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DISCUSSION AND EXPLANATION OF UNPLANNED IGNITION INCIDENT: IGNITION CAUSED BY RAPID PRESSURIZATION OF A PROPELLANT CONTAINING BUBBLES

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JULY 1988

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The unplanned incident is discussed from the point of view of adiabatic compression of gas bubbles in the liquid propellant. Reference is made to previous Army work in this field.

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INTRODUCTION

Propellants, even though they may have extremely safe handling characteristics in a vast majority of circumstances, still have to be utilized so that certain ranges of specific outside parameters are excluded during or prior to the intended detonation.

The understanding and prevention of such exceptions to safe predictable use is the subject of intense interest to anyone responsible for utilization and transportation of these materials. The latest unplanned incident involving LP (liquid propellant) 1846 has been the subject of a Red Team study and report which is summarized in the Appendix. Outlined in the present report are the reasons why first consideration should be given to adiabatic compression of gas bubbles as the most likely source of the unplanned ignition due to rapid pressurization. Also included is a discussion of this topic from a thermodynamic viewpoint, as an explanation of the recent unplanned incident, and some of the extensive Army literature on this topic (refs 1-3). It is hoped that this will also provide background and supplemental information to anyone interested in the Red Team report.

Reference 1 describes results obtained with LP NOS 365; Reference 2, a review, deals with apparently unpublished data on HAN (hydroxylammonium nitrate)-based LP 1845, 1846, and OTTO II, as well as NOS 365. Reference 3, an earlier experimental report, gives an extensive theoretical discussion. The experimental methods used in these reports are similar, the more recent ones representing improvements. The experiments consisted of the propellant starting in a storage chamber and then being forced into a combustion chamber by means of a piston. The liquid entered the combustion chamber via a valve. As the

References are listed at the end of this report.

propellant passed through this valve, it was injected with air bubbles of known and controlled size and total volume. The propellant-ullage (gas bubble) mixture was then in a condition described as prepressurized, the pressure being the result of the initial pressure and the poppet valve opening tension. This mixture was then subjected to an adiabatic compression of the order of 20,000 psi. The compression was caused when a charge exploded against a piston that suddenly impinged against another piston in which the propellant was contained. Two types of bubbles were introduced into this system: (1) the bubbles injected by the syringe, and (2) the bubbles caused by the cavitation. Cavitation is the name given to the process which produces bubbles in liquids when sudden holes are produced in the liquid which then are not eliminated because the vapor pressure is high enough to fill these "cavities" with the vapor of the liquid. The difference between these and other bubbles is that they can be reabsorbed more readily than foreign bubbles when the pressure or temperature is increased, thus providing lower barriers to absorption, i.e., shifting the equilibrium. For LP 1845 or 1846, the vapor in the cavitation bubbles is likely to be water which has complete solubility in the propellant (ref 4). The critical point here is that these experiments, in attempting to test for compression sensitivity of the propellants in question, largely reproduced the critical circumstances of the unplanned ignition.

Before the unplanned ignition, the vigorous movement of the propellant from behind the piston into the chamber mixed the propellant with the nitrogen gas used for the pressurization, thus providing the ullage. The vigorous motion might also have provided the cavitation bubbles. An exception to the analogy is that in the unplanned ignition, the approximately 1100 psi nitrogen pressure might also have supersaturated the propellant with nitrogen gas molecules. The

20- to 40-minute rest time may have had two effects which could have acted to cancel each other: (1) the nitrogen, which exists as a supersaturated state in the liquid, could come out of the solution in the form of bubbles, and (2) time might have also served to decrease the bubble volume or number in the liquid. Both effects become more pronounced with temperature. This test was run at a temperature below 32°F. The higher viscosity of the propellant due to the lower temperature tends to stop the bubbles from moving and leaving the propellant. In addition, the rate of nitrogen molecules coming out of solution is an activated process, which is temperature dependent. Therefore, the number of bubbles tends to remain more stable with time at lower temperatures. We now have a system consisting of liquid propellant and ullage.

MESSINA FINDINGS (refs 1,3)

1. Rapid injection can cause cavitation bubbles. These sensitize the propellant more to compression ignition. They tend to be eliminated, however, by a pressure pulse (hammer) which travels through the system, as well as prepressurization.

2. Ullage also tends to increase sensitivity to compression ignition. Total ullage volume, as well as bubble size, also play a role.

3. Prepressurization decreases the chances of compression ignition.

4. Pressurization rate seems to be important as well.

DISCUSSION

There are several considerations which can throw some light on the topic of compression ignition:

1. Ignition in a propellant or an explosive takes place by hot spot formation. Many regions in the liquid can have an increase in temperature due to

thermal events and some of them will cause an ignition. This is a statistical process with the probability of ignition increasing as the number of possible sites for hot spot formation and the temperature increase. Here we think of the bubbles caused by the ullage or cavitation as the sites of hot spot formation.

2. Cavitation bubbles in a liquid are filled with the vapor of the liquid which forms when a cavity is filled with the vapor of the liquid due to its own vapor pressure. The cavitation bubbles are more easily reabsorbed into 1845 than nitrogen gas since water has an unlimited solubility in the LP.

3. When matter is rapidly compressed, it tends to increase in temperature due to free energy considerations. The increase in temperature can be calculated if the pressure increase is quasistatic and adiabatic, and the equation of state of the material is known, and better yet, if it is completely described thermodynamically. Quasistatic, in effect, means that the entire system can be described by known state variables: pressure, temperature, volume. The higher the compressibility of a material, the greater the increase in temperature. This means that when a mixture of liquid and vapor (ullage and cavitation bubbles) is subjected to a rapid increase in pressure, the vapor will probably wind up at a much higher temperature than the liquid.

When Messina et al. (refs 1,3) pressurized and repressurized, they got explosions only when they had ullage. They also advocated avoidance of sharp entry points for the fluid and prepressurizing the LP before the rapid pressure rise required for start-up.

The above results by Messina et al. can be conveniently explained in terms of adiabatic compression of the gas bubbles. We also note in Messina's results that the lower the pressure of pressurization, the higher the chance that the sudden introduction of a certain pressure (20,000 psi in Messina's experiment) would induce an explosion (see Eq. (1)). This makes us think that there was a pressure leak from the combustion chamber during the 20- to 40-minute wait before the reapplication of pressure just before the unplanned incident.

We have noted that a major factor in the detonation of explosives is thought to be hot spots. Although the gas bubbles do not constitute an ideal gas, we will use the results of the ideal gas equations for qualitative illustrative purposes. For an ideal gas undergoing adiabatic compression, the initial and final temperatures before and after the compression are given in terms of the corresponding pressures as

$$T_{final}/T_{init} = (P_{final}/P_{init})^{(g-1)/g} \qquad (1)$$

where g is the ratio of the heat capacity of the gas at constant pressure to the heat capacity at constant volume. For an ideal gas, $g = 1.4$. If one assumes that the initial pressure were atmospheric, the final would be 1250 psi, and if the initial temperature were 300°K, then the final temperature would be 1161°K. That is more than sufficient for ignition. Here we note that pressure ratios are important, so it is possible that pressure leaked off during the waiting time.

From Reference 1, which deals with NOS 365, and Reference 2, which includes data for 1845 and 1846, it seems that 1845 and 1846 are just as sensitive to adiabatic compression as NOS 365. In both reports the critically necessary factors for detonation were the ullage, the repressurization, and in our opinion, the pressure ratio. These factors were present in the unplanned ignition. If we can postulate a leak during the 20- to 40-minute interval before repressurization (this should be easy to check), then the pressure difference would naturally be greater and the hot spot temperature, T_{final}, would also be higher, with a resulting higher probability for ignition.

CONCLUSION

The case for adiabatic compression of the ullage as the cause of the unplanned incident was presented. It was based on the conclusions from the work of Messina and qualitative arguments obtained from the adiabatic compression of an ideal gas. The conclusions for safe operation from Messina's work would also apply here: (1) avoid ullage, (2) decrease rate of pressurization, (3) avoid sharp entry points, and (4) prepressurize the LP before application of rapid pressure rises.

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2. John D. Knapton and Eberhard Schmolinski, "Review on Compression Ignition Sensitivity Studies of Liquid Gun Propellant," Memorandum Report BRL-MR-3497, Ballistic Research Laboratory, Aberdeen Proving Ground, MD, March 1986.
3. Neale Messina, Larry S. Ingram, Preston E. Camp, Moshe BenReuven, and Martin Summerfield, "Compression-Ignition Studies of Liquid Propellants for Guns," PCRL-FR-79-004, Princeton Combustion Research Laboratories, Princeton, NJ, July 1979.
4. Dr. N. Klein, Ballistic Research Laboratory, Aberdeen Proving Ground, MD, Private communication, May 1988.

APPENDIX

The unplanned ignition occurred during the preparation for firing of a 105-mm fixture. The following sequence of events can be surmised from Red Team Report #1, a preliminary, internal report, dated 4 May 1987:

1. PROPELLANT LOADED INTO 105-MM FIXTURE. (Please note the schematic of the download system obtained from the Red Team report (Figure A-1).) The transducer block LVDT (linear variable differential transformer) did not register properly. The decision to download was therefore reached. Normally the safety-dictated procedure would have been to inject water into the system to dilute the propellant 1846, one of whose constituents is water, and thus render it harmless. This time THE WATER INJECTION SYSTEM FAILED TO OPERATE. The temperature was below freezing and the lines were probably frozen.

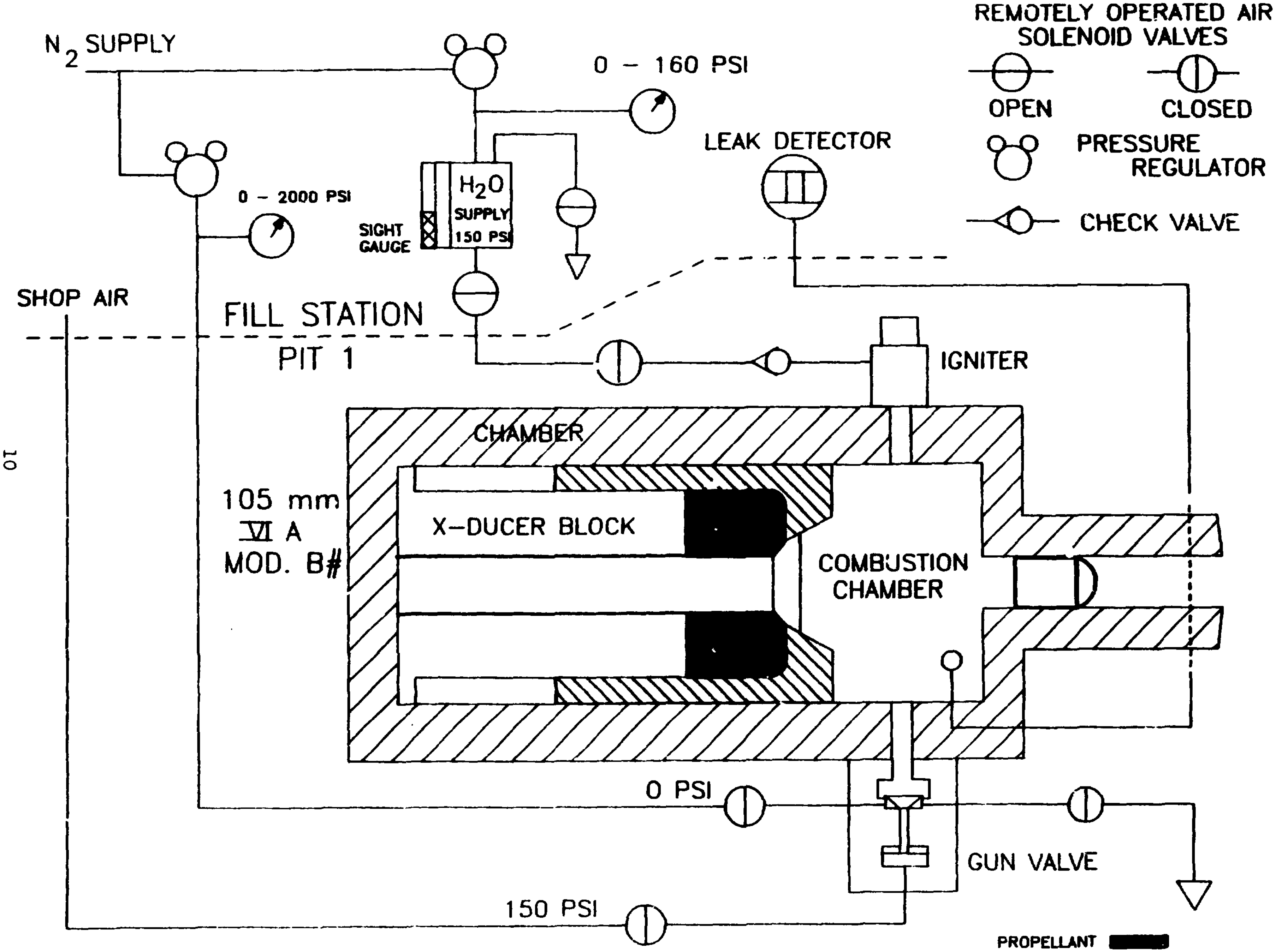
2. HIGH PRESSURE NITROGEN WAS INTRODUCED INTO THE COMBUSTION CHAMBER TO EXPEL THE PROPELLANT FROM BEHIND THE PISTON. Here the pressure on the piston from the combustion chamber side should propel the piston into the propellant region which is full, and then squirt the propellant from behind the piston to the chamber where it could either be ignited or removed through a drain. The leak detector indicated that the propellant was indeed in the chamber. The shorting clip was placed across the igniter at this point. The system was left for 20 to 40 minutes.

3. HIGH PRESSURE NITROGEN WAS INTRODUCED INTO THE CHAMBER AGAIN. DURING THE BREAK IT WAS REASONED THAT THE PISTON HAD MOVED ONLY 0.008 INCH INSTEAD OF THE 5 INCHES EXPECTED. The operators probably wanted to make sure that all of the propellant was in the combustion chamber so that it could be swept out of the test fixture. A new nitrogen tank was introduced which had 1250 psi

to replace the old one at 1100 psi. The object was to move the piston. Approximately ten seconds after the valve was opened, the unplanned ignition occurred.

The final report on this subject, "Liquid Propellant Red Team Final Report," was submitted to the Director, Ballistic Research Laboratory, in April 1988 for approval.

FIGURE A-1



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