severe, they were considered normal--possibly the result of the pentobarbital--and not noted in any of the tables. Pathological findings were noted in the lungs, kidneys, livers, and nasal mucous membranes of the hamsters. Necrosis of the convoluted tubules of the kidney and the rhinitis may be related to CTF exposure. The other changes appear to have no direct relation to the CTF since they were found in the control animals as well as those from the exposed cages.

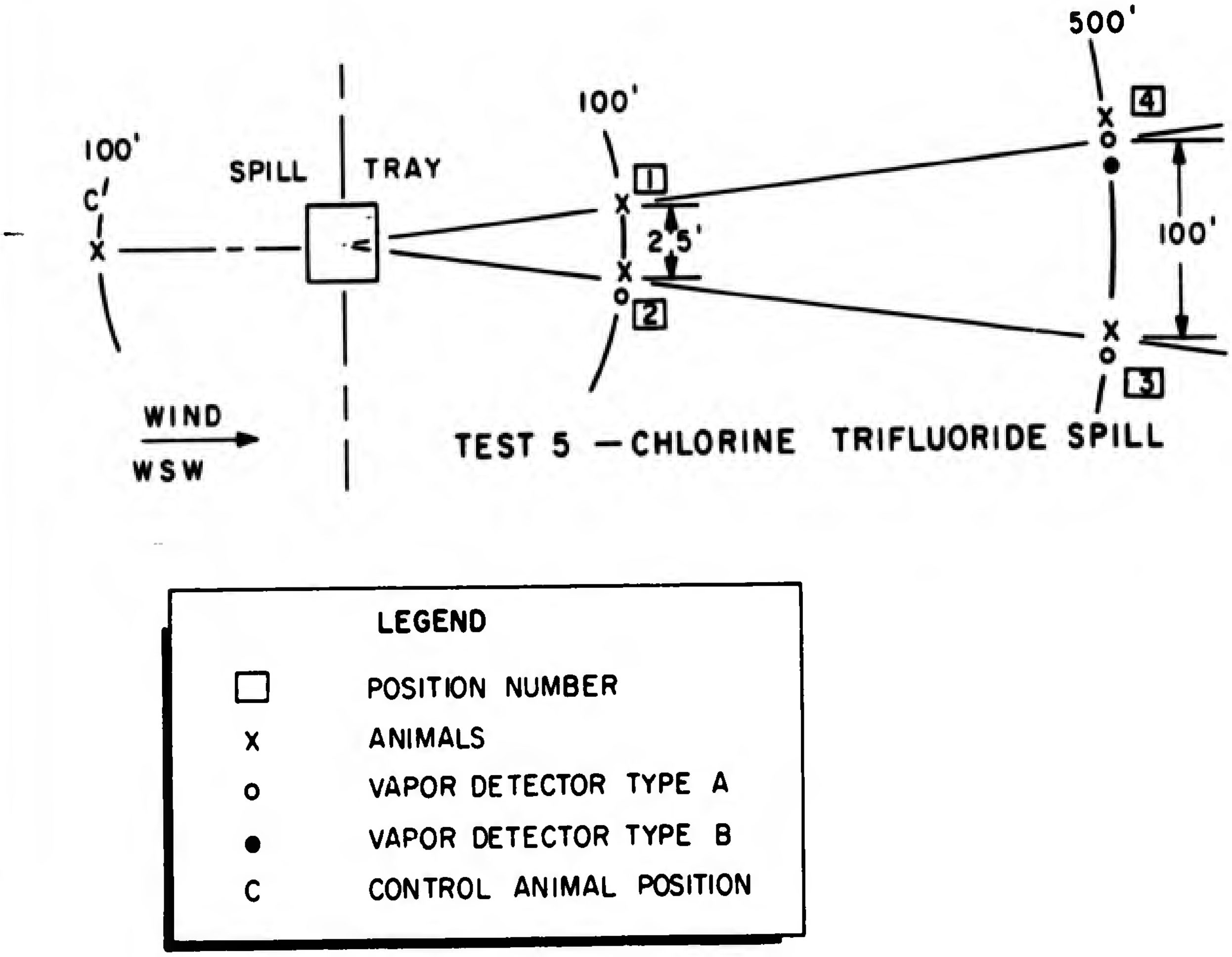

Figure C-2. Animal Exposure and Vapor Detector Positions

TABLE C-2

SUMMARY OF PATHOLOGICAL FINDINGS 24 DAYS AFTER CTF EXPOSURE

GROUP I

		Gross									Microscopic											
						Kidney		Liver			Lung				Kidney			Liver				
Cage Position	Number	Spontaneous death*	Hair loss	Pulmonary hemorrhage	Enteritis	Swollen	Mottled	Swollen	Pale	Eye opacity+	Hyperemia	Hemorrhage	Cell infiltration	Emphysema	Hyperemia	Tube cell swelling	Tube necrosis	Hyperemia	Cloudy swelling	Central necrosis	Recovered subacute atrophy	Rhinitis
C	68			X							X		X		X	X			X	X		
	72																		X	X		
	74			X			X		X					X					X			
1	40									X					X				X			
	42			X						X						X			X			X
	58													X	X				X			
2	60			X												X	X		X			X
	63			X					X					X					X			X
	73			X							X	X	X	X	X		X					
3	38			X					X			X			X				X			
	43			X															X			
	51			X							X	X							X			X
4	13			X						X		X		X						X		
	17			X						X												
	21								X													

*Unless date of spontaneous death specified, animal was sacrificed 6-7-61.

+White opaque fluid in anterior chamber.

Gross Pathology--7 Days. Three hamsters from this group died spontaneously. The rest were sacrificed with sodium pentobarbital on June 13, 1961. Table C-3 summarizes the pathological findings among these animals. Lung changes were essentially as noted in the 24-hour group with the exception that gross pulmonary hemorrhage was considerably less frequent. Eye opacities were again noted among exposed animals. Some animals from cage positions No. 1, 2, and 3 were found to have lost their hair; this hair loss was most commonly over the shoulders and back, but sometimes extended to the ventral surface. Spontaneous deaths were found in those cage positions No. 1 and 2, closest to the spill site; all of these animals showed evidence of severe enteritis and enlarged livers.

Microscopic Pathology--7 Days. Pathological findings were noted in the lungs, livers, kidneys, and nasal mucous membranes of these animals but bore no apparent relation to the CTF exposure. No reason for the gross enlargement of livers found in some animals could be determined by microscopic examination.

Gross Pathology--14 Days. Three animals from this group died spontaneously. The rest were sacrificed as before with sodium pentobarbital on June 20, 1961. The pathological findings for this group are summarized in Table C-4. All spontaneous deaths occurred in animals from cage position No. 2 which probably received the largest CTF dose. These animals showed severe enteritis and enlarged livers. These deaths all occurred in less than the two-week period, two occurring on the fourth day and one on the ninth day after exposure. Hair loss was found in animals from all exposed cages. Eye opacities were noted in animals from cage position No. 1, 3, and 4. The lung changes were as noted in the other groups, but pulmonary hemorrhage was less frequent.

Microscopic Pathology--14 Days. Pathological changes were found in lungs, livers, kidneys, and nasal mucous membranes of these animals. No relation to CTF was obvious. The grossly swollen livers of the hamsters from cage

TABLE C-3

SUMMARY OF PATHOLOGICAL FINDINGS 7 DAYS AFTER CTF EXPOSURE

GROUP II

		Gross									Microscopic											
						Kidney		Liver			Lung				Kidney			Liver				
Cage Position	Number	Spontaneous death*	Hair loss	Pulmonary hemorrhage	Enteritis	Swollen	Mottled	Swollen	Pale	Eye opacity+	Hyperemia	Hemorrhage	Cell infiltration	Emphysema	Hyperemia	Tube cell swelling	Tube necrosis	Hyperemia	Cloudy swelling	Central necrosis	Recovered subacute atrophy	Rhinitis
C	71																	X				
	76																		X			X
	78																				X	
1	56		X					X										X				
	59	6-11	X	X	X			X														X
	57		X	X						X		X		X								
2	62	6-10	X	X	X			X		X				X								
	75	6-7			X									X								X
	77		X											X								X
3	32													X								
	47		X					X		X				X								
	54		X																			
4	12									X				X				X		X		
	15			X						X												X
	18																		X			

*Unless date of spontaneous death specified, animal was sacrificed 6-13-61.

+White opaque fluid in anterior chamber.

TABLE C-4

SUMMARY OF PATHOLOGICAL FINDINGS 14 DAYS AFTER CTF EXPOSURE

GROUP III

Gross Microscopic

						Kidney		Liver			Lung				Kidney			Liver				
Cage Position	Number	Spontaneous death*	Hair loss	Pulmonary hemorrhage	Enteritis	Swollen	Mottled	Swollen	Pale	Eye opacity+	Hyperemia	Hemorrhage	Cell infiltration	Emphysema	Hyperemia	Tube cell swelling	Tube necrosis	Hyperemia	Cloudy swelling	Central necrosis	Recovered subacute atrophy	Rhinitis
C	64																		X	X		
	66																		X			
	67												X						X			
1	53		X												X				X			
	57		X																			
	55		X							X									X			
2	65	6-10		X	X			X						X	X			X				
	69	6-10			X			X			X		X		X	X		X				
	79	6-15			X			X	X				X			X					X	
3	34		X							X									X			X
	61		X							X									X		X	X
	70		X	X						X												
4	19									X					X			X	X			
	20									X									X		X	
	24		X																		X	

*Unless date of spontaneous death specified, animal sacrificed 6-20-61.

+White opaque fluid in anterior chamber.

position No. 2 could be explained by hyperemia in two cases and recovery from subacute liver atrophy in the other. Although found in one control animal in the 7-day group, recovered subacute liver atrophy was found otherwise only in animals of the 14-day group.

> NOTE: The term subacute liver atrophy is used to describe microscopic findings showing disruption of liver lobular architecture, regeneration of hepatic tissue with fibroblast and lymphocyte infiltration and the formation of new bile ductules.

Conclusions

In addition to the tissues mentioned above, hearts, spleens, tracheas, and adrenals were examined grossly and microscopically. No pathological changes were noted in these tissues. Chlorine trifluoride, in sufficient concentration and duration of exposure, will cause death in from one to nine days; the most consistent finding associated with such death is a severe enteritis. In addition, it appears that CTF exposure will cause hair loss and eye opacities and possibly an initial, but transient rhinitis and kidney damage. It seems likely that most liver, lung, kidney, and nasal mucous membrane changes found in this study are related to undetermined factors other than CTF since they were found in control as well as exposed animals. Possibly they are associated with the stress of transportation of the animals to and from the test site with resultant increased susceptibility to infection, heat, automobile exhaust, etc. However, CTF may have had an influence on these changes although it is not possible to determine to what, if any degree. The incidence of recovery from subacute liver atrophy indicates that CTF well may have had a deleterious effect on the liver.

EXPOSURE TO PENTABORANE-HYDRAZINE, TEST 8

This study was made in conjunction with a mixing spill of 200 lb of pentaborane and 100 lb of hydrazine.

Placement of Animals at Test Site

The biological study group from the Institute of Medical Research, Huntington Memorial Hospital, arrived at Edwards Air Force Base at approximately 9:30 a.m. with the hamsters to be exposed in the pentaborane-hydrazine spill test. The animals were placed in their cages at the sampling sites on the range at approximately noon. The spill took place at approximately 1:30 p.m., and the animals were collected from the sampling sites shortly after 2:00 p.m. All animals were found dead in their cages at this time. (It is to be noted that the weather on this day was extremely hot.) The animals were returned to the Institute of Medical Research and autopsies were performed on all animals that night. Figure C-3 illustrates the placement of the animals at the test site.

Pathological Findings

Gross Pathology. Lungs were uniformly found to be dark red, to fail to collapse when the thorax was opened, and to exude a bloody fluid when cut; this indicates hyperemia, edema, and possibly hemorrhage of the lungs. The livers of all animals were found to present essentially the same features: they were generally pale and yellowish with many small red areas giving the livers a mottled appearance. The kidneys were generally paler than normal. In addition, certain lesions of a traumatic nature were found. One animal from the upwind control group was found dead with the left eye missing, ribs broken, the abdominal wall ruptured, and evidence of rupture of the colon. Three animals were found to have severe bruises of the abdominal wall; it is possible that these occurred during transporation. The stomachs of a number of hamsters were found ruptured at autopsy. It seems likely that this was the result of

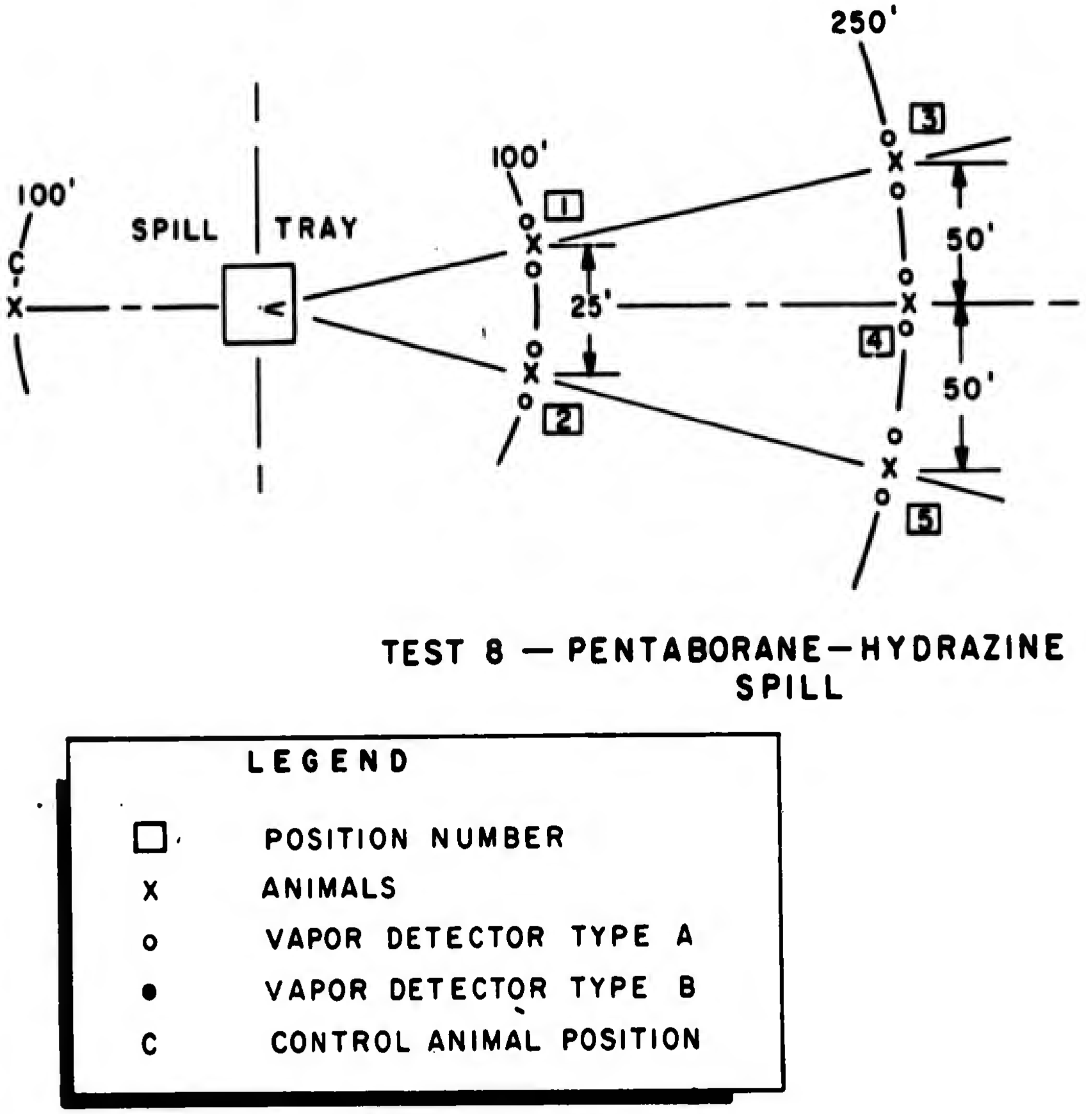

Figure C-3. Animal Exposure and Vapor Detector Positions increased bacterial activity and rapid decay which would be expected to occur in hot weather. However, because of the extent of contamination and decay in the peritoneal cavity, the possibility that these findings represented explosion-inflicted trauma could not be excluded although the fact that most of these ruptures were in animals farthest from the spill site opposes it. Table C-5 gives a summary of the findings.

Microscopic Pathology. Tissues were taken from all animals and have been mounted in paraffin blocks. However, because of the similarity of the gross findings, only a limited number of tissues have been cut, stained and studied microscopically. These have been selected, however, so that tissues of a hamster from each sampling site have received histological examination. The following animals have been studied: No. 95 (Cage position C), No. 119 (Cage position 1), No. 117 (Cage position 2), No. 138 (Cage position 3), No. 150 (Cage position 4), No. 101 and No. 109 (Cage position 5).

The findings were as follows:

1. Lung: The lungs of all animals showed severe hyperemia with edema and some hemorrhage.
2. Liver: The appearances of the livers of all animals were similar. Areas of pronounced hyperemia were found; these were usually cantrolobular with the central vein congested. Most frequently, the periphery of the lobule was devoid of blood, although areas were found in which congestion extended to the periphery too. Veins were generally filled. Hamsters No. 101 and No. 109 showed perivascular polymorphonuclear infiltration in the liver, and perivascular infiltration by lymphocytes and fibroblasts was also found in the liver of No. 101.
3. Kidney: The glomeruli were uniformly engorged with blood.
4. Spleen: The spleens appeared normal; however, the spleen from hamster No. 150 was engorged with blood.

TABLE C-5

GROSS PATHOLOGY: PENTABORANE-HYDRAZINE SPILL, 7-18-61

Cage Pos'n.	No.	Lung Hyperemic and/or Hemorrhagic	Liver Pale with Red and Yellow Mottling	Kidneys, Pale	Abdominal Wall Discolored (Bruised)	Stomach Ruptured	Colon Ruptured	Other Findings
C	80	X	X	X				
	81	X	X	X				
	83	X	?	?	?	?	X	Left eye missing, ribs broken, abdominal wall ruptured, abdominal viscera too badly damaged for examination
	84	X	X	X				
	86	X	X	X				
	88	X	X	X				
	93	X	X	X				
	95	X	X	X			X	
	99	?	?	?	?	?	?	Escaped from cage.
1	87	X	X	X				
	102	X	X	X				
	103	X	X	X				
	115	X	X	X				
	119	X	X	X				
	120	X	X	X				
	123	X	X	X				
	126	X	X	X				
	140	X	X	X				
2	94	X	X	X				
	104	X	X	X				
	107	X	X	X				
	111	X	X	X				
	112	X	X	X				
	113	X	X	X				
	117	X	X	X				
	132	X	X	X		X		
	141	X	X	X		X		

TABLE C-5
(Continued)

Cage Pos'n.	No.	Lung Hyperemic and/or Hemorrhagic	Liver Pale with Red and Yellow Mottling	Kidneys, Pale	Abdominal Wall Discolored (Bruised)	Stomach Ruptured	Colon Ruptured	Other Findings
3	45	X	X	X		X		
	128	X	X	X	X			
	130	X	X	X		X		
	131	X	X	X				
	134	X	X	X		X		
	138	X	X	X		X		
	142	X	X	X				
	144	X	X	X				
	147	X	X	X	X	X		
4	129	X	X	X				
	135	X	X	X				
	136	X	X	X				
	137	X	X	X				
	139	X	X	X		X		
	143	X	X	X				
	145	X	X					
	148	X	X	X	X			
	150	X	X	X				
5	85	X	X	X				
	89	X	X	X		X		
	98	X	X	X		X		
	101	X	X	X				
	108	X	X	X				Subserosal hemorrhage of small intestine
	109	X	X	X				
	121	X	X	X				
	124	X	X	X		X		
	125	X	X	X		X		

5. Adrenal: The adrenals exhibited medullary hyperemia; the cortex of the adrenal from hamster No. 150 was also hyperemic.

6. Heart: The hearts were normal.

7. Nasal mucous membrane: The nasal mucous membrane changes were minor. There appeared to be a slight rhinitis since some hyperemia associated with small areas of epithelial erosion and debris in the nasal cavity was found. These changes were seen in all animals. However the slides were difficult to study since cellular structure was poorly differentiated and staining was poor. Possibly some of these changes were artifacts resulting from the decalcifying process.

Conclusions

While there is some evidence of possible trauma caused by the pentaborane-hydrazine explosion, the extent to which the concussion may have been a factor is very questionable. It seems most likely that these animals died from circulatory collapse resulting from hyperthermia.

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