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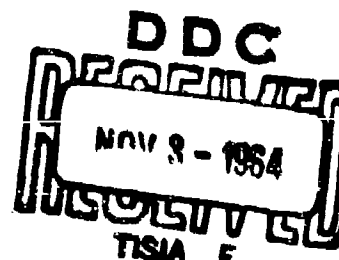
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INTRODUCTION

The need to improve propulsion systems for missiles and space vehicles has focused attention on many fuels and oxidents heretofore not considered practical for such applications. A factor in the earlier rejection of these propellants had been the extreme hazards associated with their use--at least, as revealed in laboratory programs. One of these propellants is liquid hydrogen. Although it has been a laboratory curiosity for years, there was insufficient knowledge of its characteristics to provide a sound basis for many of the design problems faced in its production and use. Its low ignition-energy requirement when mixed with air, its wide limits of flammability, and its known detonation effects under confined conditions made handling and storage hazards appear great. For these reasons, the Air Research and Development Command felt it desirable, before producing liquid hydrogen in large quantity, to initiate a research program to develop realistic safety criteria. Such criteria could bring about substantial savings in the capital equipment costs of production and storage facilities and could point out safety devices which would prevent major losses. Also a reduction in the required area for a production or storage facility might be effected thus decreasing the costs of such facilities.

POTENTIAL HAZARDS

As an initial step in devising a test program, analysis was made of the probable causes of both known accidents at liquid-hydrogen facilities and those which could conceivably occur. From this analysis a number of hazardous situations were postulated for which more information was needed. An example of these situations is a large scale spill in which failure of a storage tank releases all its contents onto the

ground with vaporization of the hydrogen and mixing with the surrounding air to form a combustible--or possibly detonable--mixture. Other such hazardous situations are a pipe-line rupture which would release a large vapor cloud or, if ignited, a large flame; solid-oxygen or air accumulation in valves, strainers, or other process equipment; and rupture of a tank with impacting fragments on other tanks.

POSSIBILITY OF DETONATION IN FREE SPACE

One of the greatest problems, at least one which could conceivably produce the most disastrous consequences, is that of the gross spillage. Such a catastrophe would release a large quantity of liquid, which would be vaporized by removing heat from the ground and the surrounding atmosphere, producing a large volume of hydrogen and air. For example, the contents of a 60,000 lb storage tank would produce 2,100,000 lb of detonable mixture if mixed with air in stoichiometric proportions. The fundamental question to be answered here therefore was--Will a hydrogen-air mixture in free space detonate when ignited?

It has been well established experimentally that a hydrogen/oxygen mixture will detonate when confined in tubes and that such detonations will occur over wide limits of mixture proportions. The addition of nitrogen inhibits detonation to some extent but does not completely suppress it. These data could not readily be extrapolated from the two-dimensional to the three-dimensional case, however, because of the differences in the method of propagation of a plane detonation wave and a spherical detonation wave. Only in recent years have various investigators (References 1-5) demonstrated the existence of stable spherical detonation waves in experiments carried out with oxygen or enriched air and with shock-wave initiators. These investigations indicated, however, the difficulty of detonating unconfined fuel-air mixtures, for limits of detonability were reduced from that in tubes and strong initiators were required.

Consequently, an experimental program was undertaken to determine under what conditions ideal, hydrogen-air mixtures in free space were capable of detonating. A number of tests were carried out in which 5-ft and 8-ft diameter latex balloons were filled with mixtures of hydrogen and air (volumes of 100 ft^3 and 400 ft^3, respectively) and initiated at the center with explosive and flame sources, hot wires, or sparks. Blast pressures were measured with ceramic gages placed at ground level 15 to 35 ft from the center of the balloon. Initial tests with near-stoichiometric mixtures containing 32% hydrogen in a 5-ft

diameter balloon established that a three-dimensional shock wave would be propagated in free space if a sufficiently strong initiating source were available. For the hydrogen-air mixtures, however, a minimum initiating source of 2 gm of pentolite was required for full explosive yield. Use of a blasting cap initiator, which is approximately 1/2 gm of explosive, reduced the yield 95%, while flame sources, sparks, and hot wires gave only combustion of the gases with no measurable pressures.

Since the 2-gm charge supplied the minimum-initiation energy for complete detonation of the near-stoichiometric hydrogen-air mixture and since this mixture is probably most easily detonated, tests with other hydrogen-air mixtures used the 2-gm charge as initiator. These results are presented in Figure 1. Evaluation of the explosive yield for the mixtures was accomplished by comparing measured overpressures to those obtained with standard C-4 charges under the same experimental conditions. The theoretical curve shown in Figure 1 was determined by assuming that hydrogen-air mixtures would have explosive yields equivalent to those of conventional explosives having the same heats of explosion (Reference 6). Maximum yields were obtained with mixtures containing 30 to 40 mol % hydrogen. The limits for at least partial detonation of the mixtures (approximately 20 to 50 mol % hydrogen) agree quite well with the 18 to 59 mol % obtained in tubes by other experimenters.

A limited number of tests were also made with stoichiometric mixtures in 8-ft diameter balloons in an effort to determine whether a greater path length would provide a transition from a deflagration to a detonation wave. As in earlier tests with the 100 ft^3 balloon, spark source initiation produced no detonation but merely a rapid combustion of the mixture with no measurable pressure. Use of a blasting cap or 2-gm pentolite initiator gave yields which were directly related to the greater mass of gas involved with no evidence of a transition to detonation occurring with the blasting cap. It was concluded, therefore, that the detonation of a hydrogen-air mixture in free space is possible only if a suitable mixture ratio is provided and a strong enough shock wave source is available. Since the probability of these idealized conditions occurring in practice is extremely remote, the chance of detonating a large mass of hydrogen gas released as a result of an accident is low.

DEFLAGRATION EFFECTS WITH LIQUID HYDROGEN

A program was also carried out to investigate deflagration effects of liquid hydrogen. A number of spills of liquid hydrogen in quantities from 1-1/4 gal to 5,000 gal were made. Ignition of the vaporized gases was by spark or flame sources. The ignition time was varied from prior to release to 8 sec after release, and depth of the pools varied from 2 - 12 in. Photographic records were taken and radiation measurements of the flame were made. Instrumentation was provided to measure overpressures in the event of a detonation.

In each case, no detonation, or tendency toward detonation resulted. In the 1.25-gal tests, partial confinement was provided by the walls of the test bay and it was observed that a stronger pressure pulse was obtained than when the liquid was spilled in the open. In fact, pressures obtained with the 1.25-gal quantities when confined were roughly equivalent to those obtained at the same distance in the 500-gal spills in the open. These results would indicate that barricading of storage vessels not only fails to provide protection, but may induce a pressure buildup which may be damaging.

The results were roughly similar in each of the tests. They were characterized by initial vaporization of a large quantity of material forming a cloud of water vapor mixed with the hydrogen and air. This cloud would remain close to the ground for some seconds and then rise slowly and drift downwind, growing in size as more liquid was evaporated. The initial tendency to remain close to the ground is not unusual when the density of hydrogen gas at the boiling temperature is considered. Upon ignition, the fireball would consume almost all of the material within the confines of the vapor cloud and the remaining material in the pool would burn in a matter of a few minutes. The results of radiation measurements taken with a thermopile are given in Figure 2. The peak source brightness of approximately 12.6 Btu/sec-ft^2 corresponds to an emissivity of about .09 based on an assumed flame temperature of 3720°F.

For comparison purposes, similar measurements made with propane are also shown in Figure 2. The emissivity at the peak of this curve is approximately that of a black body or 1. Another important point is the duration of the peak thermal flux, lasting for several minutes with propane and only a few seconds with hydrogen. Other tests with hydrocarbons demonstrated that they behave in a manner similar to propane.

A number of spill tests were also made in which the vapor clouds were initiated by means of explosive igniters such as 2-gm and 4-gm pentolite charges. In no case was there any tendency towards detonation or a significant increase in combustion pressures. Since detonation effects had been appreciable in the tests of ideal mixtures in the 5-ft balloons, it was concluded that the non-ideal mixing occurring in actual spills considerably inhibits detonation.

In other tests to assess deflagration effects, liquid hydrogen issuing from pipelines was ignited and the thermal radiation intensity and flame size measured. In these tests the average measured thermal flux level varied from 1.3 to 8.4 Btu/sec-ft^2 as compared to 12.6 Btu/sec-ft^2 for the spill tests, where contaminants were present. The wide variation in measured intensity was in part due to the lack of luminosity of the flame, making aiming of the thermopile difficult. Furthermore, as proved by infrared films developed later, the flame was quite wind-sensitive, in contrast to the spill test results when strong convection effects induced by the flame tended to overcome wind effects.

The over-all results of these deflagration tests has been to demonstrate the effects of hydrogen fires to be less than from fires with hydrocarbon fuels--both in duration and in radiation flux density. Spacing of tanks can be considerably reduced over that now required providing they are insulated to protect tanks directly in a fire. Diking is recommended to confine the fire to the area directly involved.

RADIATION EFFECTS ON PERSONNEL

In addition to the effects of liquid hydrogen flame radiation on equipment, some work has been done to establish the minimum distance at which personnel can safely approach a liquid hydrogen flame without suffering second degree burns (2+ median burns as they are referred to). AEC data provided information on thermal radiation flux density to produce such burns but these were based on short duration exposures (Reference 7). Work performed by Drs. F. C. Henriques and A. P. Moritz at the Harvard Medical School related thermal injury and skin temperature. However, these data were obtained by a number of different tests in which various heat transfer mechanisms were used (References 8 and 9). Additional work at the University of Rochester provided a simple equation relating total flux and exposure time required to cause 2+ median burns (Reference 10). This equation correlated well with the more general relationships developed by Henriques and Moritz and was used to calculate the thermal radiation effects from liquid

hydrogen/air flames. These data were combined with information on flame sizes from large spills and pipeline breaks to calculate the distance within which personnel would suffer personal injury. In order to establish recommended safe distance for unprotected personnel, it was assumed that personnel would be exposed to the flame for 30 sec. This established the recommended curve shown in Figure 3. It will be noted that for the large spill, there is little effect of the increased size and a distance of 160 ft is sufficient to prevent serious injury under all conditions. For a similar-sized fire with JP-4 fuel, the safe distance would be 675 ft, or almost four times that for the hydrogen.

CLOUD FORMATION AND GROWTH

Another important hazard which is probably peculiar to liquid-hydrogen is the possibility of ignition of the vapor cloud formed after large-scale accidental release. The spill tests carried out early in the program indicated that vapor cloud ignition produces a hot fireball which will ignite combustible material within the confines of the fireball. Two lines of investigation have been followed to determine the magnitude of this problem--one to provide data enabling the prediction of evaporation rates from the ground and the other to determine the distance downwind a hazardous condition will exist.

The following are the types of tests and their results:

1. In measurements made of the liquid-hydrogen evaporation rate, it has been determined that initially all heat supplied to the liquid comes from the ground. In later stages of evaporation (i.e., after approximately 3 min), some heat contribution is made by condensation of air into the hydrogen pool. The evaporation rate has an initial value in the order of 5-7 in/min decreasing rapidly to a steady-state value of about 1-1/2 in/min. It was also found that ignition of the vapor does not affect significantly the rate of evaporation but that use of a pebble bed of crushed rock would greatly increase the evaporation rate. It would seem desirable, therefore, to surround storage tanks with crushed rock in order to minimize the duration of the hazards of a spill.

2. In discharges of liquid hydrogen from a pipeline at rates varying from 30 to 300 gal/min, a vapor cloud is formed which persists near ground level for 500-700 ft downwind and at higher levels (but with greatly reduced density) for even further distances. Ignition of the cloud has been accomplished only within 100 ft of the vent; however, data is too preliminary to conclude that, under certain conditions, the vapor could not be ignited at greater distances. No significant concentration of hydrogen has been detected outside the limits of the visible cloud.

3. In spill tests, vapor clouds have been formed extending up to 200 ft downwind. Upon ignition at the pool the flame traveled downwind for over 100 ft.

DETONABILITY OF LIQUID HYDROGEN-SOLID AIR MIXTURES

In addition to the preceding test programs, work has been done to investigate the possibility of detonating liquid hydrogen when solid air was present. The tests were conducted by adding liquid air to a container of hydrogen and then attempting to initiate with a hot wire source. Although considerable amounts of air were added (up to 300 gm in 1.25 gal of hydrogen) explosions were obtained only when considerable oxygen-enrichment of the solid air had occurred. It was concluded, therefore, that detonation hazards were relatively slight from contamination of liquid hydrogen with solid air. Additional evidence was supplied by laboratory tests in which the detonability of liquid hydrogen-solid air mixtures were assessed by means of impact tests (Reference 11). Hydrogen-air mixtures failed to detonate even when the hammer was dropped from the full height of the impact tester. Liquid hydrogen and solid oxygen, on the other hand, evidenced an impact sensitivity comparable to RDX.

CONCLUSIONS

To sum up the results of the test work, it has been shown that liquid hydrogen is much safer to handle than many other missile propellants. When accidentally mixed with air under unconfined conditions, it does not detonate and radiation effects of any fire are less than more conventional fuels. On the other hand, its low initiation energy requirements and its wide flammability limits make ignition of any vapor cloud more likely, and for that reason, more care should be taken to remove all potential sources from an area where liquid hydrogen is stored or handled.

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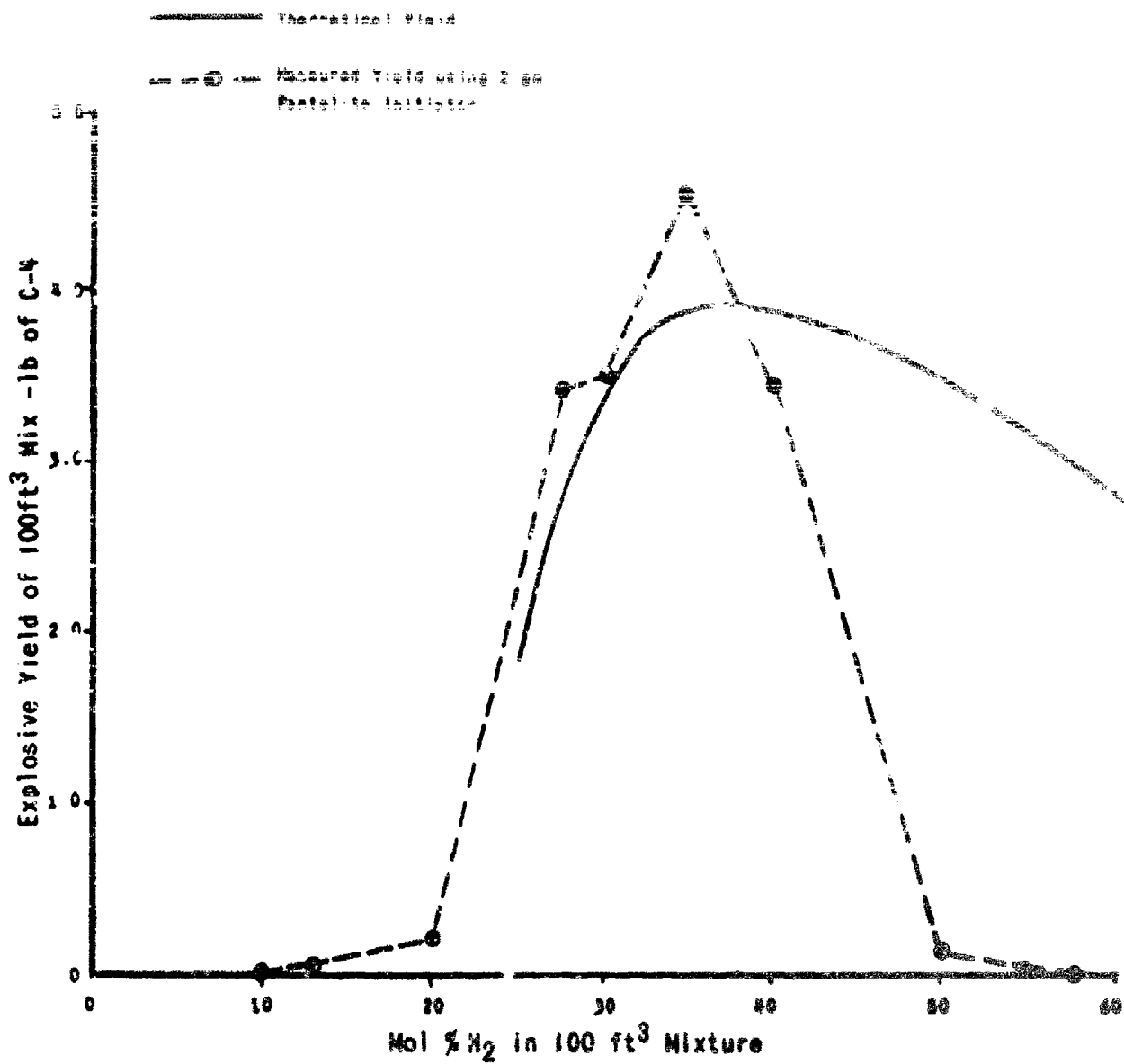
Theoretical Yield

Measured Yield using 2 gm
Pentolite Initiator

Explosive Yield of 100ft³ Mix –lb of C-4

Mol % H₂ in 100 ft³ Mixture

Fig I

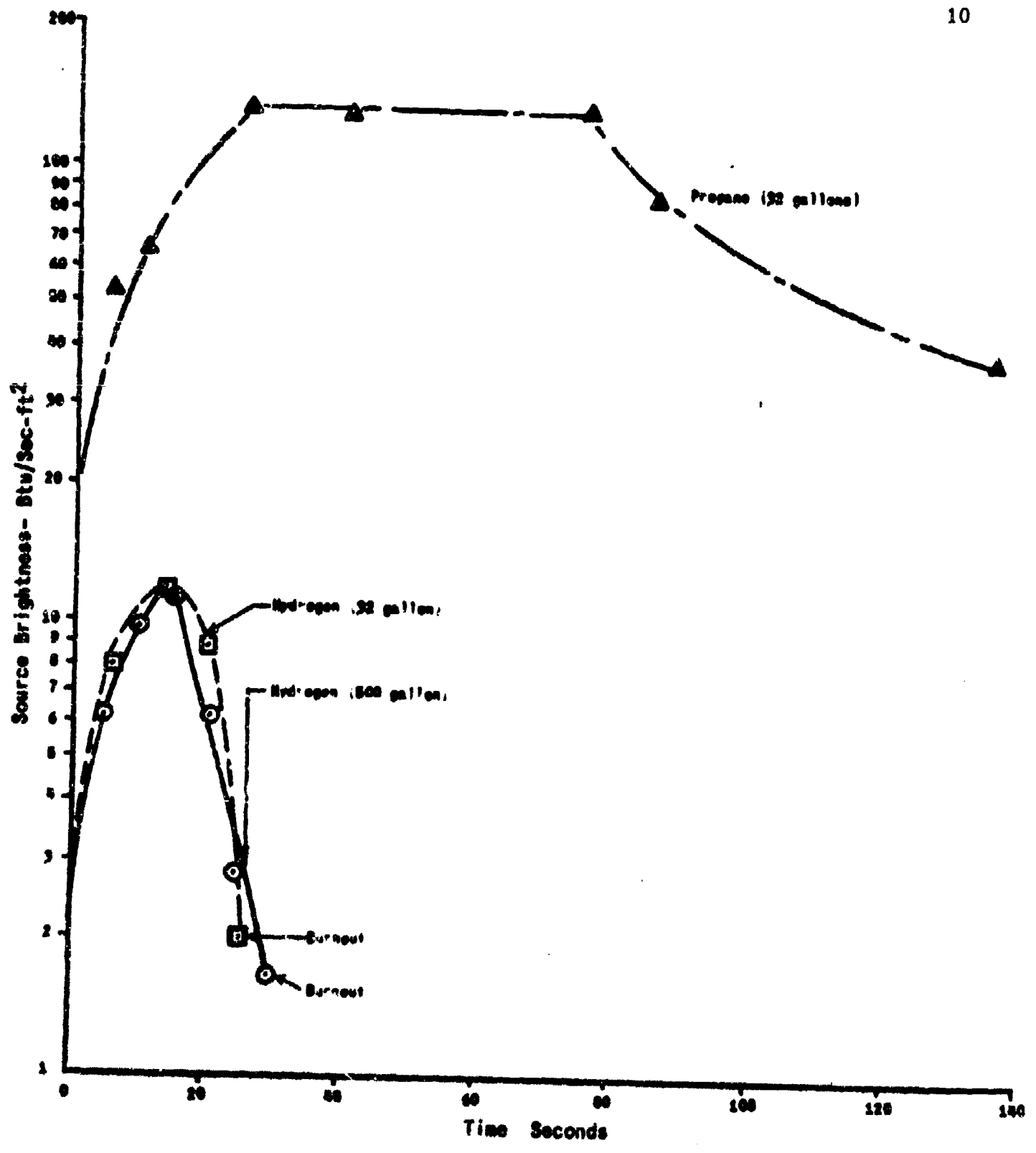EXPLOSIVE YIELD OF HYDROGEN-AIR MIXTURES IN FREE SPACE

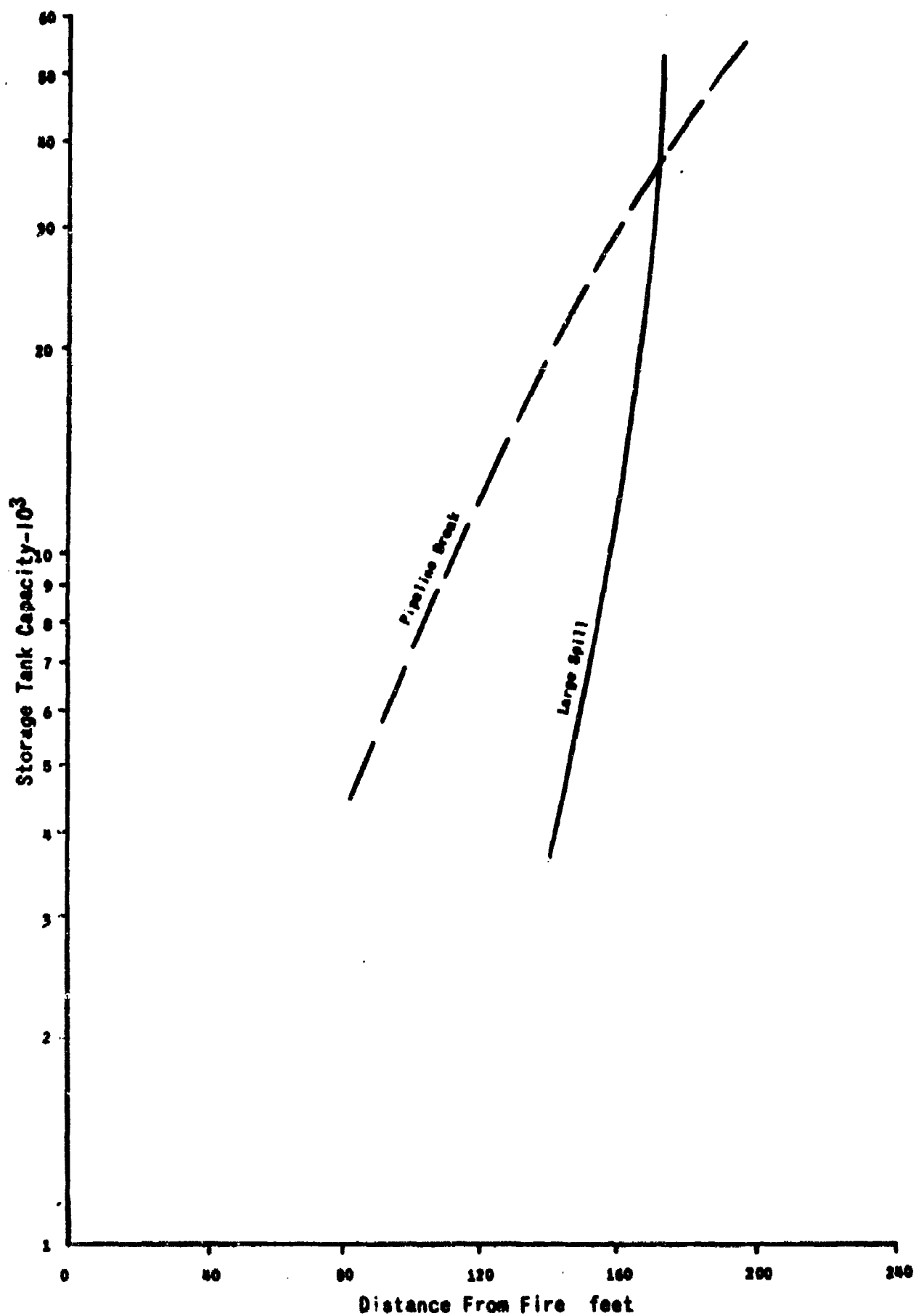Fig 2

RADIATION FROM FUEL-AIR FLAMES

Fig 3

RECOMMENDED SAFE DISTANCE FOR UNPROTECTED
PERSONNEL DURING A FIRE

Arthur D. Little, Inc.