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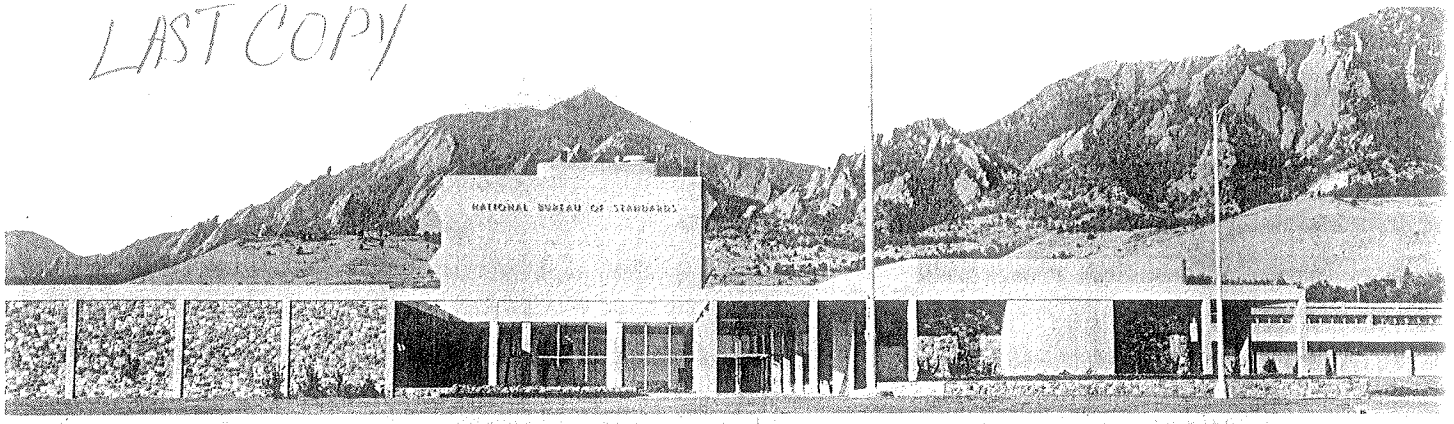

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NBS REPORT

7253

SAFETY IN THE USE OF LIQUID HYDROGEN

by

Dudley B. Chelton

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
BOULDER LABORATORIES
Boulder, Colorado

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NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT
81900

May 22, 1962

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SAFETY IN THE USE OF LIQUID HYDROGEN

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ABSTRACT

Safety in systems using liquid hydrogen is a subject of considerable present-day importance. Reducing or eliminating the potential safety hazards involved requires a basic understanding of the physical and chemical properties of hydrogen and the application of known safety technology. These factors are reviewed and recommendations are given for safety criteria. Comparisons are made with propane and methane to assist in establishing the relative hazard. Consideration is given in the use of liquid hydrogen on a large scale and on a laboratory scale.

SAFETY IN THE USE OF LIQUID HYDROGEN

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Introduction

Safety in systems using liquid hydrogen is a subject of considerable present-day importance. Although liquid hydrogen has been used for many years, activity in the missile field has vastly increased the quantity consumed. Reducing or eliminating the potential safety hazards involved requires a basic understanding of the physical and chemical properties of hydrogen and the application of known safety technology. Experimental and theoretical programs have recently been conducted on the hazards associated with the production and handling of liquid hydrogen[1, 2]. Many uncertain areas yet remain, but sufficient knowledge does exist upon which to establish satisfactory safety criteria.

Although facilities using liquid hydrogen have many problems in common, each is unique in certain respects. As in any safety program, an explicit set of adequate rules cannot be given; instead, the general criteria must be studied carefully to insure that every potential hazard has been considered.

Physical and Chemical Properties

A brief review of the physical and chemical properties of hydrogen will serve as a basis for subsequent material in this chapter. Hydrogen is the lightest of all elements. It is colorless, odorless, tasteless, and non-toxic, but can cause asphyxiation by exclusion of air. Hydrogen is a flammable gas which burns with a colorless flame in the absence of impurities; however, refraction of light passing through the flame can usually be observed.

Several properties of hydrogen which are significant when considering safety are shown in Table I. The comparative figures for propane and methane are given to assist in establishing the relative hazard with respect to these more conventional fuels. Comments on the significance of these properties follow:

Temperature and Heat of Vaporization - The temperature and heat of vaporization of the liquid phase are indicative of storage and handling problems and of damage to human tissue by freezing. Liquid hydrogen is difficult to retain in storage because of relatively low heat of vaporization and low boiling point temperature. These factors necessitate the use of high quality insulation to efficiently retard evaporation. However, once exposed to atmospheric conditions, hydrogen will evaporate quickly, greatly decreasing the duration of a possible hazard. Exposure of human tissue to cryogenic fluids can cause freezing with results similar to severe burns, although the low heat of vaporization for hydrogen may lessen the problem if small quantities are involved. The high thermal conductivity of gaseous hydrogen increases the danger of freezing by cold vapor.

Density - The ratio of the density of saturated liquid at the normal boiling point to the vapor at room temperature is a measure of the pressures that can be generated if the liquid is confined and allowed to warm. Although there is a considerable difference between the density ratio for various fuels, both hydrogen and methane can produce exceedingly high pressures in this manner. The possibility of such confinement should, of course, be avoided in practice by use of appropriate pressure relief devices. The low heat of vaporization and the low boiling point temperature cause the pressure to rise more rapidly with liquid hydrogen than with the other fuels.

Table I

PHYSICAL AND CHEMICAL PROPERTIES

Property	Fluid: Hydrogen H_2	Methane CH_4	Propane C_3H_8
Temperature of Liquid * - ^oK	20.27	111.7	230.8
Heat of Vaporization* - $\frac{cal}{gm\ mol}$	215	1950	4490
Density of Liquid* - gm/liter	70.9	425	593
Density Ratio - liq*/gas 300^oK	865	650	340
Density of Saturated Gas* -gm/liter	1.34	1.76	2.1
Diffusion Coefficient - cm^2/sec	0.63	0.2	0.1
Limits of Flammability (in air)[3]	4-75	5.3-15	2.2-9.5
Limits of Detonability (in air)	18-59[1]	6.3-13.5[4]	---
Ignition Temperature[5] ^oC	585	537	466
Ignition Energy[3] - millijoules	0.02	0.45	0.25
Heat of Combustion -K cal/mol	68	213	530
Flame Temperature[3] - ^oC	2045	1875	1925
Emissivity of Flame	0.10	---	1.0
Quenching Distance[3] (1 atm) cm	0.06	0.25	0.20
Flame Velocity[3] cm/sec	270	37	41

*Normal boiling point

Once a spill has occurred, a comparison of the density of the saturated vapors at the normal boiling point with the ambient density of air indicates the tendency for the evaporated gas to rise in its most dense state. Air at one atmosphere and 273°K has a density of approximately 1.28 gm per liter. Hydrogen vapor at saturated conditions (20°K) has a density comparable to air while propane and methane are considerably more dense. Thus, hydrogen will rise most rapidly and the result will be a faster dissipation of the evolved gas. The results of numerous spill and vent tests indicate, however, that hydrogen vapor can persist and be carried for considerable distances at ground level by strong winds.

Limits of Flammability - As the liquid evaporates, the diffusion coefficient may be regarded as a measure of how quickly the gas will disperse to the surrounding atmosphere. Spills of large quantity will generate sufficient natural convection currents to predominate over diffusion. However, for small spills or gas leaks in piping or apparatus, the rate of dilution by diffusion is pertinent. Hydrocarbons, in general, require much greater exposure times for equivalent diffusion. Although the diffusion coefficient is high for hydrogen, the limits of flammability in air are of concern. Hydrogen has one of the widest limits, while the limits for propane and methane are rather narrow. These limits of flammability indicate the volume of possible combustible mixture and perhaps are a measure of the probability of ignition. Variations exist in the published limits of flammability. Establishing these limits is, in part, dependent upon the method of determination. In tubes, flammability limits are more narrow for downward propagation of the flame and are wider as the tube diameter is increased. The limits of flammability are affected relatively little over a wide range of pressures. Normal variation of

atmospheric pressure has no appreciable effect.

Detonation - A detonation is a process in "which an exothermic reaction takes place in a high pressure wave moving at supersonic velocity with respect to the unreacted material. A deflagration process travels at subsonic velocity with respect to the unburned material"[6] being propogated by heat transfer and diffusion. With appropriate confinement and composition, most combustible mixtures can support either type of reaction. Both detonations and deflagrations are combustion processes.

The limits for detonation are relatively narrow compared to the limits of flammability. These detonation limits are of concern where possible confined conditions or strong detonating ignition sources exist. Experiments with hydrogen indicate that the partial confinement of three vertical walls (roof and one side absent) is sufficient to produce a detonation if mixtures within the detonation limits are ignited. The mixtures are determined, in part, by the volume ratio of the liquid or vapor to the confined space and by the time after exposure of the volatile liquid to the surroundings. The pressure produced by a detonation is greater than that produced by a deflagration. Every effort should be made in practice to avoid even partial confinement, particularly where large quantities of hydrogen are involved.

Ignition Temperature and Ignition Energy - Since the ignition temperature of hydrogen is higher than methane or propane, it might at first be thought that combustion of hydrogen is more difficult. Figure 1 represents the minimum spark ignition energy required for various concentrations of hydrogen in air[3]. The minimum ignition energy at stoichiometric conditions is an order of magnitude lower for hydrogen

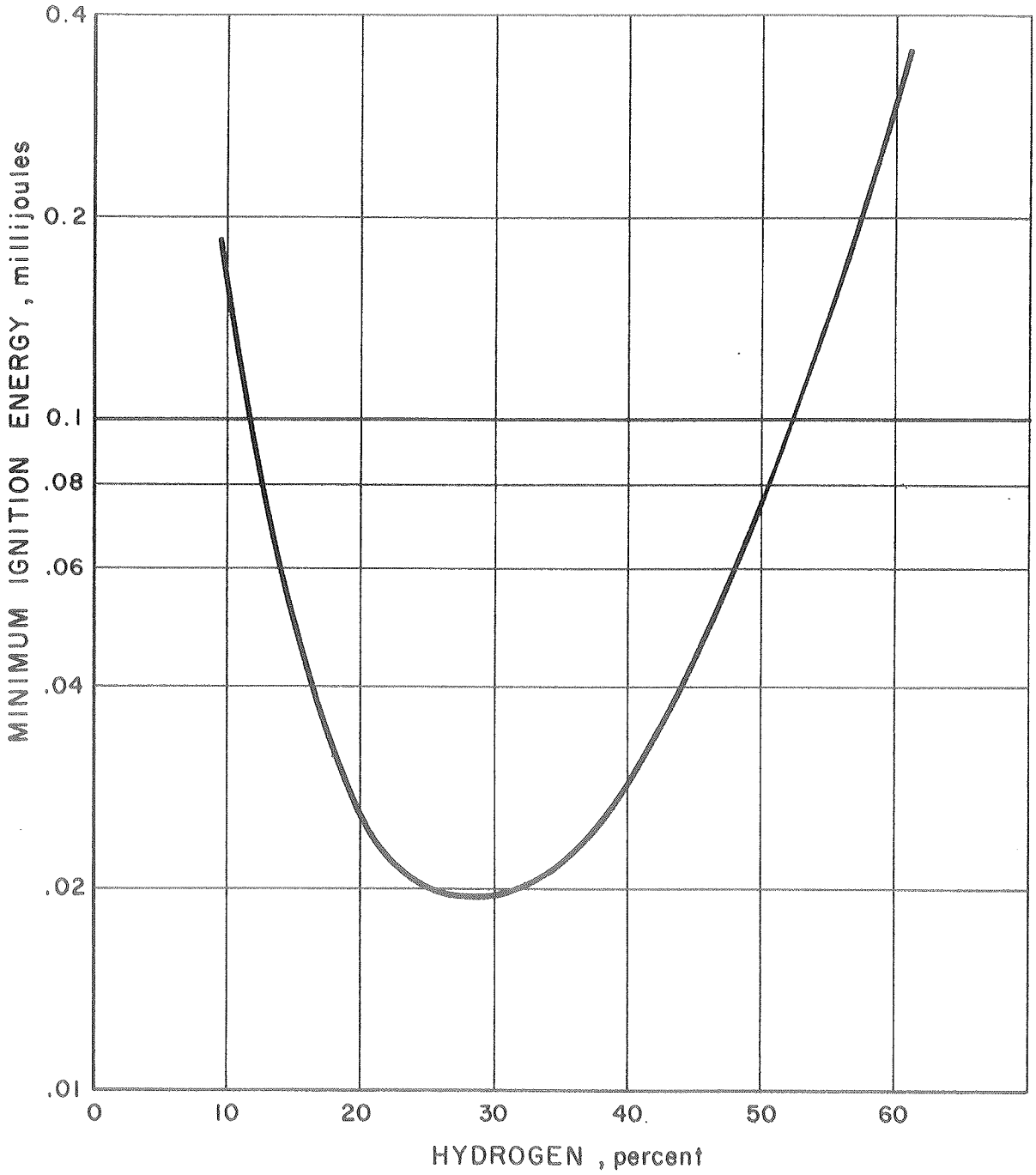

Figure 1 - Minimum Ignition Energy for Hydrogen - Air Mixtures[3]

than for the hydrocarbons. An example of the ease with which a hydrogen fire can be initiated is the relative facility with which an electrostatic charge can ignite a combustible mixture. It has been observed that an electrostatic discharge from a person could ignite a hydrogen-air mixture even though the amount of static electricity could not readily be felt on discharge. With an electrostatic voltmeter it was determined that a charge several times the minimum ignition energy could be developed by the action of removing a coat made of synthetic material.

Flame Emissivity - The flame temperatures of methane, propane, and hydrogen are of the same order. A more significant factor, however, when considering possible thermal radiation damage, is the apparent, or average, emissivity of the flame. The hydrocarbon fuels, in general, have flames with an emissivity approaching 1.0, whereas hydrogen flames range from 0.01 to 0.10[1,2]. Thus, for equivalent sized flames only 1 - 10 percent as much radiation will be transmitted from a hydrogen fire. The variations of emissivity values reported are apparently, in part, due to time delay before ignition, to the assumed flame temperature, to the quantity of liquid spilled, and to atmospheric absorption of radiation from a hydrogen flame. Because of atmospheric absorption, the radiation heat flux for hydrogen decreases rapidly with distance if the air contains as much as two percent water vapor; this is less than the saturation value at a temperature of 20°C and a pressure of one atmosphere.

Although, as has been stated, the radiation from equal sized flames is relatively small for hydrogen compared to hydrocarbons, it is important to note the effect of differences in heats of combustion, burning rate and flame size. The radiation from a flame above a pool of burning liquid, per unit area of pool surface, is about the

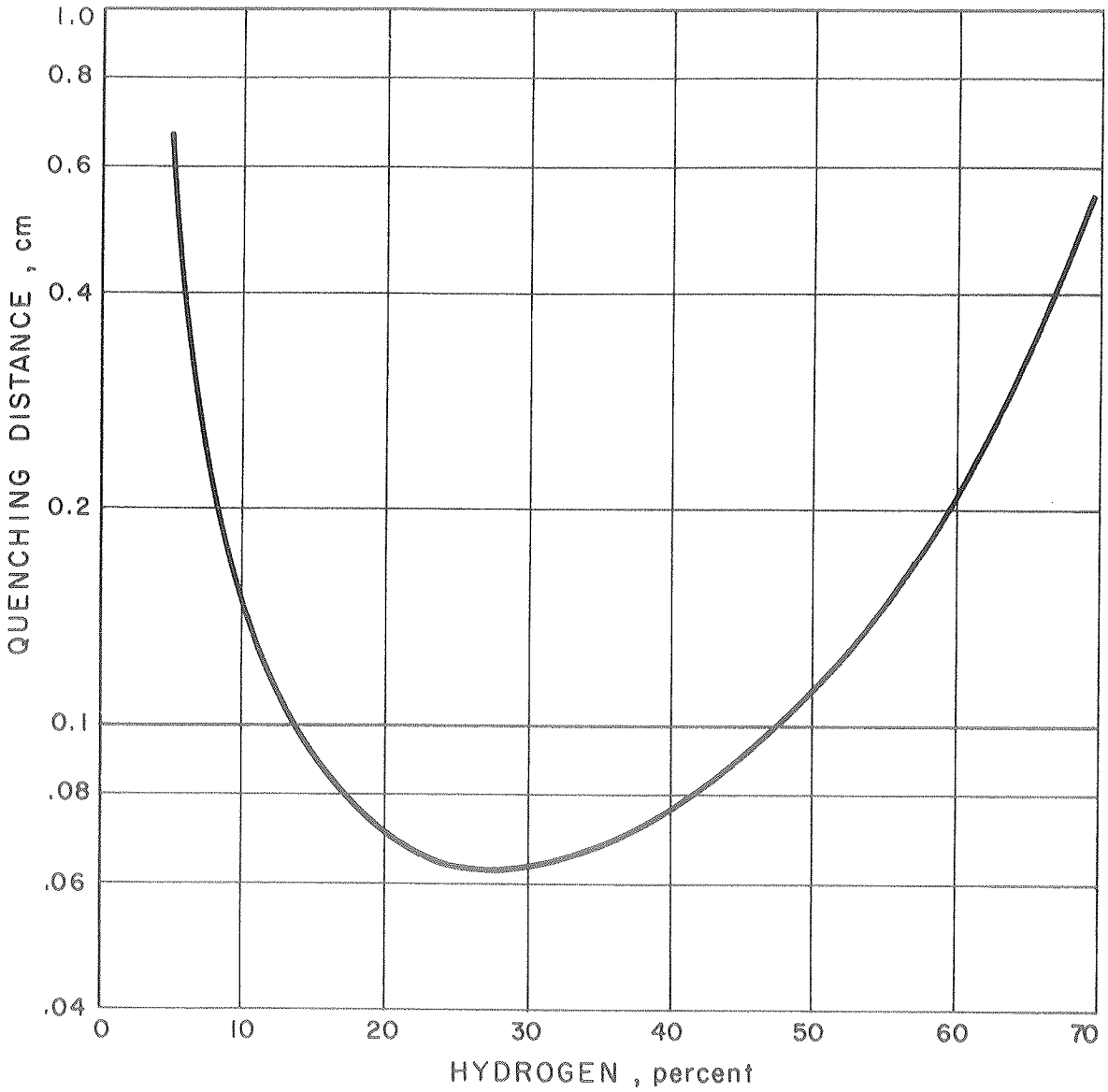

Figure 2 - Quenching Distance for Hydrogen - Air Mixtures[3]

same for liquid hydrogen and liquid natural gas (primarily methane) ~20 Kw per square foot of pool surface[6]. The rapid burning rate of hydrogen, however, reduces the total energy radiated for equal volumes of liquid.

Quenching Distance - The quenching distance is defined as the distance between surfaces that will just permit a flame to pass without being cooled to extinction. The necessary spacing in a rectangular channel is smaller than in a circular channel. Figure 2 illustrates the quenching distance for parallel plates as a function of the concentration of hydrogen in air[3]. Because of the high velocity of flame propagation, the spacing is quite small. For a stoichiometric mixture a spacing of 0.06 centimeter is required for hydrogen, while the hydrocarbons require considerably greater distances. Increasing pressure results in a significant decrease in the required quenching distance. Thus, the construction of a flash-back arrester for systems using hydrogen, particularly dynamic systems, is difficult. The placement of the arrester in the system is quite critical in order to prevent pressure increases, due to combustion on the flame side, from decreasing the required quenching distance to an impractically small dimension.

Conclusions - From the foregoing comparisons it is seen that some properties of hydrogen tend to make it more hazardous than hydrocarbon fuels, while other properties tend to make it less hazardous. Once exposed to ambient conditions, hydrogen will evaporate and more quickly dissipate, thus decreasing the time extent of a possible hazard, but increasing the size of the combustible cloud. However, for hydrogen, flammable concentrations are more readily obtained, lower ignition energies are required for combustion, and the flame is

more difficult to extinguish. Damage caused by thermal radiation to the surrounding area is usually less for hydrogen, due to the low emissivity of the flame and the rapid burning rate.

Materials of Construction for Hydrogen Handling Equipment

The structural integrity of components using hydrogen must be assured to protect against possible hazards which could result from equipment failure. Designs of cryogenic portions of a system should appropriately utilize the mechanical and transport properties of structural materials at low temperatures[7]. Component materials at ambient temperatures, and particularly those involving high pressures, should be chosen to prevent danger from hydrogen embrittlement. The choice of materials, particularly tools, to prevent ignition of combustible mixtures from sparks caused by metallic friction or impact should also be considered.

Design - Cryogenic design considerations have been adequately reported elsewhere[8,9]. The basis for design should, where applicable, include the use of a design standard or pressure vessel code[10]. The proof of proper design can be determined by an appropriate test procedure. These procedures are outlined in the usual design guide, but should include testing at ambient temperature and at least partial testing at cryogenic temperatures before use with liquid hydrogen. As a general rule, for the purpose of prior testing, reducing the temperature of the component to that of liquid nitrogen (77°K) will closely simulate the material state at liquid hydrogen temperature. Pressure tests of 1.5 times working pressure are generally accepted. Several laboratories have adapted the further restriction of testing to not less than 150 psi. A number of applications, however, prevent such strin-

gent proof testing or use of a pressure vessel code since the mass of structural material may be required to be at a minimum, e.g., apparatus for measuring specific heat and airborne components. In these instances, every possible safety precaution should be taken to protect personnel and equipment, proof tests should be to as high a pressure as possible, apparatus should be located in a well-ventilated area and operation should be performed as remotely as practical.

Hydrogen Embrittlement - Although the embrittling effect of atomic hydrogen on various materials has been known and studied for some time, recent evidence indicates harmful effects of molecular hydrogen at room temperature on some cold-worked materials. The investigation of Mills and Edeskuty[11] was initiated by the failure of several Bourdon gauges after room temperature exposure to hydrogen for times as short as one minute and at pressures of two-thirds full scale. In addition, failures had been experienced with certain cold-worked capillary tubes. Experimental results indicate magnetic materials, namely ferritic materials since little work has been performed on the other ferromagnetic materials, nickel and cobalt, are particularly susceptible to hydrogen embrittlement. In addition, cold-working significantly lowers the resistance to embrittlement.

Other laboratories have had failures of pressure gauge tubes under similar circumstances. Figure 3 shows a failure that has been attributed to hydrogen embrittlement. The Bourdon type pressure gauge (0 - 5000 psig, 403 stainless steel tube) had earlier been pressurized to 2000 psig. Failure occurred under static pressure conditions of less than 500 psig. A piece of metal approximately 1.5 x 3 cm was blown out resulting in a fire and injury to an operator.

As a result of the above investigation, it is recommended that no magnetic material be used for Bourdon gauges in hydrogen service.

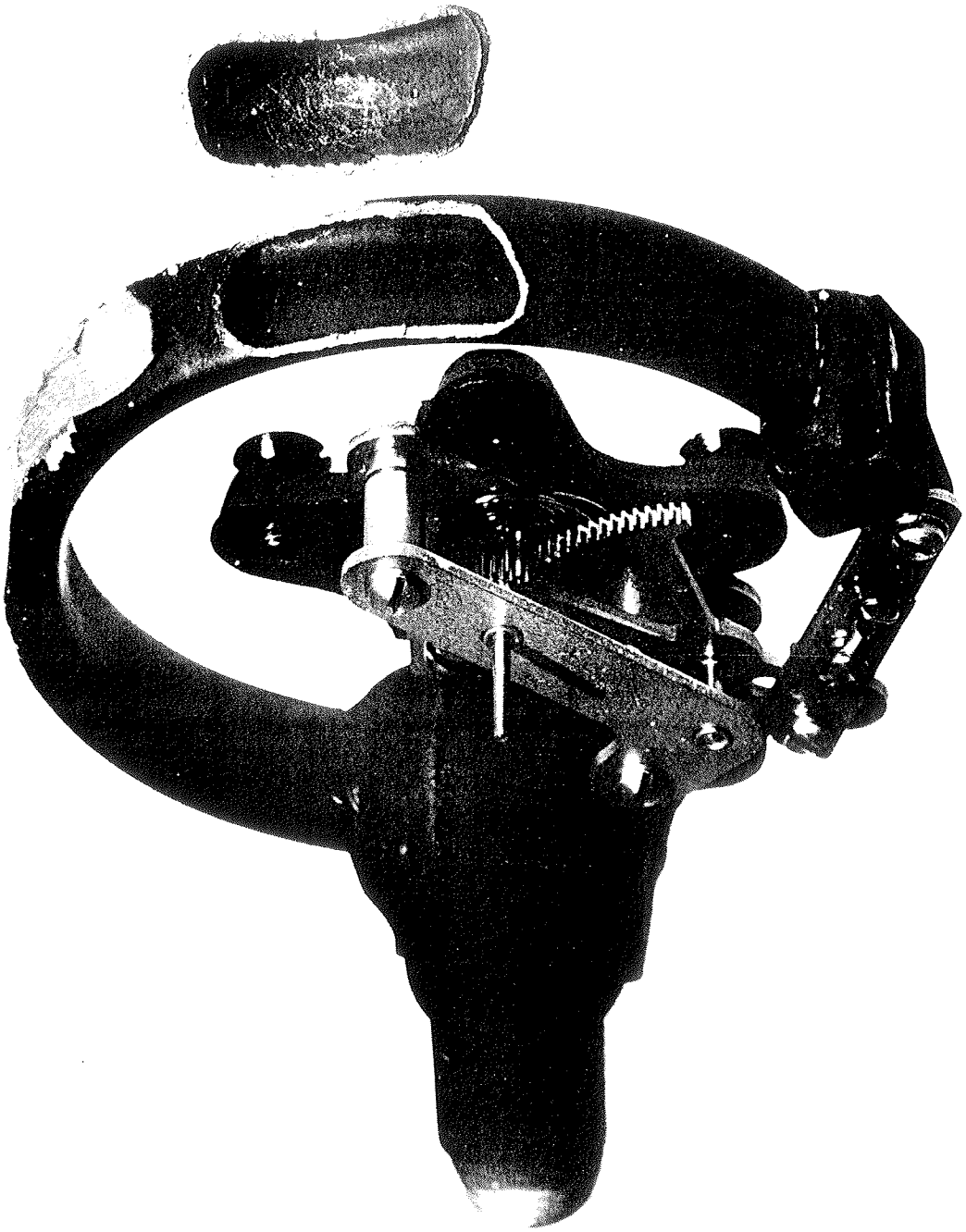

Figure 3 Gauge Failure Attributed to Hydrogen Embrittlement

Many acceptable gauge materials exist, such as the stabilized austenitic stainless steels (e.g. types 316, 321, 347), phosphor bronze and beryllium copper. It is further recommended that no cold-worked ferritic material be used in any structural application containing hydrogen gas. Applications exist where these materials are currently being used with apparent success. However, these applications should be carefully evaluated to determine the potential risk involved.

Low-Sparking Materials - "Spark-proof" tools made of low-sparking materials have frequently been used in an effort to reduce the potential hazard of igniting combustible hydrogen-air mixtures. There is some indication that sparks or impacts and subsequent ignitions can result from the use of sparking materials[12] although the number of such cases on record are extremely small. The author is not aware of any cases of hydrogen ignition from this source. Sparks caused by metallic contact of steel on steel are of high temperature, of the order of 1400°C, but of relatively low total energy. However, the low ignition energy of hydrogen-air mixtures makes combustion from this source possible. The sparks caused by metallic contact of other materials may be of a temperature considerably less than steel on steel. Copper tools on steel result in spark temperatures of about 260°C. Although the sparks of the former materials are incandescent, those resulting from copper tools are not. Copper-nickel alloys with small amounts of iron could develop spark temperatures well above 260°C.

If the energy of resulting sparks is great enough, it is theoretically possible to ignite combustible substances that have ignition temperatures at or below the resulting spark temperatures. Although it is often difficult to distinguish between impact and friction, it is the opinion of some authorities that ignition by impact offers greater hazards than by friction sparks.

On the basis of what is presently known, all materials capable of generating sparks by friction or impact should be handled cautiously. The use of hand tools made of low-sparking materials may be effective as one means of preventing hydrogen ignitions; such tools are recommended, although their use may result in a sense of security that is not warranted. Tools made of iron, steel (particularly rusted iron or steel), stainless steel and magnesium should be avoided. Rusted iron surfaces covered with aluminum paint are hazardous from the standpoint of possible thermit-type reactions, and under any circumstances, careful consideration should be given to methods of performing work in areas subject to the accumulation of combustible gas mixtures.

Large Scale Usage

Several potentially hazardous conditions exist in connection with large scale liquid hydrogen systems. Three major problem areas will be discussed. To a large degree, the conclusions reached are based upon the tests performed by Arthur D. Little, Inc.[1] and the Bureau of Mines[2].

Contamination - Occasionally, it is possible to accumulate oxygen in the presence of hydrogen. Usually, the problem exists where oxygen can be solidified because of low temperatures in a cryogenic system. In order to determine the hazard associated with such accumulation, an investigation was conducted with impact and with an electric spark from a fuse wire submerged in liquid hydrogen. The results of these experiments indicate that, although detonations were observed with accumulation of solid oxygen, no detonations were observed with solid air. Gradual combustion, however, was observed with the fuse wire and solid air. A preliminary investigation with enriched

concentrations of solid air indicated that the minimum oxygen content supporting a detonation was about 40 percent[13]. Although the probability of a detonation of liquid hydrogen and solid air accidentally entrained in a cryogenic system appears remote, it is possible to accumulate enriched concentrations of air by preferential condensation of oxygen from the atmosphere. The degree of solubility of oxygen in liquid hydrogen has been determined to be extremely small; therefore accumulation of solids would concentrate at the low point of a vessel.

Fuel Spills - Although the physical characteristics of hydrogen were known, it was found necessary to perform spill tests of liquid hydrogen to determine specific quantity - distance relationships for storage containers. These distances required further knowledge of the nature of a hydrogen spill and of a resulting fire. Several factors were studied: the rate of cloud growth, the volume of flammable cloud, the possibility of a detonation and the possible damage to surrounding materials.

Spills of liquid hydrogen were made in quantities from about one gallon to 5,000 gallons. Several conclusions were made on the basis of these tests. The majority of tests were conducted under unconfined conditions; this fact must be kept in mind in reviewing the conclusions.

During unconfined tests, no detonations of hydrogen-air mixtures occurred when ignited by a spark. The transition from deflagration to detonation requires a significant pressure build-up such as afforded by confinement or by initiation with a strong detonator. Hazards associated with fire occurring after the release of liquid hydrogen vary according to the limits and duration of the flames. In the course of experiments, it was observed that

immediate ignition of the combustible mixture decreased fireball size. In all spills, the duration of a resulting fire was extremely short as compared to other hydrocarbons, 0.05 - 0.02 of the time for equivalent quantities of gasoline or propane[1]. After the initial fireball, the flames were confined to a region directly over the diked area, but could extend 150 feet in height. Radiation effects, although less than hydrocarbons, could be significant. Radiation from flames at a break in a pipeline where shut-off is impossible would be a serious hazard because of the extended duration of burning. In pipeline-rupture tests, flames were extremely wind sensitive; winds of 18.5 mph carried flames as far as 60 feet downwind.

The Bureau of Mines, using relatively small quantities of liquid hydrogen, determined that the flammable zone does not necessarily coincide with the vapor cloud. "In general, the visible cloud height was found to be below the height of the upper flammable zone. The difference in heights varied with the relative humidity, air movement, and the time following spillage[2]". Figure 4 illustrates the extent of the flammable mixtures and height of the visible cloud formed after rapidly spilling three liters of liquid hydrogen on a dry asphalt surface in a quiescent air atmosphere at 15°C.

The pressure produced by burning a flammable mixture over evaporating liquid hydrogen is small. However, it is essential to note the significance of confinement. For instance, the pressure obtained from combustion following the spill of 1.25 gallons of liquid hydrogen in a partially confined space was equivalent to those obtained at the same distance in unconfined 500 gallon spills. The results of the partially confined test were obtained in a three-sided (plus ground) enclosure 2 x 2 x 2 feet. Thus, for four-walled enclosures (three vertical walls plus ground) of these proportions, reproducible detona-

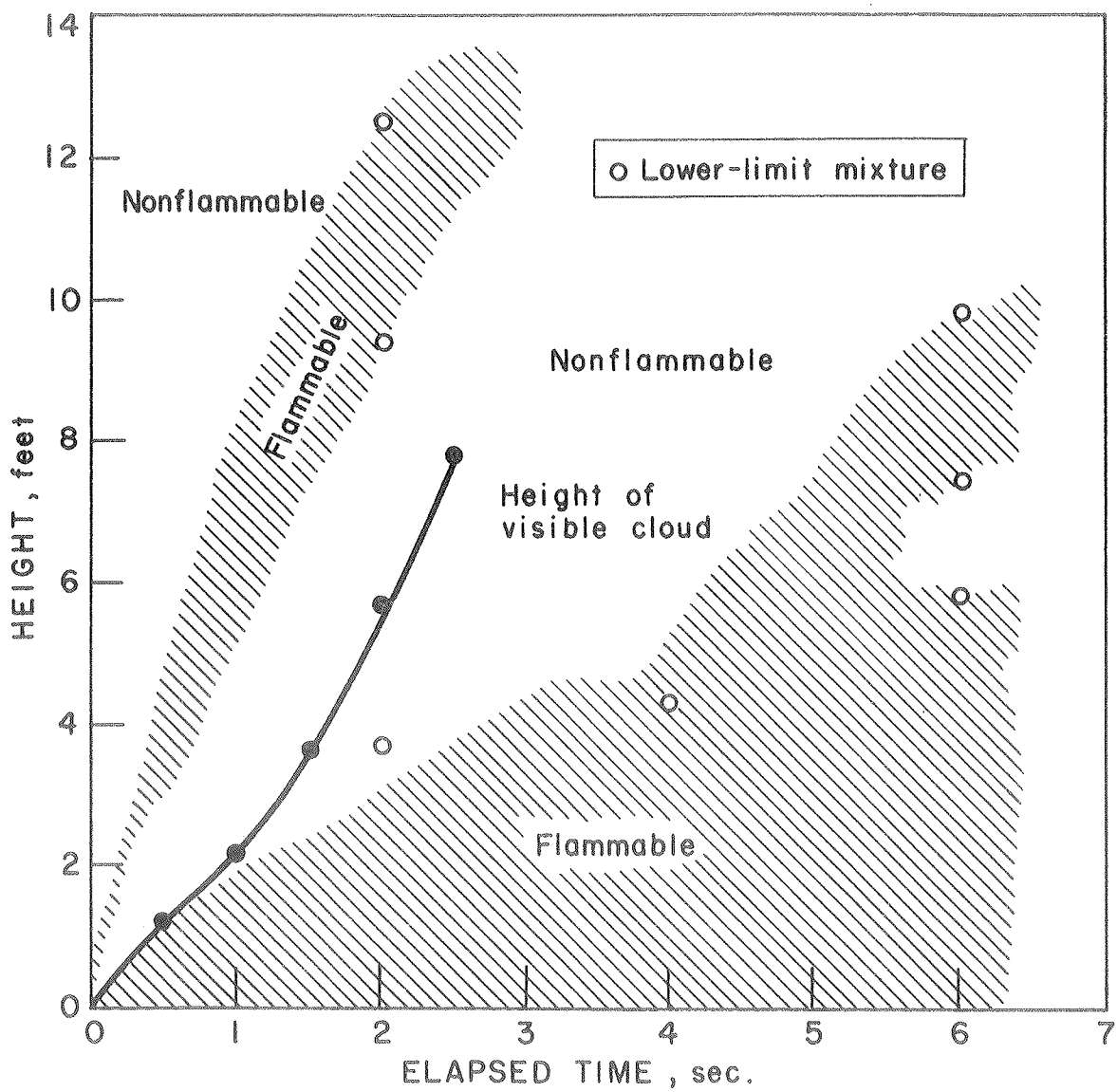

Figure 4 - Position of Flammable Zones Resulting From Liquid Hydrogen Spill (Courtesy of Bureau of Mines)

tions could be obtained. A confining structure, large compared to the volume of liquid, would not necessarily constitute confinement; therefore, detonations would not necessarily occur. No detonations were observed with a two-walled confinement (one wall plus ground).

As a result of the experiments in partial confinement, it becomes apparent that barricades should not be used to surround storage tanks. Furthermore, barricades are not necessary for the protection of adjacent tanks or buildings if proper quantity-distance relationships are followed, or if the outer walls of the dewars are externally insulated. Dikes should be used to contain the spilled liquid, but should be only large enough to prevent the liquid from flowing to an undesirable location. A base material of crushed rock yielded the highest evaporation rates for spilled liquid.

Quantity - Distance Relationships - The values of the quantity-distance relationships for liquid hydrogen, proposed by the Bureau of Mines, are shown in Table II. The distances quoted are based on one percent moisture in the atmosphere and excludes shock sensitive materials.

The quantity-distance relationships for liquid hydrogen as proposed by Arthur D. Little, Inc., are not comparable since they recommend use of a refractory material to retard heat transfer to the dewar vessel[1]. With the application of 2.5 inches of refractory material on the outer wall of the dewar, the suggested distances vary from 27 feet for 30,000 pounds to 53 feet for 100,000 pounds. The distance to adjacent work areas and potential ignition sources is to be a minimum of 200 feet for all quantities greater than 10,000 pounds. The distance to public roads should be a minimum of 500 feet.

Venting - The proper disposal of vent gas is a serious problem in handling liquid hydrogen. Many opinions have been expressed by various laboratories and safety authorities on the use of burning

Table II

QUANTITY-DISTANCE RELATIONSHIP FOR LIQUID HYDROGEN

Proposed by

BUREAU OF MINES[2]

Distance Between Storage Tanks

Liquid Quantity (Pounds)	Distance (Feet)
0 - 2,000	50
2,000 - 10,000	100
10,000 - 20,000	150
20,000 - 40,000	200
40,000 - 60,000	250
60,000 - 100,000	300

Distance to Inhabited Buildings

0 - 200	100
200 - 1,000	150
1,000 - 5,000	200
5,000 - 20,000	250
20,000 - 40,000	300
40,000 - 100,000	350

vent stacks (flare stack) versus non-burning vent stacks. The conclusions reached are often somewhat contradictory and the answer to this problem has not been solved satisfactorily for all cases. Each situation must be individually considered.

However, general guidelines can be established for venting criteria: a) It is desirable for the vent to be long enough to warm the hydrogen to at least liquid air temperature (approximately 80°K) under the most severe flow condition. This will prevent liquid air from flowing back into the vent line. b) Provisions should be made for a suitable check valve system or for a positive flow of gas from the vent line sufficient to prevent back-flow or diffusion of air. Weight-loaded or "flapper"-type discs and molecular seals have been used successfully on vent line discharge. c) Although the height of the vent stack should be sufficient to prevent accumulation in working areas, care should be taken with excessive heights since a pressure below atmospheric can be produced in the base of the stack because the density of warm hydrogen is much less than that of air. A discharge height, depending on flow rate, should be 10-30 feet above surrounding obstacles.

The Bureau of Mines advises against the use of flare stacks for disposal of excess hydrogen because of the wide range of mixture compositions over which flammable mixtures can be formed and because of the high burning velocities of such mixtures.

The conclusions reached by Arthur D. Little essentially confirmed the above recommendation if quantities less than 30 pounds of hydrogen per minute are involved, but suggest that a steam or inert gas purge be mixed with the vented hydrogen vapor to reduce the chances of ignition. It was further suggested that where flow is continuous, vented gases are to be flared if the flow rate is more than

30 pounds per minute. For high intermittent venting, a flare should be used if potential ignition sources are within 200 feet.

Care should be taken to prevent suspended solid particles from discharging with hydrogen at the end of the vent line. Considerable experience indicates that such particles may become charged and ignite the hydrogen as it is exhausted into the atmosphere. Examples of such particles are perlite or other powder insulating materials, catalyst, metal chips and dust.

Laboratory Usage

The laboratory usage of liquid hydrogen has, in many respects, additional potential hazards over the large scale usage. These hazards are primarily due to the confinement provided by the laboratory enclosure. In an effort to circumvent as many potential problems as possible, greater consideration must be given to the laboratory design and to the procedures used in carrying out experiments.

Many safety features can be built directly into the laboratory space to reduce potential hazards. Wherever practical, experiments should be performed outside where leaks of hydrogen are diluted to non-combustible proportions more easily. The primary objective is to prevent or reduce the possibility of accumulating hydrogen-air mixtures. Any enclosed laboratory containing hydrogen should be sufficiently ventilated to prevent such accumulation. Rooms should be constructed of non-combustible materials and should be without suspended ceilings, ceiling recesses, or peaks other than those required to accomplish ventilation. Exhaust fans should be located in the highest part of the room. The ventilation should be arranged so that air is conducted past the apparatus containing hydrogen. Louvers located at relatively low positions in the room are often used. Ducts

from the room to the exhaust fan should be short. The method of ventilation should insure that the room will be at a slight negative pressure to prevent leakage into unprotected areas.

The degree of ventilation required is somewhat proportional to the quantities of liquid or gaseous hydrogen involved: these quantities should be restricted to an absolute minimum. Recommended ventilation rates are from 20 to 30 air changes an hour during normal operation. Emergency operations often provide for a twofold increase in these rates. A ventilation rate of about 30 air changes an hour appears to be the threshold for personal comfort.

Conducting floors are advantageous in reducing the accumulation of static electricity by operating personnel. A variety of adequate floor constructions are commercially available. Care should be taken to prevent the floor from being covered with non-conducting paint or wax. In the absence of conducting floors, a metal sheet properly located on the floor can provide sufficient protection. All apparatus containing hydrogen should be electrically grounded to a common system, including the conducting floor, to prevent differences in electrical potential.

Combustible Gas Detection - Means for the detection of escaped hydrogen are often provided. Visual detection of a vapor cloud is not considered adequate since escaping gas is not necessarily cold enough to condense water vapor from the air. It should be noted, however, that a cloud formed by cold hydrogen gas nearly always rises, whereas clouds from nitrogen or other cryogenic fluids do not. Combustible gas analysers operating on a number of physical principles are commercially available. Although the principles involved are sound and the instruments may respond rapidly, the location of the detection, or sampling, head is extremely critical. The head must be placed

where it will sample the combustible mixture in question. Because hydrogen rises rapidly, the head should be located at an elevated point. However, a single location does not insure adequate sensing since the combustible mixture may be exhausted from the room without passing the detector. Locating the sampling device in the ventilation system is usually ineffective because of the large volume of air being handled. The number and distribution of detection points is often excessive for adequate protection. It is, therefore, concluded that a permanent combustible gas detection system may be advantageous, but should not be relied upon completely.

Portable combustible gas detectors are often used and should be provided in all installations where remote control is not required. These should be periodically checked for proper operation.

Electrical Components - Permanent electrical components of a laboratory should, where possible, be of the explosion-proof category suitable for hydrogen-air mixtures. The National Electric Code[14] describes the equipment categories. Normal laboratory operations using hydrogen are considered to be included in the Class I, Division 2, Group B designation. Although it is not considered good practice, Group D equipment has been conventionally substituted for Group B when the latter is not available. Explosion-proof equipment is constructed so that an internal combustion will not be transmitted to the environment. Thus, the housings are substantially constructed and components are close-fitting to be less than the minimum quenching distance, but are not necessarily gas tight.

Many essential components of a laboratory, and most experimental electronics, are not available in either Group B or Group D housings. In these cases, several procedures are possible. The generally applicable procedure, when laboratory quantities of

hydrogen are involved, is that sparking components shall not be located above the lowest level at which hydrogen may be expected to escape. This is, of course, not applicable for large quantity usage where appreciable liquid could be spilled at a lower level. Other non-explosion-proof equipment can be enclosed and purged with an external source of uncontaminated air or can be located remote from the equipment containing hydrogen. Electronic apparatus that requires a hydrogen gas supply (e.g. gas analysis equipment) can be purged with an inert gas or ventilated to prevent accumulating combustible mixtures.

Portable Dewars - Portable laboratory supply dewars used to replenish experimental apparatus should be stored outside in a suitably controlled area. These dewars should be in the laboratory only long enough to effect transfer. Transfer of the liquid should be performed in a closed system as much as possible. Evaporated fluid from dewars or apparatus in the laboratory should be piped to a vent discharging into the exhaust duct or directly to the roof. Although various designs exist, a large portion of the portable laboratory supply dewars are of the type shown in Figure 5, ranging in capacity from 5 - 100 liters and having liquid-nitrogen-cooled shields. The most serious problem in maintaining these dewars is providing suitable protection to the neck to prevent accumulation of solid air and water vapor. Because of the low temperature of liquid hydrogen and the low flow rate of the effluent gases from an efficient storage dewar, air and water vapor can diffuse down the neck of the dewar and solidify unless a protective device is used. Dewar vents have been obstructed in this manner at various laboratories and on occasion have resulted in a pressure rupture of the container. With proper precautions in the care of the dewar neck, combined with proper care

in removing a cold transfer line from the dewar, this hazard can be eliminated. The dewar shown in Figure 5 is fitted with such a device. An inline relief valve allows the dewar to vent at a preset pressure. A manual valve is provided to reduce dewar pressure prior to removing the protective device. The tube (not visible) extends inside to a point below the neck of the dewar. The smaller rubber hose connects the liquid nitrogen fill and vent lines and is split to form a Bunsen valve which relieves pressure and prevents diffusion of water vapor into the liquid nitrogen shield. An inverted "U" tube or rubber hose fastened to the dewar neck is not considered adequate protection for hydrogen.

Confinement - The Bureau of Mines has recently[15] performed experiments on the hazards associated with the use of liquid hydrogen in bubble chambers. Results are extremely informative in studying the added hazards accompanying the confined conditions of a laboratory. Numerous spill tests in an enclosed unventilated blockhouse 21 x 13.3 x 13.5 feet (3770 cubic foot volume) were performed. Gas samples were taken for hydrogen concentration as a function of the quantity spilled, the elapsed time after spill, and the room elevation. Quantities from 3.7 liters to about 70 liters were spilled. For quantities greater than about 25 liters, concentrations capable of supporting a detonation were rapidly achieved in appreciable portions of the enclosure.

Additional tests were conducted to determine the results of ignition following a spill. Combustion was initiated with relatively weak and with strong ignition sources. A graph of the maximum pressure produced in various spills is shown in Figure 6. In general, ignition was induced about 10 seconds after spilling. The experimental results group into several areas of interest. The pressure achieved for the smallest quantity is due to low hydrogen-air concentrations

Figure 5 Portable Hydrogen Dewar with Protective Device

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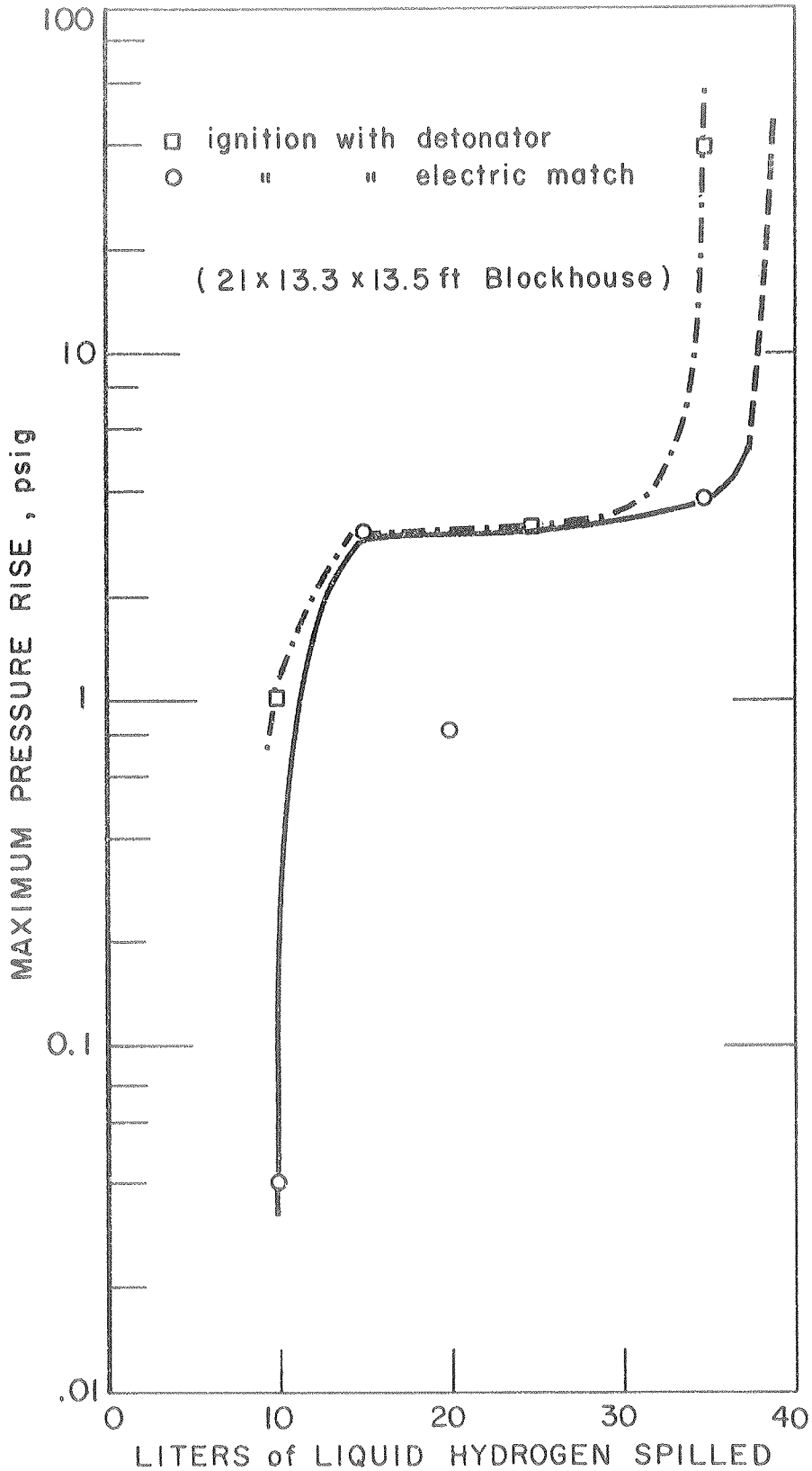

Figure 6 - Maximum Pressure Rise From the Combustion of Hydrogen Spilled in an Enclosure (Courtesy of Bureau of Mines)

existing in the enclosure. As the quantity is increased, the ratio of resulting hydrogen gas volume to enclosure volume increases to provide higher combustible concentrations. A threshold is seen to exist where transition from deflagration to detonation is possible. Extreme pressures exist beyond this threshold. The low pressure achieved with the combustion of 20 liters by an electric match may be due to early ignition, two seconds after spilling. In all cases, the flame persisted for a short period of time resulting in little fire damage.

The effect of ignition by a strong source effectively shifts the pressure curve to the left, giving higher pressures for a given liquid quantity. If appreciable ventilation rates existed in the enclosure, one would expect the curve to be shifted to the right, at least the transition from deflagration to detonation may require larger liquid quantities.

Personnel Precautions - Two personnel precautions are warranted. The first is presented by the possibility of burns by contact with cold mechanical components. Loose-fitting gloves of asbestos or leather are recommended. Danger from spilled liquid hydrogen is usually slight since every possible precaution is taken to prevent such an event in the laboratory. However, where liquid nitrogen is frequently used and small spills may be common, leather gloves are preferable for hand protection.

The low ignition energy for hydrogen-air mixtures necessitates care to prevent accumulation of static electricity on operating personnel. The type of clothing worn can be a major contributing factor. Table III gives the order of electrostatic susceptibility against synthetic rubber and indicates which fibers build the greatest electrostatic charges. On the basis of this information, cotton clothing is to be preferred. However, since it is still possible to accumulate an electrostatic charge sufficient to cause ignition, further

Table III

ELECTROSTATIC SUSCEPTIBILITY

Synthetic Rubber Against Fabric[16]

Fabric	Electrostatic Charge Volts
Cotton	50
Viscose Rayon	100
Wool	350
Acetate Rayon	550
Silk	850
Orlon	900
Dacron	1025
Nylon	1050

personnel grounding devices are often used. These devices are usually in the form of conducting-sole shoes or conducting leg-straps, and serve to maintain personnel at the same electrical potential as the conducting floor and the apparatus; several varieties are commercially available.

General - The Bureau of Mines determined that "ignition of flammable mixtures above a dewar containing liquid hydrogen produces a momentary yellow flash and then a nonluminous flame. Tests conducted in open-mouth glass dewars often ended abruptly in an orange flash following implosion of the dewar and subsequent explosive vaporization of the liquid hydrogen. Tests conducted in open-mouth stainless steel dewars resulted in failure of dewars with soft-soldered rims; as these failed, the rate of vaporization of the liquid hydrogen and consequently the flame size increased. Burning proceeded quietly above stainless steel dewars with welded rims[2]".

Glass apparatus, although essential to many experiments, should be avoided where possible. When used, a metal guard surrounding glass dewars or appreciable-sized gas volumes is advantageous. In the case of glass dewars, a metal reservoir located directly below will prevent spilling liquid at a low level in the event of failure.

Care must be taken in attempting to control or extinguish a fire from a liquid or gaseous hydrogen source. If the flame is extinguished and hydrogen continues to escape into the surrounding atmosphere, re-ignition may occur, resulting in a more serious explosion. When possible, stop the flow or remove the source of hydrogen. When the supply of hydrogen cannot be stopped it is often best to allow the fire to burn until the hydrogen is consumed, preventing the spread of the fire to other combustibles.

Conclusions

From the preceding discussion, general criteria for the safe handling of hydrogen may be summarized as follows:

1) Provide good ventilation to operating areas - outside when practical.
2) Eliminate confinements when large quantities are involved. For enclosed laboratories where confinement cannot be prevented, reduce the quantity of hydrogen as much as possible.
3) Make all transfers in properly prepared and closed systems. Pressure tests of equipment should be required.
4) Purge all equipment with an inert gas before and after using hydrogen.
5) Avoid contaminating gaseous or liquid hydrogen with oxygen or air. Maintain hydrogen equipment above ambient pressure whenever possible.
6) Provide sufficient vents and relief devices in piping systems.
7) Eliminate sources of ignition from both personnel and equipment.
8) Monitor working area for hydrogen.
9) Provide Safety Inspectors with technical ability to critically evaluate apparatus and procedures.
10) Make personnel aware of potential hazards. The best safety feature is the operating staff.

REFERENCES

1. Arthur D. Little, Inc., Final Report on an Investigation of Hazards Associated with the Storage and Handling of Liquid Hydrogen, Contract No. AF 18(600)-1687, March 22, 1960, C-61092, (Confidential).

2. Zabetakis, M. G., and Burgess, D. S., Research on the Hazards Associated with the Production and Handling of Liquid Hydrogen, WADC Technical Report 60-141, December 1959, also U. S. Dept. of Interior, Bureau of Mines, RI 5707 (1961).

3. Lewis, Bernard and Von Elbe, Guenther, Combustion, Flames and Explosions of Gases, Second Edition, New York, Academic Press, Inc., (1961).

4. Kogarko, S. M., Investigation of the Pressure at the End of a Tube in Connection with Rapid Nonstationary Combustion, Soviet Physics, Technical Physics, Vol. 3, No. 9, pp 1875-1879, (1958).

5. Fire-Hazard Properties of Flammable Liquids, Gases and Volatile Solids, National Fire Protection Association No. 325, May 1960.

6. Van Dolah, Robert W., Zabetakis, Michael G., Burgess, David S. and Scott, George S., Review of Fire and Explosion Hazards of Flight Vehicle Combustibles, ASD Technical Report 61-278, (April 1961).

7. Durham, T. F., et al, Cryogenic Materials Data Handbook, U. S. Dept. of Comm., Office of Tech. Services, Washington, D. C., PB 171, 809 (1961).

8. Cryogenic Safety - A Summary Report of the Cryogenic Safety Conference, Allentown, Pa., Air Products, Inc., July 1959.

9. Hernandez, H. P., Mark, J. W., and Watt, R. D., Designing for Safety in Hydrogen Bubble Chambers, RSI, Vol. 28, No. 7, July 1957.

10. ASME Boiler and Pressure Vessel Code, 1959 Edition, New York, ASME, 1959, Section VIII, Unfired Pressure Vessels.

11. Mills, R. L. and Edeskuty, F. J., Hydrogen Embrittlement of Cold-Worked Metals, Chemical Engineering Progress, Vol. 52, No. 11, pp 477-480, November 1956.

12. Bernstein, Harold and Young, George C., Sparking Characteristics and Safety Hazards of Metallic Materials, Technical Report NGF-T-1-57, NAVORD, Report 5205, April 8, 1957.

13. Arthur D. Little, Inc., Interim Report on an Investigation of Hazards Associated with Liquid Hydrogen Storage and Use, Contract No. AF 18(600)-1687 C-61092, January 15, 1959.

14. National Electrical Code, Boston, Mass., National Fire Protection Association, 1959.

15. Zabetakis, M. G., et al, Research on the Hazards Associated with the Use of Liquid Hydrogen in Bubble Chambers, U. S. Dept. of Interior, Bureau of Mines, Explosives Research Laboratory, Pittsburgh, Pa. (to be published).

16. Lehmicke, Static and Textile Processes, American Dyestuff Reporter, Vol. 38, p. 853.

17. Zabetakis, M. G., Furno, A. L., and Martindill, G. M., Explosion Hazards of Liquid Hydrogen, Advances in Cryogenic Engineering, K. D. Timmerhaus, Ed., Plenum Press, Inc., New York, Vol. 6, pp 185-194 (1961).

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