AFAPL-TR-65-28

FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES

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Bureau of Mines
U. S. Department of the Interior

TECHNICAL REPORT AFAPL-TR-65-28

March 1965

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Air Force Aero Propulsion Laboratory
Research and Technology Division
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FOREWORD

This report was prepared by the Explosives Research Center of the U. S. Bureau of Mines, under USAF Delivery Order 33(615)64-1007, Project No. 6075, "Flight Vehicle Hazard Protection," Task No. 607504, "Fire and Explosion Hazards of Flight Vehicle Combustibles." It was administered under the direction of the Research and Technology Division, Wright-Patterson Air Force Base, with Mr. Benito Botteri as project engineer. The report covers work done during the period January 2, 1964 to January 2, 1965, and is the final report on this contract.

ABSTRACT

Severe explosion hazards could result from a massive spill of nonhypergolic fuel and oxidizer of a missile propulsion system; this problem would be especially severe with the high-energy systems where one or both of the propellant components are cryogens. The sensitivity of two such systems, liquid hydrogen + solid oxygen + diluent and liquid oxygen + solid hydrocarbon + diluent, has been investigated employing a projectile impact to determine the shock required to detonate these mixtures. With no diluent, each explosive system is initiated by a shock stimulus of 1.0 to 2.5 kbar. The explosive yields are such that 1-lb cryogenic mixture is equivalent to 0.6 to 2.0 lb TNT. Sodium chloride, nitrogen, and methyl chloride had inert desensitizing effects upon the liquid hydrogen mixtures but did not reduce the explosive yield. Sodium chloride and nitrogen desensitized the liquid oxygen system; sodium chloride or water reduced the explosive yield of this system.

Large volumes of detonable, gaseous hydrogen-oxygen mixtures would result from a massive spill of liquid hydrogen-liquid oxygen. Inhibition of detonation initiation by dry powder particle additives was investigated. The powder additives produced insignificant inhibition in comparison to that produced by gaseous diluents.

Flammability limit determinations of four additional halogenated hydrocarbons are included in a discussion of the characteristics of 10 such compounds. Most of the compounds were flammable in oxygen atmospheres at temperatures below 200° F; their combustion products included toxic halogens or halogen halides.

This report has been reviewed and is approved.

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TABLE OF CONTENTS

INTRODUCTION

Three essentially independent investigations were conducted under DO 33(615)64-1007:

Section I. Suppression of Cryogenic Propellant Explosions
Section II. Flammability Limit Determinations
Section III. A Study of Hydrogen Heat Exchangers (Security Classified)

Final reports on Sections I and II are presented here; Section III is reported elsewhere. Data are reported for the basic explosive systems: liquid hydrogen-solid oxygen and liquid oxygen-solid hydrocarbon. Ease of initiation of detonation, the effects of diluents on sensitivity, explosive yields, and the ease of spontaneous transition from deflagration to detonation are discussed. The inhibition or extinguishment of gaseous hydrogen-oxygen detonations by powder additives is discussed and compared to similar effects from gaseous additives. Limits of flammability and minimum auto-ignition temperatures in atmospheres of air, oxygen, and nitrogen tetroxide are reported for: 1,2,2-trifluoropentachloropropane; 1,1,1-trifluorobromochloroethane; 1-bromo-2-dichloro-1,1,2,3,3,4-hexafluorobutane; and trichlorotrifluoroethane. These four compounds are discussed in conjunction with six other halogenated hydrocarbons, also investigated under U. S. Air Force sponsorship.

Manuscript released by authors March 1965 for publication as an RTD Technical Report.

SECTION I

Suppression of Cryogenic Propellant Explosions. (A) Condensed Phase

by E. L. Litchfield and M. L. Weiss

INTRODUCTION

Envisaged in these studies is a massive spill of both the oxidizer and fuel components of a missile propulsion system, such as might occur from a catastrophic failure either on the launching pad or soon after launch. Several tons of condensed explosive mixture could result from mixing of the fuel and oxidizer, since both are present and since the components (liquid hydrogen-solid oxygen and liquid oxygen-solid hydrocarbon) are not hypergolic in combination. The physical location of the spill may be uncertain so that the presence of elaborate apparatus for application of extinguishing agents cannot be assumed. Dilution with exotic materials is probably not economically or physically feasible. Accordingly, this investigation has been concerned with the explosive properties of fuel and oxidizer mixtures of cryogenic propellant combinations and with inhibition and suppression by dilution with common and easily available materials. Approximately 350 tests have been conducted with the cryogenic mixtures, in addition to the necessary noncryogenic support and calibration tests.

Both the liquid hydrogen-solid oxygen system and the liquid oxygen-solid hydrocarbon system formed quite sensitive explosive systems. Tests on diluted mixtures gave results similar to those from conventional explosives with inert diluents; appreciable dilution was required before the initiating shock requirement changed by a factor of 10 or so. Transition from deflagration occurred quite readily in small explosive samples even when the samples were lightly or moderately diluted.

PROCEDURE

The mixtures were prepared in polyethylene containers insulated with foamed urethane plastic. Materials that were gaseous at ambient temperatures were mixed as gases and then introduced into the vapor space above the liquid hydrogen or liquid oxygen where they were condensed by evaporation of the cryogen. The one exception was the liquid oxygen-solid hydrocarbon mixtures with nitrogen as the diluent; they were prepared by adding liquid oxygen to liquid nitrogen and using this mixture to condense the fuel. With gases, a spray nozzle was used to obtain maximum dispersion in the vapor space. In preparing mixtures with solid diluents, a vibrator arrangement was used to dispense the particles which were then carried into the container with the gas to be condensed. The crystals resulting from condensation of the gases were quite fine (about 0.010 x 0.040 inch or smaller).

For projectile impact tests, a 1/2 x 1/2-inch right circular cylinder of free machining brass was loaded into a .50 caliber machine gun cartridge and fired from a special smooth-bore gun. The gun was mounted so that the projectiles were fired vertically downward into the open top of the test mixture container. The occurrence of detonation was judged from the blast effect determined from the bending of aluminum strip witness gages, and, in some instances, by the signals from piezoelectric pressure gages.

Because of noise problems, the size of the sample employed in the outdoor facility (Ref 1) was limited to the equivalent of approximately 1/4 pound of TNT. Investigations of spontaneous transition from deflagration to detonation were run in an enclosed bombproof.

Projectile Impact Initiation of Detonation in Liquid Hydrogen + Solid Oxygen + Diluent

The Basic Explosive System - No Diluent:

Samples prepared with 0.85 oz of crystalline oxygen and an excess of liquid hydrogen were tested as a 15-trial statistical group and required a projectile velocity of 1660 ft/sec for a 50 percent probability of initiation of detonation. The probable error in the 50-percent velocity is estimated to lie between the limits ±15 and ±75 ft/sec. In 35 trials, only once was reaction observed at velocities of less than 1600 ft/sec; two partial reactions were observed with projectile velocities of 1600 ft/sec. For velocities higher than 1660 ft/sec, two tests, at 1800 ft/sec, failed to give detonation.

The 35 trials included the 15-shot group and approximately 20 initial control tests of the effects of the quantity and dimensions of the test sample and its container. No effect of stoichiometry was observed per se. Maximum sensitivity was observed when enough liquid hydrogen (in excess of stoichiometric) was used to fill the voids and cover the pile of crystals. Liquid hydrogen in lesser amounts desensitized the mixture because of the separation of fuel and oxidizer. Because of its low density, a considerable excess of liquid hydrogen had only a small retarding effect upon the projectile at these velocities. It is possible that the size of the oxygen crystals has some effect on the detonation sensitivity of the mixture. However, except with single crystals, this effect should be small and such investigations were not included in this program.

Initiating shock strength was interpreted from the equation $P = \rho Cu$ where ρ is the density of the explosive mixture, C is the acoustic or sonic velocity in the mixture, and u is the particle velocity at the shock front (the projectile velocity). From visual observations of the crystal packing, the known specific gravities of liquid hydrogen (0.07) and solid oxygen crystals (1.426) in the α state (Refs 2 and 3), the specific gravity of the liquid-crystalline mixture was estimated at 0.2. Sonic velocity for liquid hydrogen is 3894 ft/sec at 32° R (Ref 4) and this value is assumed applicable to the explosive mixture. Literature search has not yielded a sonic velocity for the α phase of crystalline oxygen. The data of Stewart (Ref 5) give an acoustic velocity of 4600 ft/sec for the gamma phase of solid oxygen and the velocity in the alpha phase should be quite similar. Calculation from an acoustic velocity of 3900 ft/sec should thus underestimate the required shock pressure rather than overestimate it. The calculated shock pressure for initiation is then 1.25 kbar (1 kbar = 14,700 psi) if initiation is accomplished by the incident shock and 2.50 kbar if initiation is by the reflected shock.

Comparisons can be made between the 1.25 kbar for hydrogen-oxygen and initiating shock pressures for more conventional explosives as obtained by the same techniques. Initiation of cast TNT of 1.57 specific gravity requires a projectile impact shock pressure in excess of 90 kbar; initiation of pressed TNT of 1.5 specific gravity requires about 50 kbar. Tetryl of 1.5 specific gravity requires a projectile impact pressure of about 20 kbar. A 50-50 mixture of nitroglycerin and ethylene glycol dinitrate requires about 3 kbar for initiation of the low velocity detonation.

Dilution with Nitrogen, Methyl Chloride or Sodium Chloride:

Data obtained from projectile impact studies of liquid hydrogen-solid oxygen mixtures and various dilutions are summarized in Table 1. The diluents are specified as weight percent of the solid condensate. The failure velocity is the highest velocity at which failure was observed and the initiation velocity is the lowest velocity at which detonation resulted. The ratio of the velocities to the velocity for 50-percent probability of detonation is also given for each dilution. These latter values are roughly the ratio of the initiating shock pressure in the diluted system to that in the undiluted system, and thus are a measure of the desensitization produced.

In several instances the go-no-go steps in the table are rather large, but they show comparison of the several diluents. All of the additives tested have produced some desensitization. When desensitization is expressed in terms of the weight percent of diluent in the solids, nitrogen is the most effective inhibitor. When the dilution is expressed in mole percent, nitrogen and methyl chloride produce approximately equal desensitizations for 50 percent dilution or less. Assuming equivalently intimate mixtures in the two instances, both diluents behave as inerts and the presence of the halide ion is not markedly beneficial. Even when expressed as molar percent dilution, the desensitization produced by the sodium chloride crystals is inferior to the desensitization produced by the other two diluents. It is possible that this result reflects a larger crystal size and less intimate mixing, although this does not appear to be true for the liquid oxygen system. On the basis of the above data, desensitization by at least as much as the 87 percent nitrogen dilution would be desirable since stimuli as powerful as that from the fuse must be presumed to be present in the event of the massive spill.

TABLE 1. - Projectile Impact Sensitivity of $LH_2 + O_2$ + Diluent

Dilution	Initiation Velocity ft/sec	Initiation Velocity ratio	Failure Velocity ft/sec	Failure Velocity ratio
Wt % N_2 in solid				
00	1660	1.0	1660	1.0
20	2280	1.4	1950	1.2
44	3580	2.2	3250	2.0
76	max proj vel did not initiate		4880	2.9
78	--	16-48 1/	--	--
87	--	--	--	16-48 1/
Wt % CH_3Cl in solid				
00	1660	1.0	1660	1.0
34	1910	1.2	1620	1.0
61	3580	2.2	3250	2.0
67	max proj vel did not initiate		4880	2.9
Wt % NaCl 2/ in solid				
00	1660	1.0	1660	1.0
70	1970	1.2	result not obtained	
75	2290	1.4	1970	1.2

1/ Maximum equivalent velocity ratio. Initiation was accomplished with 50-grain Primacord initiating fuse. The quoted number is actually the ratio of the maximum pressure which could have been delivered by the initiating fuse relative to the calculated pressure from the projectile. The smaller number assumes that the shock is transmitted through liquid hydrogen to the explosive mixture; the larger number assumes that the shock is delivered from the initiating fuse to a medium of 0.2 specific gravity.

2/ Crystal size was that of ordinary table salt through 25 mesh onto 40 mesh.

Explosive Yield from Liquid Hydrogen + Solid Oxygen + Diluent:

Evaluation of the air blast yield from an explosive compound is usually based upon the scaling relationship $P\ (r = r_0) \alpha\ (\text{explosive weight},\ r = 0)^{0.33}$ (Ref 6) where P is the peak pressure observed at the distance r_0 from the explosive. As tables are available (Ref 6), it is convenient to express the pressure observed in terms of the weight-equivalent of TNT required to produce the same peak pressure. Charge size limitations prevented direct evaluation of explosive yield from standard tables. Rather, peak pressures were determined for equal weights of liquid hydrogen-solid oxygen and TNT using piezoelectric pressure transducers. From the scaling relationship, liquid hydrogen-solid oxygen has the explosive yield of approximately 2 lb TNT/lb $LH_2 + O_2$. From deflection of the aluminum strip witness gages, the impulse equivalence was estimated as 3-5 lb TNT/lb $LH_2 + O_2$. Piezoelectric gage data gave an impulse from condensed hydrogen-oxygen which was five times that from an equal weight of TNT. The weight equivalent determined from pressure measurements agrees well with the estimate of Cook (Ref 7). The larger equivalents determined via the impulse comparisons are believed to arise, at least in part, from reaction of the excess liquid hydrogen with the air in the bombproof chamber (afterburning) after the primary explosive reaction had been accomplished.

Spontaneous Transition from Deflagration to Detonation:

Samples containing 0.7 and 1.0 oz of oxygen and an excess of liquid hydrogen were ignited to deflagration by firing an electric match in the hydrogen-air vapor space. Transition to detonation occurred after some appreciable delay time but in the absence of any confinement beyond that supplied by the mixture container. The delay times were of the order of one minute and are believed to correspond to the times required for the fire to consume the liquid hydrogen and expose the liquid hydrogen-crystalline oxygen interface. In the absence of diluents, detonation always resulted and the blast, as indicated by strip gage deflection, was equivalent to that obtained with projectile initiation of detonation. Transition must thus have occurred before any significant consumption of the explosive mixture in deflagration.

Samples containing 0.7 oz oxygen and diluted with nitrogen or methyl chloride detonated, after initiation to deflagration, up to dilutions of 45 and 50 weight percent of total solids, respectively. At dilutions of 50 and 65 weight percent, respectively, the samples burned to completion without detonation. Failure to achieve detonation at these larger dilutions must be attributed to the existence of a subcritical sample size. Larger samples have given transition to detonation with nitrogen dilutions of 50 weight percent.

Similar samples diluted with sodium chloride crystals transited to detonation up to 75 weight percent of sodium chloride in the combined solid phase.

The results here closely parallel the shock sensitivity results. Nitrogen and methyl chloride are approximately equivalent inhibitors; thus, by implication, the inhibitory action is that of a chemically inert diluent. The sodium chloride crystals were inferior inhibitors in comparison to the other two.

Projectile Impact Initiation of Detonation in Liquid Oxygen + Solid Hydrocarbon + Diluent

The experimental techniques were essentially those described for the liquid hydrogen system. The significant physical difference between the systems is that solidified hydrocarbon fuels float on the surface of liquid oxygen whereas crystalline oxygen falls to the bottom of a container of liquid hydrogen.

The Basic Explosive System - No Diluent:

Commercial kerosine, butane, and propane were evaluated as the fuel component of the explosive system. Within the precision of the tests--perhaps 10 percent--there was no difference in the sensitivity even though certain physical differences existed between the fuels. Kerosine was dispensed from a buret as a liquid; propane and butane were admitted as gases to the cold vapor space and there condensed. Kerosine and butane gave solid condensates whereas the propane condensate was liquid.

Projectile impact on samples prepared by condensing 0.6 cu ft of butane on liquid oxygen yielded detonations when the projectile velocity was 377 ft/sec or more, and failed to initiate at projectile velocities of 354 ft/sec or less. The velocity corresponding to 50 percent probability of initiation of detonation was about 365 ft/sec. As with the liquid hydrogen system, it was not apparent that sensitivity depended upon the relative quantities of fuel and oxidizer. Whenever the thickness of the sensitive layer, containing both butane and oxygen, was reduced below about 0.2 inch, the shock pressure required to initiate detonation was increased.

Initiating shock pressures were again evaluated from the equation $P = \rho Cu$. From values of the specific gravity of butane crystals (0.79) (Ref 8) and of liquid oxygen (1.15), and from visual observations of crystal packing density, the specific gravity of the sensitive layer was estimated as 0.96. The sonic velocity in liquid oxygen at its boiling point is not more than 3100 ft/sec (Ref 9). Sonic velocity in butane crystals was not found in the literature; the velocity for liquid oxygen has been assumed for the mixture of liquid and crystals. Initiating shock pressure was 1.0 kbar for the incident shock and 2.0 kbar for the reflected shock.

Effects of Diluents:

Data showing the effects of nitrogen and NaCl on projectile impact detonation initiation sensitivity of liquid oxygen-solid butane mixtures are summarized in Table 2. Diluents are expressed as a weight percentage of the fuel. The highest velocity at which failure was observed, the lowest observed velocity for detonation, and the ratio of the velocities to the velocity for 50 percent probability of initiation of detonation are given. The ratios compare the initiating shock pressures in the diluted and undiluted systems and thus are a measure of the desensitization.

TABLE 2. - Projectile Impact Sensitivity of LO_2 + Solid Hydrocarbon + Diluent

Dilution	Initiation Velocity ft/sec	Initiation Velocity ratio	Failure Velocity ft/sec	Failure Velocity ratio
Wt % LN_2 added to LO_2				
00	365	1.0	365	1.0
33	985	2.7	655	1.8
50	2620	7.2	2300	6.3
60	max vel did not detonate		4900	13.4
Wt % NaCl in solid				
00	365	1.0	365	1.0
11[1/]	656	1.8	541	1.5
21[1/]	1312	3.6	984	2.5
22[2/]	1970	5.4	984	2.5
31[2/]	2300	6.3	1640	4.5

[1/] From saturated aqueous solution.

[2/] Crystal size: through 25 mesh onto 40 mesh.

Both nitrogen and NaCl inhibited detonation initiation in liquid oxygen-solid hydrocarbon. The inhibiting effect of NaCl was perhaps somewhat greater than that of nitrogen but the difference in desensitization is not significant. The inhibition produced in the liquid oxygen-solid hydrocarbon is somewhat greater than that produced by the same percentage dilution of liquid hydrogen-solid oxygen.

Desensitization produced by the NaCl is remarkable in that it must result from trapping NaCl crystals in the pile of butane crystals; otherwise, the sodium chloride crystals would sink to the bottom of the LO_2, whereas the butane crystals float on the surface. Inhibitory effects would be quite unlikely to occur if physical separation of butane and diluent actually existed. Inhibitory effects result from NaCl even when added as a water solution. Water (H_2O) ice was also evaluated as a desensitizing diluent. Water had no inhibitory value in this system, although the impulse from the explosion was reduced. The fact that essentially the same results were obtained with added NaCl crystals and with crystals obtained from saturated brine suggests that crystal size is not a particularly important consideration for this system.

Methyl chloride was an unsatisfactory inhibitor. Methyl chloride in LO_2 could not be detonated with the maximum projectile velocity available. However, when combined with butane in quantities such as 10 and 25 percent, the detonation was initiated at velocities of 377 ft/sec, and the methyl chloride participated quite vigorously in the chemical reaction.

Explosive Yield from Liquid Oxygen + Solid Butane + Diluent:

Piezoelectric gage data were not obtained from this system. Evaluations were based on the aluminum strip gage deflections and detonation rate determinations.

From the strip gage deflections, the impulse from the liquid oxygen system corresponds to 0.3 to 0.5 lb TNT/lb liquid oxygen-butane mixture. The explosive combustion products are uncertain; the larger number is applicable if the carbon is oxidized to CO and the smaller number if the carbon is converted to CO_2. The impulse equivalence would approach 1 lb TNT/lb LO_2-butane if it were assumed that only the oxygen in the sensitive layer entered into the reaction. This latter condition must hold in any large charge but it is problematical whether this condition held in our determinations.

A detonation rate determined in a rather thin layer of liquid oxygen-solid butane was about 11,000 ft/sec or about 75 percent of the "ideal detonation velocity" given by Aerojet (Ref 10). Eleven thousand ft/sec is approximately one-half the detonation rate of TNT, and the pressure in the cryogenic explosive should be somewhat less than 1/4 to 1/2 that in TNT. Assuming the air blast peak pressure results from the primary explosive reaction rather than from afterburning, 0.6 to 0.8 lb TNT/lb liquid oxygen-butane is the suggested equivalence. The same sort of analysis would then give 0.36-0.64-1.0 as the impulse equivalent.

From the results above, it is reasonable to presume that the TNT equivalent of the liquid oxygen-solid butane mixture is in the region 0.6 to 0.8 lb/lb liquid oxygen-butane. This result is in reasonable agreement with the discussion by Cook (Ref 7).

Water dilution reduced the impulse but not the sensitivity. Sodium chloride dilution reduced both impulse and the sensitivity. In both cases the maximum reduction in impulse corresponded to a 50 percent reduction in explosive weight. This same maximum impulse reduction resulted from dilution with brine. These were the only cases in which a significant reduction in explosive yield was observed as a consequence of dilution.

Spontaneous Transition to Detonation, Liquid Oxygen + Solid Hydrocarbon:

When liquid oxygen-butane samples, prepared with 0.6 cu ft of gaseous hydrocarbon, were ignited to deflagration, about one in three detonated. Several of these detonations were quite low yield. Undiluted mixtures prepared from 1.2 cu ft of butane had quite high yield detonations. Transition to detonation was not suppressed for additions of NaCl up to 60 weight percent of butane or of methyl chloride up to 46 weight percent.

When 1.2 cu ft of butane was condensed by a mixture of liquid oxygen and liquid nitrogen, transition to detonation occurred whenever the amount of nitrogen was less than or equal to 33 weight percent of the liquid. Transition to detonation did not occur when the nitrogen was 40 weight percent of the liquid. As in the liquid hydrogen system, transition at one sample dilution and not at another is probably an indication of desensitization of this particular sample size. This does not mean that larger, more diluted samples would not transit to detonation. That nitrogen is the most efficient inhibitor is probably a reflection of its intimate mixture with the oxygen.

Suppression of Cryogenic Propellant Explosions. (B) Gas Phase

by E. L. Litchfield and M. H. Hay

INTRODUCTION

In addition to the condensed explosive mixtures considered above, liquid hydrogen because of its low heat of vaporization can form considerable amounts of gaseous hydrogen in case of a massive spill. This gaseous hydrogen can mix with air to form extensive flammable and detonable mixtures. In a catastrophic missile spill, explosive bolts and other devices capable of initiating gaseous detonation would be present, making it desirable to inhibit the formation of detonation. The use of gases as inhibitors was investigated earlier (Ref 1). The present study evaluated the inhibitory action of dry powders of the type ordinarily used as fire extinguishing agents.

PROCEDURE AND RESULTS

The techniques used to study suppression of detonation initiation by powder additives were the same as for gaseous inhibitors (Ref 1). They are based on the method of initiation of gaseous detonations by electric discharge used in earlier Bureau studies (Ref 11). A 60-40 hydrogen-oxygen gas mixture was prepared in a 1-liter spherical vessel and diluted with the additive. The minimum stored energy for initiation to detonation was determined for the diluted mixture and compared to the corresponding energy for the undiluted mixture. The ratio of the stored energies is considered to be an index of the effect of the diluent.

Initial efforts were directed toward obtaining float dusts which would remain in suspension long enough to permit tests in quiescent gas mixtures. Small concentrations of float dust had no detectable inhibiting effect and agglomeration of the float particles was severe (Ref 12). To avoid these effects, vibrating screens were used to rain powder into the gas mixture; with this arrangement the gases were quiescent except for the falling particles. Caking effects limited the dispensed particles to a minimum size of about 37 microns (through 400 mesh) regardless of the fineness of the original preparation. The narrow fraction around 37 microns could be dispensed in some instances, the 37-74 micron fraction could be dispensed in most instances, and the 37-125 micron fraction could be dispensed in all instances. Caking effects were not eliminated either by drying, by calcium stearate, or by commercial antistatic solutions.

With the vibrating screens, powder mass densities of about 2 oz/ft^3 were obtained with 240 mesh, commercial, floated silica powder. Equivalent powder particle number densities were obtained with potassium chloride, sodium chloride, potassium bitartrate, sodium carbonate, and expanded glass microspheres. All of these powders produced detectable inhibition at this particle number density. Sodium chloride, silica, and expanded glass microspheres produced the maximum inhibition, suppressing detonation when the initiation energy was 10 percent more than that required to detonate the undiluted mixture. However, this 10 percent increase in stored energy requirements is insiginficant in comparison to the 4000 percent, or more, increase readily obtained with gaseous diluents (Ref 1).

To permit an increase in particle number density beyond that obtained in the 1-liter spherical vessel, a tube apparatus was assembled consisting of a vertical 2-inch id glass pipe, 30 inches long. At the lower end of the tube, a gas inlet port and a housing for the exploding wire initiation source were provided. At the upper end, there were gas outlet ports, a powder container, a powder dropping slide and screens to control the dispersal rate and uniformity of pattern. Hydrogen and oxygen were mixed in the gas loading line by multiple impinging jet mixers. The 60-40 hydrogen-oxygen composition was established by flow meter readings. A minimum of five volume changes of gas were passed through the tube before closing the inlet and outlet port valves and dropping the powder. An electronic timer activated by the falling powder made it possible to vary the delay between commencement of powder flow and firing of the exploding wire initiation source. At the time of firing, the upper end of the tube was open to the atmosphere and obstructed only by the screens and such powder as had not yet been dispensed.

The inhibition tests were conducted at the 10 percent increased initiation energy corresponding to the maximum inhibition observed in the 1-liter spherical vessel. Inhibition in excess of this level was not observed in any test in the tube. Only sodium chloride powders were tested in this tube. Their maximum density was about 5 oz/ft^3 which is four times the powder density previously tested in the spherical bomb.

This tube and ignition source have the property that the discharge of an energy approximately 10 percent less than required to initiate detonation will produce quite a stable deflagration wave in the 60-40 mixture. This characteristic was utilized in control tests to determine whether inhibition might be masked by increased efficiency of the initiation source in the presence of the powder particles. The control tests gave no indication that the powder particles inhibited initiation of detonation. Transition from deflagration was observed, in the presence of the powder, with transition occurring well away from the initiation source. As a further test, 1.3 oz/in^2 powder was placed on the powder slide and dropped down the tube, without dispersal screens, into an advancing deflagration wave. Transition to deflagration was observed at approximately the anticipated meeting place of the powder and the deflagration wave.

CONCLUSIONS

The dry powders tested in particle sizes of 37 microns and more were much less effective as inhibitors of detonation initiation than the gaseous diluents investigated earlier. In fact, it appears that in a tube the presence of the dry powder particles can facilitate transition from deflagration to detonation.

Bouchet (Ref 13), Laffitte (Ref 14), and Dumont (Ref 15) have reported the extinguishment of propagating detonation waves by clouds of dry particles. Their results indicate that extinguishment is due to inerting rather than to chemical action. Inert dilution, which raises the heat capacity and reduces the reactivity sufficiently to render the mixture nondetonable, must certainly have a significant effect upon the ability of a system to undergo transition to detonation. Although the powder clouds used in the present investigation were as dense as those of the French investigators, no significant inhibition was observed. We suggest that in the French experiments an inert barrier must have formed. Reflection and attenuation of the shock wave, and possibly local turbulence, would then account for both extinguishment of the propagating detonation and the transition from deflagration to detonation. The tube diameter in the Bureau apparatus was nearly five times as high as in the French apparatus; this difference should not affect the above discussion.

SECTION II

Flammability Limit Determinations

by H. E. Perlee and G. H. Martindill

INTRODUCTION

Recent interest in the halogenated hydrocarbons as fire extinguishing agents had led to a thorough investigation of the flammability characteristics of a number of these materials in various atmospheres that might occur in missile systems. This part describes results from 10 halogenated hydrocarbons in air, oxygen, and nitrogen tetroxide.

EXPERIMENTAL PROCEDURES

The first experiments were conducted to determine the ignitibility of these materials in the three different atmospheres over the temperature range of 75° to 1200°F. Autoignition temperatures (AIT's) were measured in the standard Bureau of Mines apparatus (Ref 16) (Table 3). The autoignition temperatures listed in the table indicate the maximum temperatures at which limits of flammability of the various compounds can be measured reliably in their respective atmospheres; for example, since Freon 114B2 ignites spontaneously in an oxygen atmosphere in a glass vessel at temperatures above 860°F, limits of flammability can only be determined for this fuel-oxidant combination at temperatures below 860°F.

Following autoignition of both 12B2 and 114B2 in air or oxygen, the glass test vessel was etched; mass spectrographic analysis of the product gases showed that they contained appreciable quantities of SiF_4. As this suggested that the glass vessel may have affected the AIT results, measurements were repeated in a stainless-steel vessel. Under these conditions, 114B2-air did not autoignite up to 1200°F; however, when a short length of glass rod was introduced into the stainless-steel vessel at 1200°F, ignition occurred immediately. After the glass rod was removed from the vessel, autoignition was obtained at temperatures as low as 1076°F. Apparently trace quantities of silicon compounds affect the AIT of 114B2 appreciably.

Although the various halogenated hydrocarbons did not ignite below the temperatures indicated in Table 3, there was evidence that some chemical reaction had occurred. Such a reaction could appreciably affect the results of any limit-of-flammability experiments, particularly if the half-life of the reaction was of the same order as the time required to prepare and test the gas mixture. In view of this, a preliminary kinetics experiment was conducted to measure the rate of reaction of 12B2 (one of the more stable of the halogenated hydrocarbons studied) in oxygen at atmospheric pressure, below 1200°F, in a glass vessel. The reaction rate at each temperature was evaluated by measuring the loss of 12B2 and the carbon dioxide generated during one minute. The product gases were analyzed with a gas chromatograph.

TABLE 3. - Minimum Autoignition Temperatures (°F) of Halogenated Hydrocarbons in Various Oxidant Atmospheres at Atmospheric Pressure in a 250-cc Glass Vessel

Halogenated Hydrocarbon	Oxidant		
	Air	Oxygen	Nitrogen Tetroxide
1. CF_2BrCl	>1200[1]	1098	>1200
2. CF_2Br_2	>1200[2]	∼1100[2]	>1200
3. CF_2Br	>1200	>1200	∼1090
4. $CBrF_2 \cdot CBrF_2$	1054[2]	860[2]	910
5. CH_2BrCl	842	694	630
6. $CCl_3CF_2CFCl_2$	>1200	1155	891[2]
7. $CF_3CHBrCl$	1166	1070	702
8. $CF_2BrCFClCF_2CHFCl$	986	865[2]	752[2]
9. CCl_2FCF_2Cl	>1200	>1200	1171[2]
10. Cl_2CCClH	786	745	430

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[1] This is meant to imply that if autoignition occurs, the AIT value is greater than 1200°F.

[2] Glass vessel showed pronounced etching.

Names of the above compounds:

1. Bromochlorodifluoromethane (12B1)
2. Dibromo-difluoromethane (12B2)
3. Bromotrifluoromethane (13B1)
4. 1,2-dibromotetrafluoroethane (114B2)
5. Bromochloromethane
6. 1,1,1,3,3-pentachloro-trifluoropropane
7. 1-bromo-1-chloro-2,2,2-trifluoropropane
8. 1-bromo-2,3-dichloro-1,1,2,3,3,4-hexafluorobutane
9. 1,1,2-trichlorotrifluoroethane
10. Trichloroethylene

Table 4 gives the results of these experiments. These indicate that the reaction has a half-life of one minute at some temperature between 800° and 950°F. The other halogenated hydrocarbons showed no evidence of reaction at temperatures below 500°F. Accordingly, flammability limits for all 10 halogenated hydrocarbons in the three oxidizing atmospheres were measured below 500°F.

Limits of flammability were measured in a 2-liter glass sphere and an 8.5-liter stainless steel sphere. The apparatus was maintained at a uniform temperature between ambient and 450°F in a large oven. The criterion for a flammable mixture in these experiments was the propagation of flame from the ignition source to the wall of the sphere. The results are shown in Table 5 for five of the halogenated hydrocarbons in atmospheres of air and oxygen. The temperature at which the experiments were conducted was chosen to exceed the boiling point of the particular halogenated hydrocarbon under investigation. Neither the size nor the composition of the vessel influences the results. Consequently the glass vessel was used exclusively for the remainder of the experiments. Table 6 shows the results of these experiments for the 10 halogenated hydrocarbons and the three oxidizing atmospheres. Nine halogenated hydrocarbons are nonflammable in air, seven in nitrogen tetroxide, and three in oxygen. Three were nonflammable in all three atmospheres; in order of decreasing oxidizing potential, the atmospheres are oxygen, nitrogen tetroxide and air.

The combustion pressure-time histories were observed for the halogenated hydrocarbon-oxygen mixtures shown to be flammable. The 2-foot diameter spherical test vessel shown in Appendix I is equipped with a piezoelectric pressure transducer and a central ignition source. Because of the high dielectric breakdown potential of the halogenated hydrocarbons, a 50-mg guncotton scource was used instead of the usual spark ignition. The compositions of gas mixtures prepared in the apparatus were known to within ±0.1 volume percent.

Three trials were conducted on each of the halogenated hydrocarbons. With the exception of trichloroethylene and bromochloromethane, the concentration of halogenated hydrocarbon was chosen near the middle of the flammable zone as shown in Table 5; trichloroethylene and bromochloromethane mixtures were run under saturated conditions. A typical pressure record obtained from these experiments is shown in Figure 1. Table 6 summarizes the results for each of the gas mixtures. Comparison shows that flame speeds of the halogenated hydrocarbon-oxygen mixtures are many orders of magnitude slower than corresponding flame speeds of methane-oxygen mixtures; rates of pressure rise are also much lower. In addition, the maximum explosion pressures developed for dibromodifluoromethane-oxygen mixtures were very low compared with those of stoichiometric, unhalogenated hydrocarbon-oxygen mixtures.

TABLE 4. - Yield of Carbon Dioxide in an Oxygen Atmosphere at Various Temperatures for a Reaction Period of One Minute in a Glass Vessel

Temperature °F	Concentration After One Minute, Vol %	
	12B2*	CO_2
75	17	0
500	17	0
800	10	2
950	1	9
1100	0	11

* Initial concentration = 17 volume percent

TABLE 5. - Limits of Flammability of Various Halogenated Hydrocarbons (Volume Percent) in Glass and Stainless Steel

Halogenated Hydrocarbon	Glass Container				Stainless Steel Container				Temperature, °F
	Air		Oxygen		Air		Oxygen		
	LL	UL	LL	UL	LL	UL	LL	UL	
CF_2BrCl	NF(14-61)[1/]		NF(5-78)		NF(14-78)		NF(14-78)		75
CF_3Br	NF(10-85)		NF(12-98)		NF(21-85)		NF(12-85)		75
CF_2Br_2	NF(5-68)		29	80	NF(5-68)		29	73	122
CH_2BrCl	NF(4-85)		20[2/]		NF(4-85)		10	85	212
$CBrF_2 \cdot CBrF_2$	NF(6-68)		21	--	NF(6-68)		21	53	212

1/ The quantities in parentheses indicate the fuel percentage range over which the experiments were conducted.

2/ Apparatus destroyed by explosion.

NF - Nonflammable
LL - Lower limit
UL - Upper limit

TABLE 6. - Limits of Flammability of Various Halogenated Hydrocarbons (Volume Percent) in Air, Oxygen and Nitrogen Tetroxide Atmospheres in Glass Vessels

Compound	Air LL	Air UL	Oxygen LL	Oxygen UL	Nitrogen Tetroxide LL	Nitrogen Tetroxide UL	Temperature °F
CF_2BrCl	NF(14-61)[1]		NF(14-78)		NF(6-88)		75
"	NF(14-95)		NF(14-95)				450
CF_3Br	NF(10-85)		NF(12-98)		NF(4-97)		75
"	NF(10-95)		NF(12-98)				450
CF_2Br_2					NF(4-95)		80
"	NF(5-68)		29	80			122
"	NF(5-95)		29	80			450
CH_2BrCl	NF(4-85)		10	85			212
"	NF(2-95)		13	--[2]			450
"					21		100
$CBrF_2CBrF_2$	NF(6-68)		21				212
	NF(6-95)		21	52			450
					NF(6-73)		104
$CCl_3CF_2CFCl_2$	NF(3-67)		18	52	NF(8-23)[3]		302
$CF_3CHBrCl$	NF(4-73)		21	59	NF(6-75)		212
$CF_2BrCFClCF\ CHFCl$	NF(6-58)		7.5	58	14	28	302
CCl_2FCF_2Cl	NF(5-68)		NF(14-36)		NF(5-85)		212
Cl_2CCClH	10.5	41	7.5	91	13.5	69	212

[1] The quantities in parentheses indicate the fuel percentage range over which the experiments were conducted.
[2] Decomposition excessive.
[3] Range investigated limited by vapor pressure.

NF - Nonflammable
LL - Lower limit
UL - Upper limit

The bromine concentrations found in the combustion products of some of the mixtures are listed in Table 7. Such large quantities of bromine would create toxicity problems if these halogenated hydrocarbons are used in oxygen-rich atmospheres.

TABLE 7. - Maximum Pressures, Rates of Pressure Rise and Bromine Concentrations Developed During Combustion of Five Halogenated Hydrocarbons in Oxygen and Air Atmospheres

Halogenated Hydrocarbon	Mixture Composition, vol %		P_{max}, psig	τ, sec	P_{max}/τ, psi/sec	Bromine Concentration, vol %
	Combustible*	Oxidant				
CF_2Br_2	50	Oxygen	6.1	2.3	2.6	--
	51	"	5.3	2.1	2.5	--
	50	"	3.8	1.5	2.5	--
	49	"	--	1.6	--	13
$CBrF_2 \cdot CBrF_2$	31	Oxygen	54	4	13	15
	31	"	31	5	6.2	20
	28	"	67	4	17	21
	30	"	71	3.5	20	21
CH_2BrCl	16	Oxygen	75	1	75	--
	16	"	79	1	79	--
$CF_3CHBrCl$	21	Oxygen	115	2.1	53	--
	41	"	133	1.2	110	--
	41	"	158	0.7	210	--
	40	"	146	0.7	200	--
CCl_2CHCl	13	Air	49	5.0	10	--
	14	"	50	5.2	10	--
	15	"	51	7.0	7	--
	16	Oxygen	96	0.9	10	--
	15	"	138	0.2	70	--
	15	"	129	0.3	10	--

* Halogenated hydrocarbon.

CONCLUSIONS

Of the 10 halogenated hydrocarbons studied only three were nonflammable in atmospheres of oxygen, air and nitrogen tetroxide below 200°F temperature. The seven remaining halogenated hydrocarbons were flammable in oxygen. One was flammable in air at 212°F. In each case the products of combustion were highly contaminated with toxic halogens and/or halogen halides. Consequently, the use of these seven materials as fire extinguishing agents in oxygen-enriched atmospheres would be undesirable.

CONCLUSIONS

The liquid hydrogen-solid oxygen system requires a projectile velocity of 1660 ft/sec for initiation of detonation. The incident shock pressure at this velocity is about 1.25 kbar and the explosive yield from the cryogenic mixture is such that 1 lb $LH_2 + O_2$ = 2 lb TNT. Addition of nitrogen, methyl chloride, or NaCl crystals produces desensitization, apparently due to an inert diluent effect, but the addition of 50 mole percent diluent with the oxygen only increased the shock strength needed for initiation by a factor of 2. To prevent initiation with 50-grain Primacord, 78-87 weight percent dilution of the oxygen is required. Spontaneous transition from deflagration to detonation occurs readily in the neat mixture and in mixtures containing up to 50 weight percent nitrogen in the oxygen.

The liquid oxygen-solid hydrocarbon system requires a projectile velocity of about 365 ft/sec for initiation of detonation. The incident shock pressure is about 1.0 kbar and the explosive yield from the cryogenic mixture is 1/2-1 lb TNT/lb LO_2 + hydrocarbon. Desensitization results from dilution with nitrogen or NaCl. The explosive yield is reduced as much as 50 percent by dilution with NaCl or with H_2O. Spontaneous transition from deflagration to detonation occurs readily in the neat mixture and in mixtures containing up to 33 weight percent diluent in the oxidizer.

Because of their higher specific gravity, the liquid oxygen-solid butane mixtures are more sensitive to projectile initiation than liquid hydrogen-solid oxygen mixtures. Calculated shock initiation pressures are also apparently less for the liquid oxygen-hydrocarbon mixtures. However, the lesser effect of diluents and the extreme ease of transition to detonation even with small samples of $LH_2 + O_2$ suggest that this system may be the more sensitive. The difference between the specific gravities of the two mixtures is appreciable and small inaccuracies in the test method would be sufficient to reverse the shock initiation pressures. In any case, both of these cryogenic mixtures are sensitive and energetic explosive systems.

Powders consisting of 37 microns or larger particles do not effectively inhibit initiation of gaseous detonation. The maximum inhibition observed was negligible as compared to that easily obtained with gaseous inhibitors. The powder densities needed to produce a significant effect on initiation or propagation may actually facilitate transition to detonation if the powder clouds are formed from particles as large as 37 microns.

For the 10 halogenated hydrocarbons investigated the efficiency of oxidizing atmospheres decreased in the order: oxygen, nitrogen tetroxide, and air. Only three of the halogenated hydrocarbons investigated were nonflammable in all three atmospheres below 200°F. Appreciable quantities of halogens, particularly bromine, occurred in the combustion products. This would create toxicity hazards if the compounds were used in oxygen-rich atmospheres.

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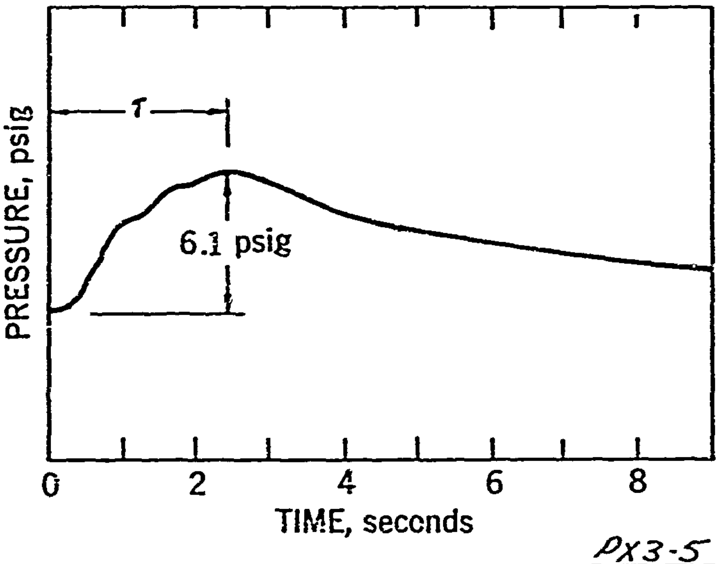
APPENDIX I

EXPERIMENTAL TECHNIQUE FOR FLAMMABILITY LIMIT DETERMINATIONS

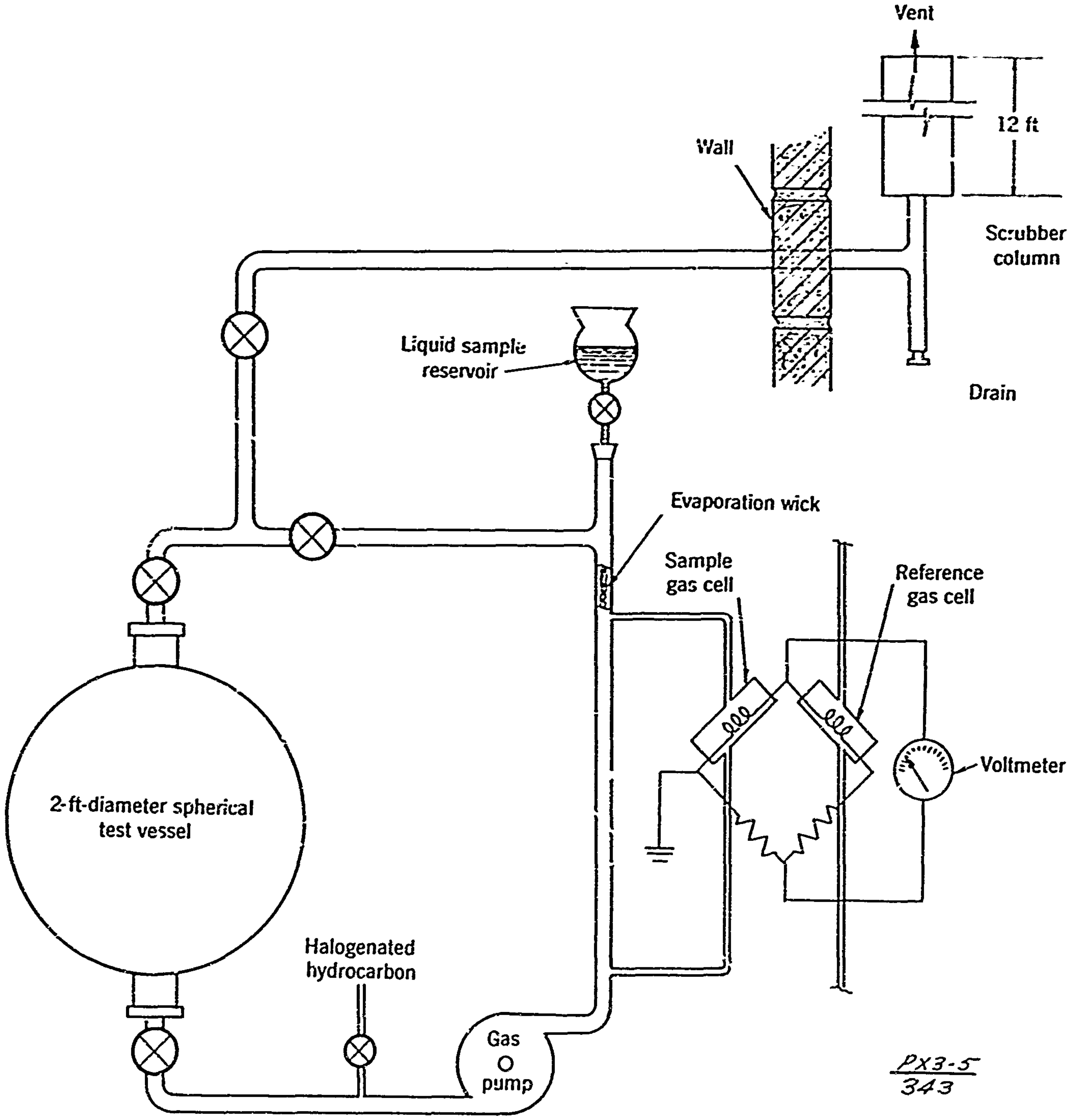
Figure 2 shows the apparatus constructed to record the combustion pressure histories for the halogenated hydrocarbon-oxygen mixtures. The 2-foot diameter spherical test vessel shown in the figure is equipped with a piezoelectric pressure transducer and a central ignition source. Specific gas mixtures can be prepared in the apparatus with the composition known to at least ±0.1 volume percent; use is made of a hot-wire gas detector bridge which works on a null balance principle. Gaseous halogenated hydrocarbons are added to the system through the piping indicated in the figure; those that are normally liquids are added as liquids and vaporized in the gas stream on a 36-inch asbestos wick. A small portion of the pumped gas is bled through the sample gas cell. Addition of halogenated hydrocarbon is continued until the bridge attains a null state against the reference gas mixture.

Since an appreciable quantity of bromine gas is generated when brominated hydrocarbons are burned, a 12-foot long, 4-inch diameter sodium thiosulfate adsorption column was incorporated into the vent system to remove the bromine and chlorine prior to dumping the products into the outside atmosphere. To conduct an experiment, the desired gas mixture is first prepared in the apparatus, then the mixture is ignited by fusion of a short length of No. 40 nickel wire wrapped with 50 mg of guncotton. The pressure history following ignition is recorded by means of a piezoelectric pressure transducer in conjunction with an electronic amplifier and an oscilloscope.



Px3-5
342

Figure 1 Typical Pressure History Record Obtained During Combustion of 50 Volume Percent CF_2Br_2 in an Oxygen Atmosphere in a 2-foot Diameter Sphere



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343

Figure 2 Apparatus Used to Measure Maximum Explosion Pressures During Combustion of Confined Gas Mixtures

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