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FIRE AND EXPLOSION HAZARDS OF FLIGHT VEHICLE COMBUSTIBLES

QUARTERLY PROGRESS REPORT NO. 2
April 1 to June 30, 1964

BUREAU OF MINES, PITTSBURGH, PA.

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Quarterly Progress Report 2

April 1 to June 30, 1964

by

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INTRODUCTION

This study is comprised of three independent portions. One is concerned with the possibility of suppression of cryogenic propellant explosions and results are presented in Part A of this report. Another investigation is the determination of flammability characteristics of selected halogenated hydrocarbons; these results are reported in Part B below. The third study is concerned with hydrogen heat exchangers and is reported separately by reason of its security classification.

The work on cryogenic propellant explosions includes determinations of detonation initiation sensitivity of: liquid hydrogen-oxygen-diluent mixtures, liquid oxygen-hydrocarbon-diluent mixtures, and gaseous hydrogen-oxygen-diluent mixtures. Exploratory investigations of the condensed-phase systems are being conducted to obtain a rapid survey of the desensitization resulting from various diluents. Desensitization of the liquid hydrogen-oxygen system results if the oxygen is in intimate mixture with either nitrogen or methyl chloride. Desensitization of the liquid oxygen-hydrocarbon system has not yet been observed in this investigation but is known to result from nitrogen dilution of the LOX.1/ The work with powder suppressants of the gas-phase detonation initiation continues to indicate that powders are inferior to gases and vapors for gas-phase inhibition.

Minimum autoignition temperatures and information on thermal stability are presented for: 1,2,2-trifluoropentachloropropane, 1,1,1-trifluorobromochloroethane, 1-bromo-2,4-dichloro-1,1,2,3,3,4-hexafluorobutane, and trichlorotrifluoroethane in atmospheres of air, oxygen, and nitrogen tetroxide. The halogenated butane has the lowest ignition temperatures in air and oxygen and nearly the lowest ignition temperature in nitrogen tetroxide.

PART A: SUPPRESSION OF CRYOGENIC PROPELLANT EXPLOSIONS

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

1-a. Shock Sensitivity of Liquid Hydrogen + Solid Oxygen + Solid Nitrogen

Oxygen and nitrogen were mixed in the gas phase and then condensed to solids by cooling with the vapors from boiling liquid hydrogen. The dilution is specified as mole percent nitrogen relative to oxygen +

1/ Private conversation with Dr. John B. Gayle, George C. Marshall Space Flight Center, Huntsville, Alabama.

nitrogen. Seven-tenths of an ounce of oxygen was used in all cases and the amount of liquid hydrogen was varied so that the condensate was covered with liquid hydrogen at the time of the projectile firing. Total hydrogen was not in stoichiometric proportions to the total oxygen; the mixture was richer than the balanced proportions, $2H_2 + O_2$, by an amount depending upon the nitrogen dilution. As discussed in the last report,[2] the varying quantity of liquid hydrogen had no significant effect upon the initiation sensitivity.

The lowest velocity observed to produce initiation, the highest velocity not producing initiation, and their ratios to the 50 percent velocity of the undiluted mixture are tabulated below for various nitrogen dilutions. The velocity of the undiluted mixture is the 1,660 ft/sec previously determined[2] to have a 50 percent probability of initiation of the undiluted liquid hydrogen-solid oxygen mixture. The velocity ratio is then the approximate ratio of the pressure produced in the quoted test and the pressure having the 50 percent probability of initiation. The 47 percent dilution of the oxygen with nitrogen doubles the shock strength required for initiation. An increase in the shock strength by at least a factor of three would be required for initiation with 78 percent nitrogen dilution of the oxygen.

	Initiation		Failure	
Percent N_2 in condensate	Velocity, ft/sec	Velocity ratio	Velocity, ft/sec	Velocity ratio
0	1,660	1.00	1,660	1.00
23	2,280	1.39	1,950	1.20
47	3,580	2.16	3,250	1.96
78	insufficient velocity available		4,880	2.94

1-b. Shock Sensitivity of Liquid Hydrogen + Solid Oxygen + Solid Methyl Chloride

The method of preparation was similar to that used for nitrogen dilution. The 25 and 50 percent dilutions with methyl chloride and nitrogen appear to produce equivalent desensitization. The possibility that nitrogen and methyl chloride are similar at 57 percent dilution will be investigated in the near future.

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[2] Fire and Explosion Hazards of Flight Vehicle Combustibles. Quarterly Progress Report No. 1, January 2 to March 31, 1964.

Percent CH_3Cl in condensate	Initiation Velocity, ft/sec	 Velocity ratio	Failure Velocity, ft/sec	 Velocity ratio
0	1,660	1.00	1,660	1.00
25	1,910	1.18	1,620	0.98
50	3,580	2.16	3,250	1.96
57	insufficient velocity available		4,880	2.94

1-c. Explosive Initiation of Liquid Hydrogen + Solid Oxygen + Solid Nitrogen

Primacord is representative of one type of initiating fuse in common use. Fifty-grain Primacord has been used to initiate liquid hydrogen + oxygen + nitrogen mixtures in which nitrogen was as much as 80 percent of the nitrogen + oxygen. The maximum nitrogen dilution permitting initiation with this Primacord has not yet been determined.

It is estimated that the pressure transmitted from the Primacord was 7-10 kbar. It is believed that modifications of the experimental arrangement will permit reduction of the transmitted pressure by a factor of three and thus permit a comparison with the projectile impact tests.

2. Shock Sensitivity of LOX + Solidified Kerosine

The shooting containers were the same as those used for the determinations with liquid hydrogen except for an asbestos paper liner in the polyethylene container. Subsequent experience has shown that LOX and the polyethylene liner do not react at the highest projectile velocities available (4,880 ft/sec).

The mixtures were prepared by slowly ejecting kerosine from a burette into the container of LOX. As an example, a mixture of approximately 30 percent kerosine by weight was prepared by placing an initial quantity of 5 oz of LOX in the container and slowly adding 1.4 oz kerosine. Allowing for evaporation by heat from the surroundings and by condensation of the kerosine, 4.7 oz of LOX should have been present at the time of the test firing. The kerosine formed a frost-like layer which floated on the LOX.

Mixtures containing 30 and 50 percent kerosine by weight were initiated with projectile velocities of 420 ft/sec[*/] and were not initiated with projectile velocities of 325 ft/sec.

Mixtures containing 10 and 75 percent kerosine by weight were not initiated with projectile velocities of 650 ft/sec but were initiated with projectile velocities of 975 ft/sec. It is not thought that the percentages of oxidizer and fuel are, per se, of any greater importance than in the liquid hydrogen system.[2/] Rather, it is believed that the thickness of the fuel or oxidizer layer and the momentum transfer mechanisms represent the differences in the two instances. Only 80 percent as much kerosine was used in the 10 percent mixture as in the 30 percent mixture; for the 75 percent kerosine mixture the LOX layer thickness at time of test was only 0.3 to 0.5 that present for the most sensitive mixtures at the time of testing. The thinnest layers were about 0.3 inch for the kerosine and about 0.2 inch thick for the LOX. This combined dimension, 0.5 inch, may then be a lower limit on the thickness required to produce the most sensitive system. Additional investigation will be required to prove or disprove this point.

At its boiling point LOX has a specific gravity of 1.15 and its sonic velocity is not more than 3,100 ft/sec.[3/] Assuming an initiating projectile velocity of 407 ft/sec and inserting these values in the equation $P = \rho Cu$, the initiating pressure is calculated to be 1.4 or 2.8 kbar (1 kbar = 14,700 psi), depending upon whether initiation results from the incident or reflected shock. The use of a specific gravity of 1.00 for the LOX-kerosine mixture gives a calculated pressure of 1.2 or 2.4 kbar. The latter numbers are essentially those previously computed for the liquid hydrogen-solid oxygen initiating shock. At the present precision of the determinations, the LOX-kerosine and liquid hydrogen-oxygen systems must be considered to have equivalent shock sensitivity.

2-a. Shock Sensitivity of LOX + Solidified Butane

These tests were conducted as controls in anticipation that the sensitivity of LOX + butane would be comparable to LOX + kerosine. Use of butane rather than kerosine would permit intimate mixtures of the fuel and normally gaseous diluents. At the present precision of the determinations, no difference in sensitivity exists between the two systems.

2 b. Shock Sensitivity of LOX + Liquefied Propane

Propane is still liquid at the boiling point of liquid oxygen so that propane was a liquid fuel layer floating on the LOX rather than a

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[*/] In the LOX-kerosine investigations, the velocities were sufficiently low that reproducibility from round to round was appreciably less than for higher velocity projectiles. Nominal velocities are presented here; future reports will give actual velocities.

[3/] American Institute of Physics Handbook, 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p. 3--72.

layer of frost crystals. We cannot yet differentiate between the sensitivities of kerosine, butane, and propane.

2-c. Shock Sensitivity of LOX + Solid Butane + Solid Methyl Chloride

Methyl chloride in LOX was not initiated at 4,880 ft/sec, the maximum projectile velocity available. However, when methyl chloride was added to butane (50-50 in the gas phase), desensitization was not observed, 420 ft/sec projectiles produced initiation. The explosive yields (from air blast measurements) from the composite mixtures showed the methyl chloride to participate quite vigorously in the reaction.

2-d. Shock Sensitivity of LOX + Solid Kerosine + Ice

Water added with the kerosine formed a sheet of ice rather than dispersed crystals. No increase was required in the velocity of the projectile to produce initiation of the syste

3. Suppression of Gas-Phase Detonation by Inert Powder Additives

As indicated in the last quarterly report,[2] attempts to prepare stable mixtures of hydrogen-oxygen-inert powder with large concentrations of float particles were unsuccessful because of coagulation. Screening experiments with several powders were conducted to assess their inhibiting value. The maximum increase in initiation energy was about 10 percent. It was necessary to simultaneously drop the powder and use a gas jet for dispersal in order to obtain even the 10 percent increase. No particle size effect was observed within the range 120-400 mesh. About 2 oz/ft^3 powder concentration required 10 percent increase in stored energy to produce detonation; by comparison, 0.2 oz/ft^3 of methane required 400 percent increase in stored energy.

Potassium chloride, sodium chloride, potassium bitartrate, sodium bicarbonate, sodium carbonate, silica sand, and expanded glass beads were investigated. The various materials all produced effectively the same maximum inhibition. These results imply that the suppression of detonation is from thermal quenching rather than the action of free radicals.

PART B: FLAMMABILITY OF HALOGENATED HYDROCARBONS AT ELEVATED TEMPERATURES

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

The minimum autoignition temperatures (MAIT) of four additional halogenated hydrocarbons were determined in air, oxygen and nitrogen tetroxide atmospheres. The procedure and the apparatus used in these experiments were the same as those reported earlier.[4] Since it was previously found

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[4] Fire and Explosion Hazards of Flight Vehicle Combustibles. Progress Report No. 13, August 1 to October 31, 1963.

that lower MAIT's were obtained in glass test vessels than were obtained in steel vessels, the experiments were conducted in 250-cc glass vessels. The results of these determinations are given in the table below.

Minimum autoignition temperatures (°F) of four halogenated hydrocarbons in various oxidant atmospheres at atmospheric pressure in a 250-cc glass vessel.

Halogenated hydrocarbon / Oxidant	1,2,2-trifluoro-pentachloro-propane $CCl_3CF_2CFCl_2$	1,1,1-trifluoro-bromochloro-ethane $CF_3CHBrCl$	1-bromo-2,4-dichloro-1,1,2,3,3,4-hexafluoro-butane $CF_2BrCFClCF_2CHFCl$	Trichloro-trifluoro-ethane CCl_2FCF_2Cl
Air	>1,200	1,170	986	>1,200
Oxygen	1,160*	1,070	865*	>1,200
Nitrogen tetroxide	891*	702	752*	1,171*

* Glass vessel showed pronounced etching.

As observed in the earlier experiments,[4/] these halogenated hydrocarbons appear to be unstable in heated atmospheres. In order to obtain meaningful results from limit-of-flammability experiments at elevated temperatures, one must be sure that the operating temperatures are low enough to avoid thermal degradation. Consequently, a series of simple kinetic experiments was conducted with these compounds to determine their stability at elevated temperatures. These experiments were conducted by determining the loss of the parent halogenated hydrocarbon as a function of time at a specified temperature in atmospheres of helium and oxygen; a gas chromatograph equipped with an 8-ft column of silicone 200 oil on a firebrick substrate was used in these studies. The results showed that the halogenated hydrocarbons tend to pyrolyze extensively in helium at temperatures above 300° C. The experiments conducted in the oxygen atmosphere showed that many of the products were the same as in helium atmospheres. As many as six products were discernible in each case; however, only with two of the halogenated hydrocarbons, $CF_3CHBrCl$ and CCl_2FCF_2Cl, was there evidence of CO_2 formation after 15 minutes of reaction; furthermore, CO_2 was found only at temperatures above 500° C. It appears from these observations that the halogenated hydrocarbons are primarily undergoing thermal decomposition rather than chemical reaction with oxygen at temperatures between 300° and 500° C. At the same time, several of the products of pyrolysis may have been oxidized since these were present in the helium atmosphere experiments but absent in the oxygen atmosphere experiments. The experiments of Park, Lamb and Lacher[5/] have demonstrated that the pertinent reactions are primarily (1) pyrolysis in which hydrogen halide is split out and olefins, acetylene, or hydrocarbons are produced, (2) rearrangements of halogen groups within the parent compound, and (3) pyrolysis in which molecular halogens are split out. The latter pyrolysis has been observed in our experiments. No attempt has been made to identify any of the remaining pyrolysis products, although it is possible that some of these would be flammable in air and the other atmospheres of interest here.

SUMMARY AND CONCLUSIONS

The initiating shock strength for cryogenic mixtures of liquid hydrogen and solid oxygen and of mixtures of liquid oxygen and hydrocarbons is 1.2 to 2.5 kbar.

Inert diluents produce desensitization of the liquid hydrogen-oxygen system. Equal molar dilution of the oxygen with either nitrogen or methyl chloride increased the initiating shock strength by about a factor of two.

Kerosine, butane, and propane all have nearly the same sensitivity when combined with LOX. Methyl chloride is a relatively insensitive individual fuel; but as an additive to a LOX-hydrocarbon mixture, it showed no desensitization effect.

Powders are much less effective detonation suppressants in the gaseous 60-40 hydrogen-oxygen system than are some of the previously tested gaseous inhibitors. The suppression effects of the powders appear to be entirely thermal in nature.

1-bromo-2,4-dichloro-1,1,2,3,3,4-hexafluorobutane has the lowest, or nearly the lowest, minimum autoignition temperatures of the four halogenated hydrocarbons tested. It would appear to be the least attractive fire extinguishment agent. Future tests will further differentiate between the other three compounds.

PLANS FOR FUTURE WORK

The desensitization resulting from nitrogen dilution of LOX and from carbon dioxide dilution of the hydrocarbon will be determined in the next quarter together with suitable statistical values for the sensitivity of the undiluted LOX-hydrocarbon system. The values of powder diluents will also be assessed for both the liquid hydrogen and LOX systems.

[5/] Private communication from R. W. Lamb, Office of Aerospace Research, U. S. Air Force Academy, Colorado, June 6, 1964.

The gas-phase suppression studies will be continued with a changed apparatus which is patterned after that used by Laffitte[6/] in his propagation studies. The new apparatus will permit both initiation and propagation studies.

Rates of pressure rise and concentration limits of flammability are yet to be determined for the four halogenated hydrocarbons.

[6/] Laffitte, P., and R. Bouchet. Suppression of Explosion Waves in Gaseous Mixtures by Means of Fine Powders. Seventh Symposium (International) on Combustion, Butterworths Scientific Publications, London, 1959, pp. 504-508.