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RESEARCH AND TECHNOLOGIC WORK ON EXPLOSIVES, EXPLOSIONS, AND FLAMES: FISCAL YEAR 1968

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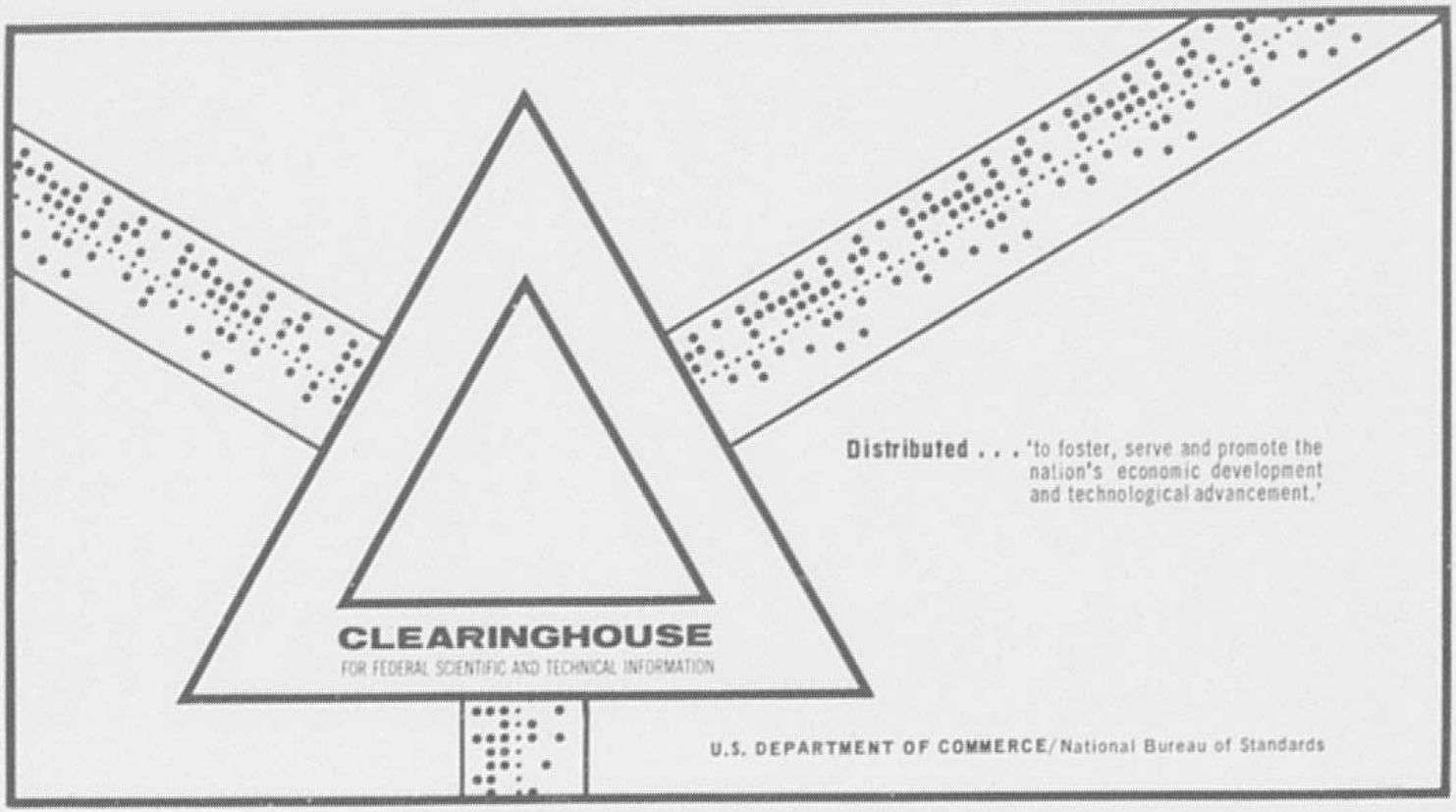

IC bureau of mines information circular 8442

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UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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RESEARCH AND TECHNOLOGIC WORK ON EXPLOSIVES, EXPLOSIONS, AND FLAMES

Fiscal Year 1968

By Staff, Safety Research Center

information circular 8442

UNITED STATES DEPARTMENT OF THE INTERIOR
Walter J. Hickel, Secretary

BUREAU OF MINES
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RESEARCH AND TECHNOLOGIC WORK ON EXPLOSIVES, EXPLOSIONS, AND FLAMES

Fiscal Year 1968

by

Staff, Safety Research Center[1]

INTRODUCTION

The principal activities of the Bureau of Mines Explosives Research Center (now Safety Research Center) during fiscal year 1968 (July 1, 1967, to June 30, 1968) are reviewed in part 1. Part 2 presents short abstracts of the publications issued during this period in the Bureau series and in other media. Part 3 describes a short study on the thermal decomposition of RDX and HMX not destined for publication elsewhere.

ACKNOWLEDGMENTS

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The Manufacturing Chemists Association.

It also acknowledges the sponsorship by the following Government agencies of research conducted during that period:

Department of the Air Force
Department of the Army
Department of Health, Education, and Welfare
Department of the Navy
Federal Aviation Administration
National Aeronautics and Space Administration
Space Nuclear Propulsion Office

PART 1.--SUMMARY OF EXPLOSIVES RESEARCH CENTER ACTIVITIES IN FISCAL YEAR 1968

The activities of the Explosives Research Center were again divided into two major programs--Explosions, Flames, and Combustion Research; and Explosives Research and Evaluation. The basic objectives remained the same: to

[1]Safety Research Center (formerly Explosives Research Center), Bureau of Mines, Pittsburgh, Pa. On July 1, 1969, the Explosives Research Center and the Health and Safety Research and Testing Center merged to form the Safety Research Center.

promote safety in the coal mining and other mineral industries through a better understanding of the fundamental mechanisms involved in combustion and detonation processes; through more extensive knowledge of the flammability and detonability of individual combustibles and explosives; and through the development of safer and more efficient procedures for utilizing fuels and explosives.

In research relating to coal mine fires and explosions, two programs continued to explore the cooperative effects of methane gas and coal dust from both the chemical and the physical standpoints. An investigation was completed on the special hazard created by accumulations of methane gas near the mine roof. A program was initiated to study the role of radiant energy in ignition and combustion processes, using laser beams to irradiate micron-size particles singly and in groups. Other ignition processes under study included the initiation of detonations in gases by exploding wires, electric sparks, and electric arcs. The role of gaseous detonations in initiating condensed-phase explosive systems was investigated further. Controlled shots with permissible explosives in atmospheres of methane and coal dust continued to provide more realistic evaluation of the safety of these formulations under actual mining conditions. The effect of added sodium nitrate on the incendivity of certain permissible explosives was evaluated. A low-strength permissible explosive was formulated suitable for replacing black powder used until recently in certain small underground coal mines. A test procedure for determining the initiating ability of nonincendive detonating cord was evaluated, and a number of commercial blasting caps were studied for incendivity in 8 percent natural gas-air mixtures using a procedure recently developed by this center.

In support of the National Manned Space Flight Program, research continued to improve operation of Apollo attitude control engines; the problem of prevention and extinguishment of fires from hypergolic fuels was the subject of an intensive investigation. A study on the safe disposal of large quantities of hydrogen was essentially completed. Additional information was obtained on the behavior of conventional explosives at the very low temperatures and pressures to be expected on the moon.

The Bureau's long-term work to improve the safety of aircraft with respect to fire hazards was extended by an experimental study of flame arrestors based on polyurethane foam and hollow polyethylene spheres. A system was developed for rating crash fire hazards of gelled aircraft fuels.

Fundamental research was continued to establish meaningful relationships between physical and chemical properties of condensed explosive systems and their performance. Experimental studies with explosive systems included target penetration by explosive jets, destruction of earthen tunnels by detonable gas mixtures, and the fracturing of rock to stimulate gas and oil flows. The problem of low-velocity detonation in liquid explosives continued to be the subject of extensive experimental and theoretical effort. Work was initiated on the use of desensitizers to improve the safety of liquid explosives without diminishing their performance significantly. Two patent disclosures were filed, one for a gelled ammonium nitrate slurry suitable for packaging in

cartridges, the other covering the stabilization of AN-FO blasting agent to permit their use in pyrite bearing ores. Detonation characteristics were evaluated for a number of explosives and potentially explosive systems including condensed-phase nitric oxide, three haloalkylamines, and mixtures of nitromethane, hydrazine, and methanol. Thermal decomposition of RDX and HMX at high temperatures was investigated. A study was completed on factors governing the emission of air pollutants by gas burners. Considerable progress was made in writing high-speed computational programs suitable for application to various combustion and detonation problems.

A new limit of flammability apparatus was completed. A pond designed for underwater research on explosives was constructed at the Bruceton, Pa., facility.

Assistance was given the city officials of Richmond, Ind., in investigating a major fire and explosion disaster. Consultative services were provided as needed to industry and other Government agencies.

A fourth course on Explosion Problems in the Chemical Industry was presented.

Thirty-six papers were published in the Bureau series and other scientific publications during fiscal year 1968. Nineteen papers were presented at meetings and conferences.

Explosion, Flame, and Combustion Research

Hybrid Mixture Studies

Earlier work on flame propagation in lower limit hybrid coal dust-methane-air mixtures (23)[2] was extended by studies in which the quenching of flames of coal dust-methane-air mixtures by other dusts was examined in a 12-foot-long duct with a 6-inch inside diameter. Lean and rich coal dust-air flames were quenched within the duct; only a near stoichiometric mixture propagated the entire duct length. The range of flammable coal dust concentrations could be extended by adding small amounts of methane (less than 5 percent). In the unheated duct, potassium bicarbonate inhibited ignition of coal dust-methane-air flames more effectively than sodium chloride or rock dust. Heating the walls to 150° to 200° C reduced wall quenching enough so that lean, stoichiometric, and rich coal dust-air mixtures propagated through the entire duct.

The radiant energy passing a slit at right angles to the path of a coal dust-air flame propagating in the 6-inch id duct was measured. Radiation was viewed by a phototube, the area under the curve of phototube voltage versus time being related to the radiation from the flame. Experiments with lean to rich flames indicate that for laboratory-scale flames of ultrafine coal dust particles (90 percent between 3 to 14 microns) afterburning beyond the primary combustion wave is a comparatively minor source of radiation.

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[2] Underlined numbers in parentheses refer to publications in part 2.

Aerodynamics of Formation of Clouds of Float Coal Dust

In experiments to study the formation of potentially explosive clouds of float coal dust, techniques simulating disturbances from weak gas explosions were used to disperse coal dust piled in ridges. It was observed that dust usually was lifted from these ridges by a combination of denudation and erosion. Frequently the ridge was fractured and clumps weighing up to 0.3 mg were lifted into the airstream where they were dispersed. The time required for complete entrainment of a 2-gram ridge varied from 100 to 300 milliseconds. Average dust concentrations in the wind tunnel, estimated from motion pictures, were about 15 mg coal per liter of air in the denudation and erosion stage, increasing to 80 mg per liter following partial fracturing of the ridge and finally to about 500 mg per liter when all the dust had been dispersed.

Radiant Ignition of Heterogeneous Systems

This is a new program to study the rate of radiant energy transport in flame propagation in heterogeneous systems. The systems investigated include both metallic and nonmetallic micron-size particles suspended in an oxidizing environment. A neodymium-doped glass laser with a maximum radiant energy output of about 30 joules was used to radiant-heat these small particles to their boiling point in fractions of a millisecond. Schlieren and streak photography were used to detect the onset of the ignition and to study the combustion reaction.

The incendivity of these radiantly heated particles to methane-air was also investigated. The radiant energy required to ignite micron-size coal in air was measured as a function of the particle diameter for diameters from 5 to about 100 microns.

Flame Propagation in Layered Gas Systems

This investigation was completed during the year. In these studies, the velocities of flames propagating along the region separating a methane layer from an air layer were measured under different conditions in and around the layers (10). Some experiments were conducted with fuel-oxygen mixtures to determine the effect of the increased flame velocity on the flame. Interferometric and particle track techniques were used to investigate the flame structure. The thickness of the flammable zone and the burning velocity of the stoichiometric mixture were found to be the most significant factors in controlling the flame speed, although the higher velocity flames formed by the fuel-oxygen systems exhibited an unexpectedly large growth rate which was attributed to forced convective mixing ahead of the flame.

Experiments in which the flames propagated through a stratified fuel-air mixture in the direction of a concentration gradient made it possible to determine the burning velocity of various fuel-air mixtures and their limits of flammability. These studies also reconfirmed earlier observations that the propagation characteristics of limit flames are determined by the convective gas motion produced at the flame front by the buoyancy of the product gases. This technique could provide a rapid and reasonably accurate method for

determining limits of flammability and burning velocities of various fuel-oxidant mixtures.

Hydrogen Safety

Several combustion characteristics of hydrogen diffusion flames were determined in the course of studies seeking to improve the safety of operations involving large quantities of hydrogen. Photographs of hydrogen diffusion flames on stacks varying in diameter from 12 to about 30 inches were used to calculate the burning rates of such flames. These range from about 0.1 to 1 ft/sec, depending on the flow rate, and can be used to predict approximate flame heights for other stacks and flows.

Flare stacks are frequently operated with hydrogen and inert gases such as nitrogen or steam. Whether or not stable diffusion flames result depends on the dilution of the hydrogen and on the flow velocity. The dilution limits at which diffusional flames of hydrogen-inert gas will no longer burn on a given flare stack were determined.[3]

Electrical Initiation of Gas Detonation

An earlier investigation of acetylene-oxygen mixtures was extended to the ethylene-oxygen system (12). In experiments using a 30-70 ethylene-oxygen mixture at 0.25-atmosphere pressure and an exploding wire ignition source, the reaction front was followed essentially to the critical size for detonation. Although the transition to detonation could not be observed directly with the technique used, the incipient detonation waves were observed to be rough and uneven, in contrast to the smooth outline characteristic of combustion waves.

Computer programs for wire heating in pulse discharge and for gas detonation, written in connection with two other investigations, will be incorporated into a program for computing the development of the gas ignition kernel.

Pulse Transformer Initiation of Deflagration

Experiments showed that under optimum conditions a pulse transformer can initiate gas mixtures with an electrical efficiency averaging about 70 percent, as compared with direct condenser discharge (13), whereas under least favorable conditions this efficiency can be less than 0.01 percent.

For energetic gas mixtures such as saturated hydrocarbons with air, pulse discharge cannot compete with direct condenser discharge as a technique for determining minimum ignition energies. It appears promising for less energetic mixtures but specific calibration of the transformer is required.

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[3]Grumer, J., A. Strasser, J. M. Singer, and P. M. Gussey. Hydrogen Flare Stack Diffusion Flames: Low Flow Instability, Burning Rates and Dilution Limits. Pres. at meeting at AIChE, Tampa, Fla., May 1968. Available from the authors as BuMines Preprint ERC No. 4030.

Ignition Temperatures Versus Induction Time With Dynamic Ignition

Metallic conductors fastened to terminal points or to other metallic conductors ordinarily introduce an electrical impedance discontinuity. Such a discontinuity also occurs at the junction of two wires of the same material but with different diameters. When a composite conductor is heated by the rapid discharge of energy stored on an electrical condenser, visible gaseous discharges frequently occur at the impedance discontinuities. These discharges are usually associated with the ejection of hot metallic particles which may produce ignition without any particular contribution from bulk heating of the metallic conductor. For pulse heated conductors, these "contact arcs" and "sparklers" are the usual ignition sources unless extreme care has been taken in preparing the electrical joint. With carefully prepared electrical joints, the electrical pulse energy can be increased by an order of magnitude, before ignition occurs due to bulk heating of the metallic conductors.

Hypergolic Ignition and Combustion

The causes of hard starts in a vacuum sometimes experienced by Apollo spacecraft attitude control engines were investigated in an earlier program (21). This investigation has been extended to determine the agent responsible for the explosive ignition of these small engines under simulated space conditions. Experiments to date have successfully established the chemical constituents of the engine residue at the time of ignition which are responsible for the explosive process (unreacted propellants, fuel nitrates, ammonium nitrate, and traces of azide), but some questions remain regarding the ignition mechanism leading to these explosions. The rates of vaporization and decomposition of the residue species were determined. The chemical kinetics of the vapor phase reaction between the fuel and oxidant that produces these explosive materials is currently being investigated.

Prevention and Extinguishment of Fires Involving Hypergolic Propellants

An intensive, short-term investigation was made of the effectiveness of bromotrifluoromethane (Halon 1301) as an inerting agent for spills of either Aerozine-50 (A-50) or nitrogen tetroxide which make up the propellant mixture used in manned spacecraft. Experiments showed that it provides some inerting in case of A-50 and could extinguish secondary fires of many flight vehicle combustibles in an N_2O_4-enriched atmosphere. However it was not effective against established A-50 fires. Toxic combustion products and considerable smoke were generated except when water was used simultaneously.[4]

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[4]Burgess, D., and others. Prevention and Extinguishment of Fires Involving Hypergolic Propellants. BuMines Explosives Research Center Final Rept. No. 4053, Oct. 31, 1968, 56 pp.

Fire and Explosion Hazards Assessment and Prevention Techniques for Aircraft

The flame quenching effectiveness of reticulated polyurethane foams was evaluated. Full-scale experiments in a 450-gallon fuel tank indicated that a 20-pore/inch foam quenches flame effectively up to pressures of at least 5 psig with a 40-percent gross void volume. A 10-pore/inch foam also evaluated at the Bureau is being used for explosion protection in the fuel tanks of military aircraft.

The flame arresting action of various configurations of perforated hollow polyethylene spheres was investigated. These materials are of interest for possible use in reducing the fuel tank explosion hazard and the external fuel tank fire hazard. Present results indicate that 1-inch-diameter spheres with 0.1 inch perforations are less effective than the 10-pore/inch polyurethane foam in suppressing explosions.

A survey was completed of the ignition and flammability characteristics of some 90 lubricants and hydraulic fluids (6).

Controlled Flammability Fuels

A number of research programs have established that addition of a gelling agent to aircraft fuels may greatly reduce fire hazards following fuel spillage. Accordingly a system was developed by the Bureau for use by the Federal Aviation Agency in rating crash fire hazards of various candidate gelled and emulsified fuels for commercial aircraft. Based on this rating scheme, the thickened fuels were found to be noticeably less flammable than the base fuels.

Flame Characteristics Causing Air Pollution

Factors that influence the emission of oxides of nitrogen, carbon monoxide, and light hydrocarbons by gas appliances such as space water heaters have been determined. This information can serve as guide in the design of these appliances.

The formation of oxides of nitrogen and the decay of carbon monoxide in the secondary combustion zones of propane-air and methane-air gas burner flames were studied as functions of temperature and the amount of secondary air entering the secondary combustion zone of the flame; the concentration of residual hydrocarbons was measured. Trends and general characteristics were the same for both propane and methane; concentrations of nitrogen oxides and carbon monoxide were a little lower in methane-air flames and hydrocarbon concentrations were a little higher. It was found that the most effective way to reduce the concentration of oxides of nitrogen was to depress peak temperatures and cool the secondary combustion zone rapidly. The carbon monoxide concentration was limited most effectively by rapid induction of secondary air. Hydrocarbon concentrations were controlled most effectively by designing for well-seated, stable flames.

Flammability Limits and Autoignition Temperatures: New Concepts and Experimental Methods

A prototype model of a new limit-of-flammability apparatus was completed. The apparatus is designed to determine flammability semiautomatically. Velocity and concentration profile data indicate that "plug" flow can be obtained with the porous plate gas-mixing piston controlled by an extendable stem.

Explosive Effects

In work to establish the destructiveness of explosions in underground tunnels, earlier experiments established that uncoupled condensed-phase explosives at very low loading densities could collapse tunnels several times as deep as those destroyed by gaseous explosive systems.[5] During the year, attention was focused on the trade off between performance and safety and between performance and cost. The performance of the candidate explosives was evaluated from the pressure-time history of the pulse transmitted by the explosive when fired under water in the new pond at Bruceton.

Explosives Research and Evaluation

Evaluation of Permissible Explosives in Predispersed Coal Dust

Eighteen permissible granular explosives were tested for incendivity to coal dust-natural gas-air mixtures using the modified test procedure developed recently (17). The charges were fired unstemmed from a cannon into 4 percent natural gas plus 0.2 ounce coal dust dispersed per cubic foot of air. The charge weights for 50 percent probability of ignition (W_{CDG}) ranged from 399 to more than 906 grams.

The effect of sodium nitrate on the incendivity of gelatinous permissible explosives was evaluated at the large explosive gallery using five gelatinous experimental explosives containing 0, 5, 10, 15, and 20 percent sodium nitrate respectively and fired under different test conditions. Under the conditions of Schedule 1-H test 7, the sodium nitrate content had little effect on the incendivity of the explosives examined. As against that, the incendivity of the explosives increased markedly with the $NaNO_3$ content when the charges were fired unstemmed from a cannon into coal dust-air (0.3 ounce dust dispersed per cubic foot air) or coal dust-natural gas-air (4 percent gas plus 0.2 ounce dust dispersed per cubic foot air).

Explosive Characteristics of Ammonium Nitrate Slurries

Development of a stable gelled slurry composition suitable for packaging in cartridges was made possible by the addition of potassium dichromate and urea to ammonium nitrate slurries. The composition gelled led to a rubbery consistency in 8 hours and remained stable and sensitive to initiation by a No. 6 electric blasting cap (EBC) for at least 60 days. It had a critical

[5]Burgess, D. S., J. N. Murphy, N. E. Hanna, and R. W. Van Dolah. Large-Scale Studies of Gas Detonations. BuMines Rept. of Inv. 7196, 1968, 53 pp. Murphy, J. N., N. E. Hanna, D. S. Burgess, and R. W. Van Dolah (20).

diameter of less than 0.5 inch and a detonation velocity of 3,450 m/sec. Its density was 1.03 g/cm^3, and the charge value for 50 percent probability of ignition (W_{50}) was 757 grams. It maintained a pH of 4.5. The energy developed by the composition was 95 percent of that generated by TNT in the ballistic mortar. A patent disclosure was filed.[6]

Experiments were conducted on the long-term effect of various additives investigated earlier.[7] Thirteen slurry formulations with 15 to 30 percent water, 3 to 10 percent sodium chloride, and 4 to 8 percent aluminum were stored for 1 year. Eleven remained cap-sensitive over that time, and exhibited no significant segregation or gassing.

The effect of density on detonation velocity was evaluated using a cross-linked gelled slurry composition sensitized with aluminum. Detonation velocities were determined by the continuous probe method.[8] The density was varied by varying the amount of air entrained in the gel from 0.96 to 1.16 g/cm^3. The corresponding detonation velocity ranged from 2,900 to 3,500 m/sec.

Keeping all other constituents in the slurry constant, the sodium chloride and water concentrations were varied independently from 0 to 50 percent and 10 to 45 percent, respectively, to determine the water and salt limits for cap sensitivity. In mixtures without salt, increasing the water content from 10 to 45 percent decreased the ballistic mortar value from 123 to 54 percent TNT equivalent. In mixtures containing salt and 10 percent water, the TNT equivalent decreased from 98 to 45 percent as the salt increased from 10 to 45 percent. With 20 percent water, increasing the salt content from 10 to 30 percent decreased the TNT equivalent from 91 to 38 percent. With higher water contents the sensitivity was too marginal to obtain reliable TNT equivalents in the ballistic mortar.

The fumes produced by aluminum-sensitized slurries were determined in the Crawshaw-Jones apparatus. Compositions with 3 and 10 percent sodium chloride, 4 and 8 percent aluminum, and oxygen balances from 0.70 to -1.95 (excluding water) were examined. Carbon monoxide ranged from 0.092 to 0.131 cu ft per lb and oxides of nitrogen ranged from 0.001 to 0.014 cu ft per lb.

Initiation of Condensed-Phase Detonation by Gas-Phase Detonations

A versatile Algol computer program for polynomial fitting of data was written and applied to the pressure-time relation in the condensed explosive following the impact of the gas detonation. Calculations, supported by experimental pressure transducer records, indicate that the reaction in the

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[6]Forshey, D. R., and E. C. Lisotto. Nonincendive Rigid Cap Sensitive Slurry Explosive. Report of invention MIN-1410.

[7]Van Dolah, R. W., C. M. Mason, and D. R. Forshey. Development of Slurry Explosives for Use in Potentially Flammable Gas Atmospheres. BuMines Rept. of Inv. 7195, 1968, 9 pp.

[8]Ribovich, J., R. W. Watson, and F. C. Gibson. Instrumented Card-Cap Test. AIAA J., v. 6, No. 7, July 1968, pp. 1260-1263.

condensed sample attains a virtually constant propagation velocity soon after the arrival of the gas detonation wave. This constant velocity persists until some disturbance causes transition to detonation. Preliminary experiments indicate that the propagation velocity is higher for oxygen-rich gas mixtures.

Static calibration of expendable resistive pressure transducers greatly increased the confidence in these devices. Justification was also obtained for their use at long detonation induction times (100 μsec or more).[9]

Computer Studies of the Growth of Explosion in Condensed-Phase Explosives

Investigation of mathematical techniques for solving simultaneous partial differential equations encountered in the formulation of quantitative models of explosions was continued. The objective is to develop a suitable procedure that is not as costly in terms of computer time as the particle-in-cell codes.

Energy Transfer Studies

Methods are being sought to utilize more efficiently the energy developed by explosives. Energetics of a number of permissible explosives were measured from the radial expansion of an expanding metal cylinder, as observed with a high-speed smear camera. Corresponding detonation pressures were measured by the Bureau's expendable pressure transducer (27). The results were compared with the incendivity, air-gap sensitivity and ballistic mortar value of the explosives. Best correlation was found between the energy released by the explosive and its incendivity to coal dust-air-methane atmospheres.

An attempt was made to relate the composition of commercial explosives to the energy and pressure which they generate. A linear relation was established between the pressure and the explosive oil content; no significant relation was found for the ammonium nitrate content or the oxygen balance. Use of the experimental results in a computer program to predict explosive performance in function of composition gave an orderly ranking of energies.

Multidisciplinary Research Leading to Utilization of Extraterrestrial Resources

The effect of temperature on the sensitivity to shock initiation of loose and pressed charges of granular RDX was examined. The ease of initiation to detonation was virtually temperature-independent between 25° and 115° C; it decreased only slightly down to -195° C.

Experiments were started to develop a scaling law to predict the probability of explosive charges being initiated by micrometeors that may be encountered on the moon.

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[9]Durpee, R. L., and A. Maček. Generation and Measurement of High Amplitude Square Shocks in Solids. AIAA J., v. 6, No. 5, May 1968, pp. 977-978.

Propellant Ingredient Safety

Means are being sought to desensitize liquid explosives and propellant ingredients sufficiently to make their manufacture, handling, and usage less hazardous without affecting their energy content significantly. The instrumented card-gap and its wedge experiment analog are used in these studies.

Shock sensitivities of neat nitroglycerin and nitroglycerin-ethylene glycol dinitrate (50-50 by weight) were determined at temperatures ranging from ambient down to -75° C. For the mixture, no low-velocity detonations were observed below -65° C, whereas for neat nitroglycerin they were observed down to -75° C. Increasing the viscosity of ethylene glycol dinitrate from 6 to 15,000 centipoises by addition of nitrocellulose reduced the detonation velocity only slightly but decreased the peak pressure by about one-third.

Studies on the initiation and propagation of low-velocity detonations were continued. Attempts were made to observe the growth of initiation in a single cavity created by spark discharge across needle gaps and by hot-wire techniques. The precavitation technique was extended to less sensitive materials by increasing the scale of the explosive donor to provide the photographic quality necessary for detailed analysis. Flash radiographic techniques were applied to a number of explosives systems known to undergo low-velocity detonation. Comparison of the radiographs with high-speed conventional framing camera records provided support for a low-velocity detonation model proposed earlier.

Detonation Zone Structure and Reaction Kinetics

Research conducted on the electrical conductivity of the detonation products of a number of condensed-phase secondary explosives, showed that this conductivity depends more on the conditions of the experiment than on the explosive used.

A study was begun of the time-space relation in liquid explosives between the shock front and the leading edge of the reaction zone, as indicated by the onset of electrical conduction. A shock-wave detector with a resolution of the order of 1 nanosecond was developed for use in this work.

State-of-the-Art Survey on Fragment Impact

A literacure review was completed on the initiation of detonation of explosives and ordnance devices by the impact of fragments.

Oil and Gas Well Stimulation by Explosives

Assistance was given to the Bureau's Bartlesville (Okla.) Petroleum Research Center in evaluating candidate explosives for fracturing underground oil- and gas-bearing formations. These included ammonium nitrate-water slurries and nitromethane sensitized with amines. Excessive solubility in water resulted in desensitization of the explosives. To improve water compatibility,

a procedure was developed for sensitizing nitromethane with water-resistant nitrate esters.[10]

Detonation Characteristics of Condensed-Phase Nitric Oxide

An investigation into the detonability of condensed-phase nitric oxide showed it to be very sensitive to shock in the liquid phase but somewhat less sensitive in the solid phase. In the liquid phase it was initiated to high-velocity detonation across a 10-inch card-gap, whereas in the solid phase initiation of high-velocity detonation ceased with a gap of between 3 and 5 inches.

New Methods of Hazard Evaluation

The reactivity of AN-FO with pyrite-bearing ores was investigated, using ore samples from five different mining regions.[11] Reaction was observed as low as 150° F in AN-FO pyrite mixtures containing 5 percent sulfuric acid. Addition of 0.5 to 1 percent of MgO, ZnO, urea, or $CaCO_3$ stabilized the AN-FO-pyrite ore mixtures, delaying reaction up to temperatures around the melting point of AN. A patent disclosure was filed covering the addition of stabilizers to AN-FO destined for use in pyrite-bearing ores.[12] In a corollary study, the cook-off temperatures were determined for a series of U.S. detonators.

The sensitivity to impact and detonation shock of three haloalkylamines was evaluated. Neat N,N-dichloromethylamine and N,N-dibromomethylamine were easily initiated by mechanical impact in the drop-weight test. They were also initiated to detonation in small diameters at ordinary temperatures.

A study of binary and ternary systems of nitromethane, hydrazine, and methanol showed that addition of hydrazine strongly sensitizes nitromethane and nitromethane-methanol mixtures to detonation shock, but does not sensitize them to mechanical impact (drop-weight test). Hydrazine increased the tautomeric aci form of nitromethane relative to the nitro form; this shift in equilibrium may be related to the sensitization of nitromethane by hydrazine. Theoretical calculations agreed with the experimental detonation velocity data and yielded reasonable estimates of the energy content of the mixtures.

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[10] Ribovich, J., J. E. Hay, and J. N. Murphy. Water-Compatible Liquid Explosive Detonable in Thin Layers. Report of invention MIN-1363.

[11] Forshey, D. R., T. C. Ruhe, and C. M. Mason. Reactivity of Ammonium Nitrate-Fuel Oil Mixtures With Pyrite-Bearing Ores. BuMines Rept. of Inv. 7187, 1968, 10 pp.

Forshey, D. R., T. C. Ruhe, and C. M. Mason. Reactivity of AN-FO Mixtures With Pyrite-Bearing Ores. Min. Cong. J., v. 55, No. 1, January 1969, pp. 34-35.

[12] Mason, C. M., and D. R. Forshey. The Use of Urea, $CaCO_3$, MgO, and ZnO Decrease the Reactivity of Ammonium Nitrate-Fuel Oil With Pyrite Ores. Report of invention MIN-1362.

Evaluation of Nonincendive Detonating Cord

An "extra wrap" test was explored as a means of evaluating the initiating action of detonating cords (18). In this test, several layers of 6-mil kraft paper are wrapped around a standard 1-1/4- by 8-inch cartridge of explosive. A length of detonating cord is then attached along the cartridge and the cord is initiated with a No. 6 electric blasting cap. If the cord fails to initiate the cartridge, wraps of paper are removed until an initiation occurs. If the cord initiates the cartridge, more wraps are added until initiation no longer occurs. Applying the Bruceton up-and-down method, the number of wraps required for initiation in 50 percent of the trials (EW_{50}) is determined. Eight detonating cords with N_{50} values[13] ranging from 8.2 to more than 30 were examined. Except in one case, all the detonating cords examined were found to initiate the explosive through a thickness of paper greater than the case of an ordinary cartridge, indicating that a cord which passes the "extra wrap" test will perform satisfactorily in actual use.

Two detonating cords with N_{50} values greater, respectively, than 25 and 30 were evaluated for their effect on the incendivity of permissible explosives under the conditions of Schedule 1-H test 7 which was modified to allow the explosive to be initiated by the detonating cord rather than by the standard No. 6 EBC; the detonating cord itself was initiated by the No. 6 EBC in the gas chamber of the gallery. W_{50} values of 591 and 624, respectively, were obtained for a permissible explosive with a W_{50} value of 412 grams in the usual gallery test 7 which employs an electric blasting cap alone.

Incendivity of Electric Blasting Caps

(1) Sixteen commercial millisecond delay and four commercial No. 6 instantaneous electric blasting caps (obtained from four different manufacturers) were examined for incendivity in an 8-percent natural gas-air mixture. The caps were bundled and suspended in the center of a 45-cubic-foot steel gallery fitted with a replaceable paper diaphragm on one end. Each bundle of caps was fired in series with a permissible blasting machine having a 12- to 15-millisecond cutoff. The number of caps required to ignite the gas-air mixture with fifty percent probability (N_{50}) was determined using the Bruceton up-and-down method.[14]

(2) The same test procedure was used to evaluate three additional types of No. 6 electric blasting caps having, respectively, a copper shell with iron leg wires, an aluminum shell with iron leg wires, and a steel shell with iron leg wires. N_{50} values of 3.3 caps were observed for both copper-shell and steel-shell caps. The aluminum-shell caps gave 10 ignitions in 10 trials using one cap per trial. The effect of initiating a permissible explosive with a No. 6 electric blasting cap with aluminum leg wires in gallery 7 test was examined.

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[13] N_{50} is the number of 3-foot lengths of cord in a bundle which will initiate an 8-percent gas-air mixture in 50 percent of the trials.

[14] Dixon, W. J., and F. J. Massey, Jr. Introduction to Statistical Analysis. McGraw-Hill Book Co., Inc., New York, 2d ed., 1957, ch. 19, pp. 318-327.

These experiments confirm that electric blasting caps with aluminum leg wires and/or aluminum shells are hazardous for use in underground gassy mines; electric blasting caps with steel shells appeared to be as safe as those with copper shells. Some millisecond-delay caps appeared to be as incendive as aluminum-shelled caps.

Evaluation of Black Blasting Powder and Development of a Low-Strength Permissible Dynamite

Black blasting powder (3F) and black pellet powder were examined in the large explosive gallery in 8 percent natural gas-air (test 7) and in a modified version of the test, replacing the natural gas with 0.3 ounce coal dust dispersed per cubic foot air. With the gas-air mixture, 25 grams of either black powder (3F) or black pellet powder produced ignition. In coal dust-air mixtures, ignition occurred for 11 grams of black powder and 14.5 grams of black pellet powder.

A low-density, low-strength permissible explosive containing 30 percent sodium chloride was developed to replace black powder used until recently in some underground coal mines. In field tests, the new dynamite was equivalent to black powder in strength and coal breakage. Three explosives manufacturers are now marketing permissible explosives based on the formulation suggested by the Bureau.

Testing of Explosives and Hazardous Materials

One new formulation was submitted for schedule testing and approved as a permissible explosive. Seventeen field samples were examined--of these, five met all of Schedule 1-H requirements; three samples passed but two were out of chemical tolerance and one was out of tolerance in the rate of detonation; nine samples failed gallery test 7.

A number of potentially explosive compounds and mixtures were examined for their reaction to impact and static spark. Strength was determined for one material (table 1).

TABLE 1. - *Compounds examined during fiscal year 1968*

	Impact test, height, cm[1]		Static spark test energy, joules[4]	Ballistic mortar, strength of TNT, percent
	Method 1[2]	Method 2[3]		
Mixture of 60 percent magnesium, 40 percent Teflon	315	>330	12.5	-
Iso-sorbide dinitrate	72	-	6.25	-
Tritonal	187	98	-	-
Minol II	171	51	-	-
Ferrophosphorus dust	>330	100	-	-
Unsymmetrical dimethyl hydrazine carboxylate	>330	-	12.5	-
Diperisophthalic acid	4	-	.0005	57

[1]Height of drop of a 5-kg weight for 50 percent probability of ignition.
[2]One-half-inch-diameter cup with a closely fitting striker pin.
[3]Type No. 12 tool.
[4]Maximum energy for zero probability of ignitions using a potential of 5,000 volts.

Investigation of Actual and Potential Disasters

An investigation was made of a fire in a heat-exchanger cell at the Hanford facilities of the U.S. Atomic Energy Commission, Richland, Wash. (June 21, 1967). The accident was attributed to excessive oil leakage from a coolant pump. It was demonstrated experimentally that insulation soaked with the oil could ignite spontaneously at the operating temperatures of the pump.

Consultation was provided to city officials of Richmond, Ind., following a fire and explosion at a small arms ammunition store (April 6, 1968) that killed 41 people, injured over 100 people, and caused estimated damage in excess of $10 million. A report submitted to the Indiana State Public Service Commission was cited in the Congressional Record.

The Commonwealth of Puerto Rico was advised on safety problems associated with the anticipated shutdown of liquid petroleum gas facilities supplying San Juan with gas.

Consultative services were provided to the National Aeronautics and Space Administration regarding explosion hazards of the hydrogen-oxygen-water mixtures at high pressures and to the Army Materiel Command on the use of reticulated polyurethane foam as a flame arrestor in ground vehicles.

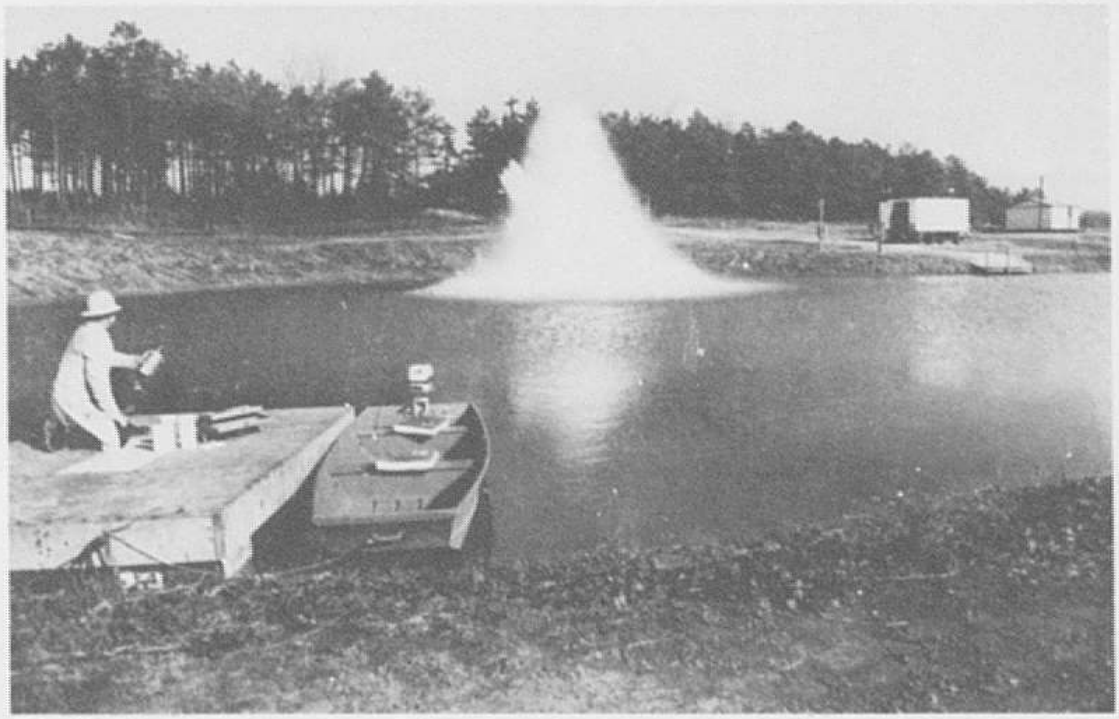

FIGURE 1. - New Bureau of Mines Facility for Underwater Shooting of Large Explosive Charges at Bruceton, Pa.

New Facilities and Installations

A pond about 180 feet wide and 25 feet deep with a capacity of 2.5 million gallons was constructed at Bruceton, Pa. (fig. 1). It is designed for underwater evaluation of explosives--a procedure which does not place the usual limitations on the charge weight and makes it possible to determine shock and bubble energy independently in a single shot.

Courses and Seminars

A fourth course on Explosion Problems in the Chemical Industry was presented in January 1968 by the Explosives Research Center. The course which ran for 5 days was attended by 28 participants representing 19 companies belonging to the Manufacturing Chemists Association.

A series of monthly seminars on current Explosives Research Center programs and related problems was held throughout the year. Speakers included ERC research personnel and a number of invited guest speakers.

Meetings and Conferences

Explosives Research Center personnel presented 10 papers at the following international and national meetings and conferences:

Twelfth International Conference of Directors of Safety in Mines Research, Dortmund, Germany, September 1967:

Mason, C. M., J. L. Uraco, and J. C. Cooper. Development of a Method for Measuring Relative Incendivity of Detonating Cord (18).

Van Dolah, R. W., C. M. Mason, and D. R. Forshey. Development of Slurry Explosives for Use in Flammable Gas Atmospheres (subsequently published as RI 7195).

Singer, J. M., N. B. Greninger, and J. Grumer. Some Aspects of the Aerodynamics of Float Coal Dust Clouds.

Mason, C. M., P. A. Richardson, and R. W. Van Dolah. The Incendivity of Permissible Explosives in Coal Dust-Gas-Air Mixtures (17)

Liebman, I., H. E. Perlee, and J. Corry. Investigation of Flame Propagation Characteristics in Layered Gas Mixtures (10).

American Institute for Aeronautics and Astronautics Third Propulsion Joint Specialist Conference, Washington, D.C., July 1967:

Perlee, H., T. Christos, Y. Miron, and H. K. James. Preignition Phenomena in Small A-50/NTO Pulsed Rocket Engines (21).

Armed Services Explosives Safety Board, Ninth Annual Explosives Safety Seminar, San Diego, Calif., August 1967:

Van Dolah, R. W. The Threat of Sonic Booms to Explosives Facilities.[15]

American Chemical Society 154th National Meeting, Chicago., Ill., September 1967:

Murphy, J. N., N. E. Hanna, D. S. Burgess, and R. W. Van Dolah. Potential Destructiveness of Gas Detonations (20).

Weiss, M. L., T. J. Schellinger, and E. L. Litchfield. Initiation of Condensed Explosives by Gas Detonation (31).

Twenty-fourth Annual Meeting, East Central Section, Air Pollution Control Association, Columbus, Ohio, September 1967:

Singer, J. M., E. B. Cook, M. E. Harris, V. R. Rowe, and J. Grumer. Flame Characteristics Causing Air Pollution: Production of Oxides of Nitrogen and Carbon Monoxide.

National Safety Congress, Chicago, Ill., October 1968:

Litchfield, E. L. Static Problems in Chemical Operations (11).

Sixtieth Annual American Institute of Chemical Engineers Meeting, New York. N.Y., November 1967:

Grumer, J., M. E. Harris, V. R. Rowe, and E. B. Cook. Effect of Recycling Combustion Products on Production of Oxides of Nitrogen, Carbon Monoxide, and Hydrocarbons by Gas Burner Flames.

Eastern Section, Combustion Institute, Pittsburgh, Pa., November 1967:

Kuchta, J. M., A. L. Furno, G. H. Martindill, and A. C. Imhof. Ignition Temperatures and Flame Spread Rates of Materials in Oxygen Enriched Atmospheres.

Litchfield, E. L., and T. A. Kubala. Ignition Energy for Condensed Materials.

Perlee, H. E., H. K. James, and Y. Miron. Preignition Mechanism of the Hydrazine-Nitrogen Tetroxide System.

Central States Combustion Institute, Columbus, Ohio, March 1968:

Grumer, J., M. E. Harris, V. R. Rowe, and L. F. Miller. Oxides of Nitrogen, Carbon Monoxide, and Light Hydrocarbons in Premixed Methane-Air and Propane-Air Flames.

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[15]Published in ASSE J., v. 13, No. 9, September 1968, pp. 12-14.

Second Joint Meeting of the American Institute of Chemical Engineers and Instituto de Ingenieros Quimicos de Puerto Rico, Tampa, Fla., May 1968:

Grumer, J., A. Strasser, J. M. Singer, and P. M. Gussey. Hydrogen Flare Stack Diffusion Flames: Low Flow Instability, Burning Rates, and Dilution Limits.

Cryogenic Technology Symposium, CRYO-68, Chicago, Ill., June 1968:

Van Dolah, R. W. Fire and Explosion Hazards of Cryogenic Liquids.

Course on Super-Conducting Devices and Accelerators, Brookhaven, N.Y., June 1968:

Zabetakis, M. G. Cryogenic Safety.

Other international meetings attended by the Research Director of the Explosives Research Center included an International Colloquium of Gas Dynamics of Explosions at Brussels, Belgium, September 1967, and a meeting of the Subcommittee on the Carriage of Dangerous Goods of the Intergovernmental Maritime Consultative Organization at London, England, May 1968.

Other meetings attended by Explosives Research Center personnel included the USA Standards Institute, Committee Z21, Cleveland, Ohio, July 1967; the Coast Guard Panel on Chemical Compatability of Hazardous Chemicals, Washington, D.C., July 1967; the Pennsylvania Hazardous Substances Transportation Board, Harrisburg, Pa., July 1967; the Ninth Annual Explosives Safety Seminar, San Diego, Calif., August 1967; the 23d Meeting of the Interagency Chemical Rocket Propulsion Group on Liquid Propellant Test Methods, Monterey, Calif., March 1968; the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

Members of the Explosives Research Center served on committees of the National Fire Protection Association, USA Standards Institute, and the American Society for Testing and Materials, and participated in conferences as well as in meetings with various agencies and research groups.

PART 2.--PUBLICATIONS DURING FISCAL YEAR 1968[16]

1. Christos, T., Y. Miron, H. James, and H. E. Perlee. Combustion Characteristics of Condensed-Phase Hydrazine-Type Fuels With Nitrogen Tetroxide. J. Spacecraft and Rockets, v. 4, No. 9, September 1967, pp. 1224-1229.

An investigation was made of the combustion characteristics of hydrazine-type propellants and their reactions in low-thrust engines prior to ignition. When mixed with nitrogen tetroxide at liquid nitrogen temperature, frozen hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine and Aerozine-50 all underwent violent exothermal reactions upon warming to between -50° and 70° C. The Aerozine-N_2O_4 mixture consistently gave a detonation-like reaction.

[16]Publications are listed alphabetically according to first author.

The other mixtures reacted less violently. Hydrazine underwent an explosive reaction with a TNT equivalence of about 130 percent when fired explosively in air, oxygen, or nitrogen tetroxide. For stoichiometric mixtures of the liquid fuels and liquid N_2O_4, the TNT equivalences were about 160 percent in all cases. The structural and inertial response of simulated rocket engines to internal explosions was also studied.

2. Furno, A. L., A. C. Imhof, and J. M. Kuchta. Effect of Pressure and Oxidant Concentration and Autoignition Temperatures of Selected Combustibles in Various Oxygen and Nitrogen Tetroxide Atmospheres. J. Chem. and Eng. Data, v. 13, No. 2, April 1968, pp. 243-249.

Minimum autoignition temperatures were determined at various pressures from 25 to 740 mm of Hg for the following combustibles in air, oxygen, and nitrogen tetroxide with nitrogen or helium as diluent: hydrogen, n-butane, n-hexane, n-heptane, 1-chlorobutane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, methylene chloride, hydrazine, mono-methylhydrazine, and unsymmetrical dimethylhydrazine.

Autoignition temperatures were lower in nitrogen tetroxide than in oxygen for all the combustibles except n-heptane and 1-chlorobutane. Generally, the AIT values increased slightly with decreasing pressure and oxidant concentration to some critical value, from where they tended to increase noticeably; they also varied with the size of the reaction vessel.

3. Grumer, J., A. Strasser, and R. A. Van Meter. Safe Handling of Liquid Hydrogen. Cryogenic Eng. News, v. 2, No. 8, August 1967, pp. 60-63.

Based on an extensive survey of the literature and current safety practices in research and industrial installations, recommendations are made for the safe handling of liquid hydrogen. Areas considered include safety in plant design (liquid hydrogen systems, electrical installations, ventilation, detectors, separation by distance and/or barriers); safety in operations (general precautions, precautions against accidental ignition, exclusion of air and oxygen, purging and filling of containers, and maintenance); personnel safety (training, clothing, general precautions, quenching agents).

4. Hay, E. J., J. Ribovich, F. H. Scott, and F. C. Gibson. The Effect of Physical and Chemical Properties on the Sensitivity of Liquid Explosives. Proc. 4th Symp. (Internat.) on Detonation, ONR, U.S. Navy, ACR-126, 1967, v. 1, Sec. C-149, pp. 412-425.

Sensitivities of several liquid explosive systems to low-velocity and high-velocity detonation were determined by means of an instrumented modification of the card-gap test. The systems investigated included nitroglycerin-ethylene glycol dinitrate with various diluents; experimental casting solvents for double-base propellants; nitromethane alone and in mixtures with tetranitromethane and hydrogen peroxide-glycerol. Emphasis was placed on the relationship between apparent sensitivity and the physico-chemical characteristics of the system and its mechanical interaction with its environment. Results indicate that, while the energy content, viscosity and homogeneity of the

system as well as the charge diameter and container material are very important, other fundamental factors still to be determined affect the tendency of a liquid explosive system to undergo low-velocity detonation.

5. Karn, F. S., and J. M. Singer. Photographic Study of Laser Irradiation of Coal and Graphite. Fuel, v. 47, May 1968, pp. 235-240.

Irradiation of coal or graphite by a normal laser pulse produces a luminous plume which has been recorded by high-speed photography. Photographs taken at the rate of 21,000 frames per second were used to measure the rate of plume growth. The effective measured laser pulse was 1.2 msec which is longer duration than giant laser pulses. The plume growth rate was 1.1×10^4 cm/sec for bituminous coal and 0.9×10^4 cm/sec for graphite which is much slower than for graphite plumes formed by giant pulse laser irradiation. The vaporization rate for graphite was 14 g/cm^2 sec^{-1}, approximately the rate expected at atmospheric pressure based on boiling-point data for carbon.

6. Kuchta, J. M., and R. J. Cato. Review of Ignition and Flammability Properties of Lubricants. Air Force Aeropropulsion Lab., AFAPL-TR-67-126, January 1968, 16 pp.; AD 665121.

The ignition temperature and flammability properties of combustible fluids are useful in determining safety guidelines and in assessing the fire or explosion hazard which may exist in the environment where the fluids are employed. Information for some 90 lubricants and hydraulic fluids has been reviewed and assembled. Particular emphasis is given to those fluids used in aircraft applications. Data are presented for petroleum-base fluids and for synthetic fluids in air, oxygen, and oxygen-nitrogen at pressures from 1/8 to 1,000 atmospheres. The temperature requirements for ignition in heated vessels, by heated wires, and by hot-gas jets are compared over a range of heat source dimensions. Flash points, flammability limits, decomposition temperatures, and other related properties are compared for the various classes of lubricants.

7. Kuchta, J. M., R. J. Cato, I. Spolan, and W. H. Gilbert. Evaluation of Flame Arrestor Materials for Aircraft Fuel Systems. Air Force Aeropropulsion Lab., AFAPL-TR-67-148, February 1968, 30 pp.; AD 82014.

Flame arrestor experiments were conducted with reticulated (20-pore/inch) polyurethane foam materials currently used for fire protection in fuel systems of military aircraft. In small-scale experiments, pressure rise measurements showed that dry samples of this foam prevent flame propagation at arrestor length/ignition void length ratios (ℓ_2/ℓ_1) as low as about 0.17 at ordinary temperature and pressure. For $\ell_2/\ell_1 \geq 1.5$, the material was effective at pressures up to about 15 psig and temperatures to 200° F. Improved performance was obtained when the foam was wetted with liquid fuel or when a more porous foam was used. Full-scale experiments in a 450-gallon fuel tank, with the arrestor packed to give a 40-percent gross void volume, indicated that the 20-pore/inch foam is effective to pressures of at least 5 psig. However the foam tends to be less effective when additional air is supplied following ignition. Results obtained with electrical spark ignition sources were

comparable to those found with tracer or incendiary ammunition. In general, the 20-pore/inch foam was noticeably more effective than the 10-pore/inch material examined in previous experiments.[17]

8. Kuchta, J. M., E. L. Litchfield, and A. L. Furno. Flammability of Materials in Hyperbaric Atmospheres. BuMines Explosives Research Center Final Rept. No. 4016, Aug. 30, 1967, 51 pp.; PB 176528.

To evaluate the potential fire hazards of combustible solids in hyperbaric atmospheres, hot-plate ignition temperatures, flame spread rates, and minimum ignition energies were determined for cotton sheeting plain and treated with fire retardants, cotton balls, paper drapes, conductive rubber sheeting, blanket wool, polyvinyl chloride sheet, plexiglass sheet, cellulose sheet, wood strips and dowels, and a Nomex[18] fabric. Air, oxygen, and various oxygen-nitrogen atmospheres were employed at pressures from 1 to 6 atmospheres. Some determinations were also made in oxygen at reduced pressures.

The hot-plate ignition temperatures of the combustibles correlated reasonably well with the oxygen partial pressure. Flame spread rates tended to depend more on oxygen percentage than total pressure. Materials treated with certain fire retardants can ignite in oxygen-enriched atmospheres at lower temperatures than untreated materials. In several instances combustible solid materials were ignited by electrical sparks or arcs with electrical energies comparable to those which a human may discharge under conditions of low humidity (10 to 20 mj). Minimum ignition energy requirements were determined for several anesthetic agents including cyclopropane, diethyl ether, divinyl ether, trichloroethylene, Fluoromar, Fluothane, and chloroform.

9. Kuchta, J. M., and G. H. Martindill. Thermal Oxidation of n-Octane Vapour-Oxygen-Nitrogen Mixtures at Reduced Pressures. Combustion and Flame, v. 11, No. 3, June 1967, pp. 21-216.

The slow oxidation of n-octane vapour-oxygen-nitrogen mixtures was investigated at reduced pressures ($P_t \geq 35$ mm Hg) and at temperatures where rapid reactions or "cool" flames may occur. At 250° C, the rates of pressure rise were more dependent upon total pressure than upon the fuel and oxygen concentrations. The critical pressure for rapid reaction (abrupt pressure rise) decreased with increasing temperature, fuel concentration and vessel radius. However, above approximately 290° C, there were no abrupt pressure rises and the reaction became a less temperature- and pressure-dependent process.

10. Liebman, I., H. E. Perlee, and J. Corry. Investigation of Flame Propagation Characteristics in Layered Gas Mixtures. BuMines Rept. of Inv. 7078, 1968, 34 pp.

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[17]Cato, R. J., A. L. Furno, A. Bartkowiak, and J. M. Kuchta. Evaluation of Flame Arrestor Materials for Aircraft Fuel Systems (U). Air Force Aeropropulsion Lab., AFAPL-TR-36, March 1963, 30 pp.

[18]Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

An investigation was made of the factors which determine the velocity of flames propagating along the boundary between gaseous fuel and air. These included flammable zone thickness, flammable zone concentration gradient, fuel type, and position of the flame relative to various environmental surfaces. The flammable zone thickness and the burning velocity of the stoichiometric mixture were found to have the most significant effect on the flame speed. The aerodynamic motion of the gases near the interfacial flame was examined by the particle track and interferometer methods. The relative velocity of the interfacial flame with respect to the unburned gas on the central streamline was found to equal the burning velocity of a stoichiometric homogeneous fuel-air mixture. The composition of the lean fuel-air mixture at the boundary of the combustion zone was observed to be less than the theoretical lower flammability limit of the fuel.

11. Litchfield, E. L. Static Problems in Chemical Operations. Nat. Safety Cong., Trans. Petrol. Ind., v. 19, 1967, pp. 19-22.

Triboelectrification and associated hazards encountered in industry are discussed. It is shown that since triboelectric phenomena are extremely difficult to eliminate, measures should be taken to prevent the occurrence of easily ignited combustible mixtures. In practice only a narrow range of flammable mixtures is readily ignitible by discharges likely to result from triboelectrification.

12. Litchfield, E. L., M. H. Hay, and D. J. Cohen. Initiation of Spherical Detonation in Acetylene-Oxygen Mixtures. BuMines Rept. of Inv. 7061, 1967, 6 pp.

Minimum energies for direct initiation of expanding gaseous detonation waves in acetylene-oxygen mixtures were determined. Composition limit ranges for the initiation of detonation with fixed energies were compared with data in the literature. Assuming that the stored electrical energy was completely converted to thermal energy, the agreement between the energy of primary explosive initiators and the energy of electrical discharge initiators was good. Minimum energies for initiation of detonation in the most sensitive composition (40 percent C_2H_2 + 60 percent O_2) were 0.64 joule at an initial pressure of 1/4 atmosphere, 5.0×10^{-2} joule at 1/2 atmosphere, and 3.7×10^{-3} joule at 1 atmosphere. Fuel concentrations in mixtures initiated to detonation by 4.9×10^{2} joules ranged from 10 to 65 percent C_2H_2 at 1/4 atmosphere, 10 to 67 percent C_2H_2 at 1/2 atmosphere, and 9 to 68 percent C_2H_2 at 1 atmosphere.

13. Litchfield, E. L., M. H. Hay, T. A. Kubala, and J. S. Monroe. Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures. Techniques and Apparatus. BuMines Rept. of Inv. 7009, 1967, 10 pp.

Techniques and apparatus used by the Bureau of Mines to determine flat plate ignition quenching distances and minimum spark ignition energies are described. Vessel materials and electrode configurations are discussed. Spherical, hemispherical, or flat plate electrodes are recommended. The preferred metals for electrodes and electrode supports is stainless steel; flat plate electrodes incorporate flanges of low electrical conductivity which are

frequently of glass. Various aspects of the electrical energy supply system are discussed and suitable arrangements of components are indicated. The concept of a thermal relaxation time is introduced as a basis for selecting a minimum interspark time in testing of a gas mixture. These techniques were utilized at mixture pressures between 10 mm Hg and 45 psig and initial temperatures between -78° and +198° C. The gaseous mixtures represented a wide range of chemical reactivity and corrosiveness. The minimum ignition energies determined varied from about 10^{-7} joule to nearly 10^{3} joules.

14. Litchfield, E. L., M. H. Hay, and J. S. Monroe. Electrification of Ammonium Nitrate. BuMines Rept. of Inv. 7139, 1968, 17 pp.

Electrification of ammonium nitrate-fuel oil (AN-FO) blasting agent by pneumatic loaders is described. Its consequences are considered in terms of the conditions required to initiate electric blasting caps.

The use of semiconductive loading tubing and the control of the resistivity of the AN-FO are recommended. In addition, the operator should (1) test to insure continuity of the electric detonator legwire-bridgewire-legwire circuit before inserting the cap into the charge or borehole; (2) keep the legwires shunted but not otherwise connected to ground during loading of the blasting agent; (3) make sure that the borehole is discharged before hooking up the detonator leads; (4) make sure that he himself is discharged before he handles the detonator leads; (5) make sure that the blasting cap leads are never carried to the AN-FO loader.

15. Mason, C. M., D. R. Forshey, and F. J. P. Perzak. Fire Hazards of Ammonium Nitrate-Sulfur Systems. Agric. Food Chem., v. 15, No. 6, November/December 1967, pp. 954-966.

The addition of sulfur to ammonium nitrate-based fertilizers has raised questions regarding the hazard of these mixtures when exposed to fire. Ammonium nitrate-sulfur (AN-S) mixtures detonated when initiated by an explosive shock under sufficiently long diameter. Diammonium phosphate, triple superphosphate, and potassium chloride decreased the shock sensitivity of AN-S. At pressures above 1,000 psi, AN-S mixtures burned rapidly; deflagration to detonation transition was accomplished experimentally in some cases. Sulfur has the same effect on detonability as other fuels when added to AN or AN systems. The thermal stability of AN-S mixtures was about the same as that of AN mixed with fuel oil or polyethylene. Addition of chloride ion materially reduced the thermal stability.

16. Mason, C. M., and P. A. Richardson. Active List of Permissible Explosives and Blasting Devices Approved before December 1, 1967. BuMines Inf. Circ. 8371, 1968, 9 pp.

The Bureau of Mines active list of permissible explosives include 95 brands. Twelve are gelatinous and the rest are the more commonly used granular ammonium nitrate type. The list of permissible blasting devices comprises five Cardox models.

17. Mason, C. M., P. A. Richardson, and R. W. Van Dolah. The Incendivity of Permissible Explosives in Coal Dust-Gas-Air Mixtures. BuMines Rept. of Inv. 7127, 1968, 12 pp.

Mechanical mining produces large quantities of very fine coal dust, called float dust. The resulting increase in hazard requires a reexamination of the Bureau of Mines method of evaluating the incendivity of explosives in coal dust-gas-air mixtures. A technique recently developed by the Bureau for evaluating the incendivity of explosives in coal dust-air mixtures was applied, with modifications, to coal dust-natural gas-air mixtures. A series of permissible explosives were evaluated by this modified technique. Results indicate that the modified technique could be the basis of a more discriminatory procedure than the current one.

18. Mason, C. M., J. L. Uraco, and J. C. Cooper. Development and Evaluation of Nonincendive Detonating Cord. BuMines Rept. of Inv. 7149, 1968, 9 pp.

A method was developed for evaluating the relative incendivity of detonating cord in natural gas-air mixtures. Short lengths of cord in bundles were fired to determine the number of strands per bundle which would ignite natural gas-air mixtures 50 percent of the time in the Bureau of Mines 45-cubic-foot gallery. The relative efficiency of a flame quenching agent, potassium acid tartrate, incorporated in the pentaerythritol tetranitrate core and in the polyethylene sheath, was explored. The effects of sheath thickness, sheath composition, core weight, and core composition were evaluated.

19. Murphy, E. J. A Rapid Colorimetric Method for Field Determination of Nitrogen Dioxide in Fumes From Explosives. BuMines Rept. of Inv. 6981, 1967, 20 pp.

The Bureau of Mines has developed a fast, reliable modification of the Griess-Ilosvay procedure suitable for field analysis for NO_2 in fumes from explosives. Known concentrations of NO_2-air mixtures were analyzed for the nitrous acid or nitrate formed by diazotizing and coupling reactions with three Griess-Ilosvay-type reagents. Results from the Rider-Mellon, the Saltzman, and the Patty-Petty methods were in good agreement if contact between NO_2 and the reagents was sufficiently prolonged. In experiments to obtain an accurate factor for converting NO_2 to nitrite, overnight contact was allowed to ensure complete conversion. The factor was found to be 75 percent with a standard deviation of $\pm$3.2 percent. The Saltzman and Patty-Petty reagents gave low and erratic results when used as absorbing liquids unless several hours' contact was allowed. When dilute NaOH solution was used as the absorbing liquid instead of a Griess-Ilosvay-type reagent, 92 percent of the overnight conversion factor was found after a 3-minute shaking time and a 10-minute standby. The Saltzman reagent was preferable for fieldwork with the dilute NaOH solution as the absorbent because of its easy application, rapid reaction, and intense color even at low NO_2 concentrations.

20. Murphy, J. N., N. E. Hanna, D. S. Burgess, and R. W. Van Dolah. Potential Destructiveness of Gas Detonations. ACS Div. Fuel Chem. Preprints, v. 2, No. 4, September 1967, pp. 135-141.

Gas detonations were studied in acetylene-air propane-air and methylacetylene-propadiene-propylene (MAPP)-air mixtures. Limits of detonability were determined in a closed pipe 7 inches in diameter by 12-foot long length. Pressure-time transients were observed in a 24-inch diameter by 163-foot long steel tube which could be closed at one end. The conversion of detonation energy to destructive work was observed in tunnels in earth which were generally 3 feet wide, 5 feet high and 162 feet long with several right angle turns. Initiation to detonation was accomplished with boosters ranging from 1.1 grams PETN to 130 grams tetryl. Acetylene/air and propane/air mixtures were detonable at all concentrations within the reported limits of flammability, MAPP/air was detonated over a wider range of concentration than the reported flammable limits. Peak (Chapman-Jouguet) pressures could be measured reproducibly within about 53 feet of the initiation source in the steel tunnel; at longer distances both high and low values were observed as though the detonation were departing from a one-dimensional model. Other deviations from the accepted model are reported. Impulses were surprisingly high in lean mixtures. At optimum concentration the impulses of propane/air, MAPP/air, acetylene/air, and gasoline/air were nearly identical although there was considerable variation in detonation pressure.

21. Perlee, H. E., T. Christos, Y. Miron, and H. K. James. Preignition Phenomena in Small A-50/NTO Pulsed Rocket Engines. J. Spacecraft and Rockets, v. 5, No. 2, February 1968, pp. 233-235.

Recent studies at the NASA Manned Spacecraft Center and at the Bureau of Mines indicate that accumulation of hydrazine nitrate may contribute to the ignition spikes often observed in low thrust Aerozine-50/nitrogen tetroxide rocket engines. Residues taken from such engines following pulsed operation at about 0.005 psia consisted of about equal parts by weight of hydrazine nitrate and water. Experiments showed that hydrazine and monomethylhydrazine react with nitrogen tetroxide in these engines during the preignition period to form the corresponding fuel nitrate, unsymmetrical dimethylhydrazine reacts with nitrogen tetroxide to form ammonium nitrate. The accumulation of these nitrates on the engine walls with each successive pulse can eventually become sufficient to cause permanent engine damage if initiated to detonation.

22. Singer, J. M. Influence of Amount of Ash on Ignitibility of Coal Dust-Methane-Air Mixtures. Fuel, v. 47, May 1968, pp. 223-234.

The hot-gas ignition method for determining lower ignition limits was applied to hybrid mixtures containing coals with approximately the same volatile content (34 to 36 percent) but with varying percentages of ash (2.6 to 12.7 percent). The ignitibility of a de-ashed coal with less than 0.2 percent ash content and a relatively high volatile content (59.7 percent) was compared with that of the ash-containing coals.

As the ash content of the coals was increased, the ignitibility of the experimental hybrid mixture decreased for mixtures containing more than 30-35 mg/l coal dust; for hybrid mixtures containing less than 30 mg/l coal dust this effect was negligible. Chemical inhibition by the metal salts present in the coal is favored as an explanation for the decreased ignitibility of hybrid mixtures containing coals with relatively little ash. The elutriation process by which float coal dust suspensions form in mines may remove some of the ash matter from the suspended coal, thus increasing its ignitibility. De-ashed coal mixtures appear to be more ignitible than mixtures of coals with a lower volatile content.

23. Singer, J. M., A. E. Bruszak, and J. Grumer. Limits of Flame Propagation of Coal Dust-Methane-Air Mixtures. BuMines Rept. of Inv. 7103, 1968, 12 pp.

Flame propagation in lower limit hybrid coal dust-methane-air was investigated in vertical and horizontal flame ducts (15.2 cm id and 1.8 m long). Fuel concentrations at lower limits of flame propagation and equivalences of coal dust and methane were much higher for continuing flame propagation than for short-span flame propagation in the vicinity of an "overdriving" ignition source. As the energy of the ignition source was increased, the flame speed and the distance of flame propagation from the ignition source increased, whereas the total fuel concentration at the lower limit decreased.

24. Staff, Explosives Research Center. Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1966. BuMines Inf. Circ. 8349, 1967, 21 pp.

Major activities of the Bureau of Mines Explosives Research Center during fiscal year 1966 (July 1, 1965, to June 30, 1966) are reviewed briefly. Part 1 summarizes significant accomplishments of the projects that were active during that period. Part 2 presents short abstracts of the publications that appeared in the Bureau series and in other media during fiscal year 1966.

25. Strasser, A., I. Liebman, and S. R. Harris. Hydrogen Detectors. Cryogenic Eng. News, v. 2, No. 12, December 1967, pp. 16-20.

The performance of several types of hydrogen detectors was examined to determine their limitations and potentialities. The instruments were distinguished primarily by the way in which the sample was collected, and the hydrogen was sensed and its concentration displayed. Factors considered in evaluating the detectors were accuracy and reproducibility; effect of exposure to large hydrogen concentrations; effect of temperature and humidity; response and recovery; response to other gases; ignition hazards; effect of wind; zero drift.

26. Van Dolah, R. W. Explosives. Ch. in Standard Handbook for Mechanical Engineers. McGraw-Hill Book Co., New York, 7th ed., 1967, pp. 7-35--7-38.

Explosives used in the United States are described briefly. Commercial explosives include ammonium nitrate-fuel oil blasting agents, ammonium nitrate-water slurries, various dynamites, permissible explosives and liquid oxygen explosives.

27. Watson, R. W. Gage for Determining Shock Pressures. Rev. Sci. Instr., v. 38, No. 7, July 1967, pp. 978-980.

The pressure gage described is simple to construct (fig. 2). It uses an expandable transducer and measures shock wave pressures in the kilobar range. Calibration procedures and data are presented for the range from 10 to 70 kilobars. A method for extending the useful range to include pressures developed by detonating explosives is indicated.

28. Watson, R. W., J. Ribovich, and F. C. Gibson. The Shock Sensitivity of Explosive Films. Pyrodynamics, v. 6, May 1968, pp. 39-51.

A highly instrumented two-dimensional analog of the card-gap test was used to determine characteristics of the initiation and propagation of detonations in thin films of liquid explosives. Both the high-velocity and low-velocity detonation regimes were observed, depending upon film thickness, explosive material, and the strength of the initiating stimulus. The high-velocity detonations were close to the ideal hydrodynamic detonation velocity for the particular system under investigation. At lower stimulus levels, low-velocity reactions occurred at velocities both above and below the velocity of sound in the unreacted material. Qualitatively, the low-velocity detonations in films closely resembled low-velocity detonations in liquid columns. A simple physical model, based on fluid cavitation, has been developed to describe this latter case. The effects of desensitizing additives on the threshold values of the initiation stimulus required to produce high-velocity or low-velocity detonations are discussed. The behavior of the thin film systems is compared with the behavior of detonating columns for the same explosives.

29. Watson, R. W., C. R. Summers, F. C. Gibson, and R. W. Van Dolah. Detonations in Liquid Explosives. The Low Velocity Regime. Proc. 4th Symp. (Internat.) on Detonation. ONR, U.S. Navy, ACR-126, 1967, v. 1, Sec. A-121, pp. 117-125.

Certain liquid explosives can detonate both at high and low rates, depending primarily on the strength of the initiating stimulus. Earlier experimental and theoretical work, at the Bureau of Mines and elsewhere, indicated that inhomogeneities in the form of cavities play an important role in the initiation of both high- and low-velocity detonations. The present work was designed to define more clearly those features that are characteristic of low-velocity detonation in liquids. Photographic studies of low-velocity detonations in 50/50 nitroglycerin-ethylene glycol dinitrate have yielded a simple physical model which suggests that fluid cavitation ahead of the chemical reaction zone is generated by precursor wall waves with associated rarefactions. These cavities act as incipient reaction centers where initiation occurs when they are overtaken by the high-pressure field associated with the

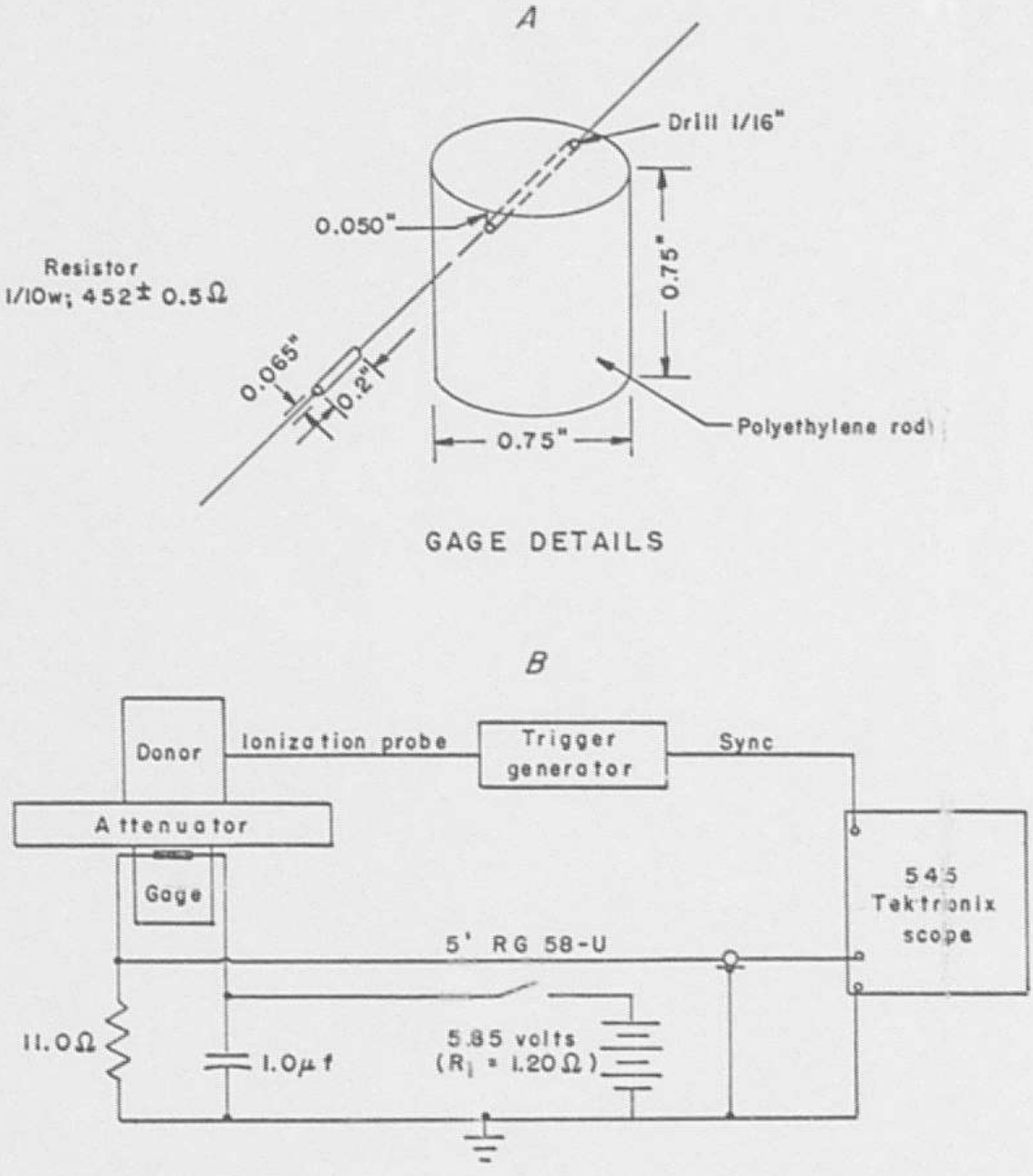

FIGURE 2. - Pressure Gage Construction Details and Monitoring Circuit Used To Determine Gage Resistance Under Shock Loading. The specific values of the components shown were used in establishing the gage calibration.

reaction zone. Correlating experiments using hemispherical cavities located on the free surface of fluids and air-filled bubbles in a bulk of the liquid explosive indicate that the reaction in the cavities may be initiated by liquid micro-jetting.

30. Weiss, M., and E. L. Litchfield. Projectile Impact Initiation of Condensed Explosives. BuMines Rept. of Inv. 6986, 1967, 13 pp.

Explosive samples were subjected to the impact of metal right cylinders fired from a 0.50-caliber gun. The physical model of the projectile-explosive interaction describes, in principle, the duration of the peak shock pressure in terms of the projectile and explosive geometry and the steady-state penetration of the explosive. Of the explosives studied, liquid hydrogen-solid oxygen and liquid oxygen-solid or liquid hydrocarbon were the most shock sensitive (initiating shock, about 1.0 kb or 987 atmospheres pressure); cast TNT was the least sensitive (initiating shock, more than 110 kb pressure). The appearance of the recovered projectiles and the calculated initiation shock pressures suggest that the solid explosives were initiated directly to high-order detonation, whereas the liquid explosives were probably initiated to low-order detonation, with subsequent transition to high-order detonation.

31. Weiss, M. L., T. J. Schellinger, and E. L. Litchfield. Initiation of Condensed Explosives by Gas Detonation. ACS Div. Fuel Chem. Preprints, v. 11, No. 4, September 1967, pp. 142-151.

The possibility of detonation of a large pile of explosive exposed to conflagration conditions was investigated. Because there appears to exist a critical pressure for the initiation of detonation, it was concluded that an unconfined gas detonation external to the pile will not cause sympathetic detonation of the condensed explosive. A gas detonation loading technique was employed to initiate detonation in solid condensed explosives. At higher gas charging pressures, detonation in the condensed explosive was initiated close to the gas-solid interface with a time delay $\leq$1 microsecond. At lower charging pressures, the condensed explosive detonated after a longer delay. At still lower pressure, no detonation occurred although a portion of the explosive may have been consumed. The shock pressure for initiation of detonation with a delay $\leq$1 microsecond was comparable to the shock pressure required for initiation by solid explosive donors or by projectile impact. The pressurization of the explosive sample at the appearance of detonation was only weakly dependent upon the induction time. For PETN, RDX, and tetryl, at densities of about 0.7, 0.9, and 1.0 gm/cc, respectively, the initial gas charging pressures for initiation with a delay $\leq$1 microsecond were 20, 26, and 26 atm gage. Pressures for appearance of detonation in these same explosives were 2, 3, and 3 kbar, respectively.

32. Zabetakis, M. G. Flammability Characteristics of Combustible Gases and Vapors. Ch. in Handbook of Laboratory Safety, ed. by N. V. Steere. The Chemical Rubber Co., Cleveland, Ohio, 1967, pp. 140-163.

Topics include definition and theory of limits of flammability and ignition; graphic presentation of flammability data; deflagration and detonation

processes; preventive measures; mathematical expressions for calculating flammability data.

PART 3.--THERMAL DECOMPOSITION OF RDX AND HMX

The thermal decomposition of RDX (1,3,5-trinitro-1,3,5-triacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) at elevated

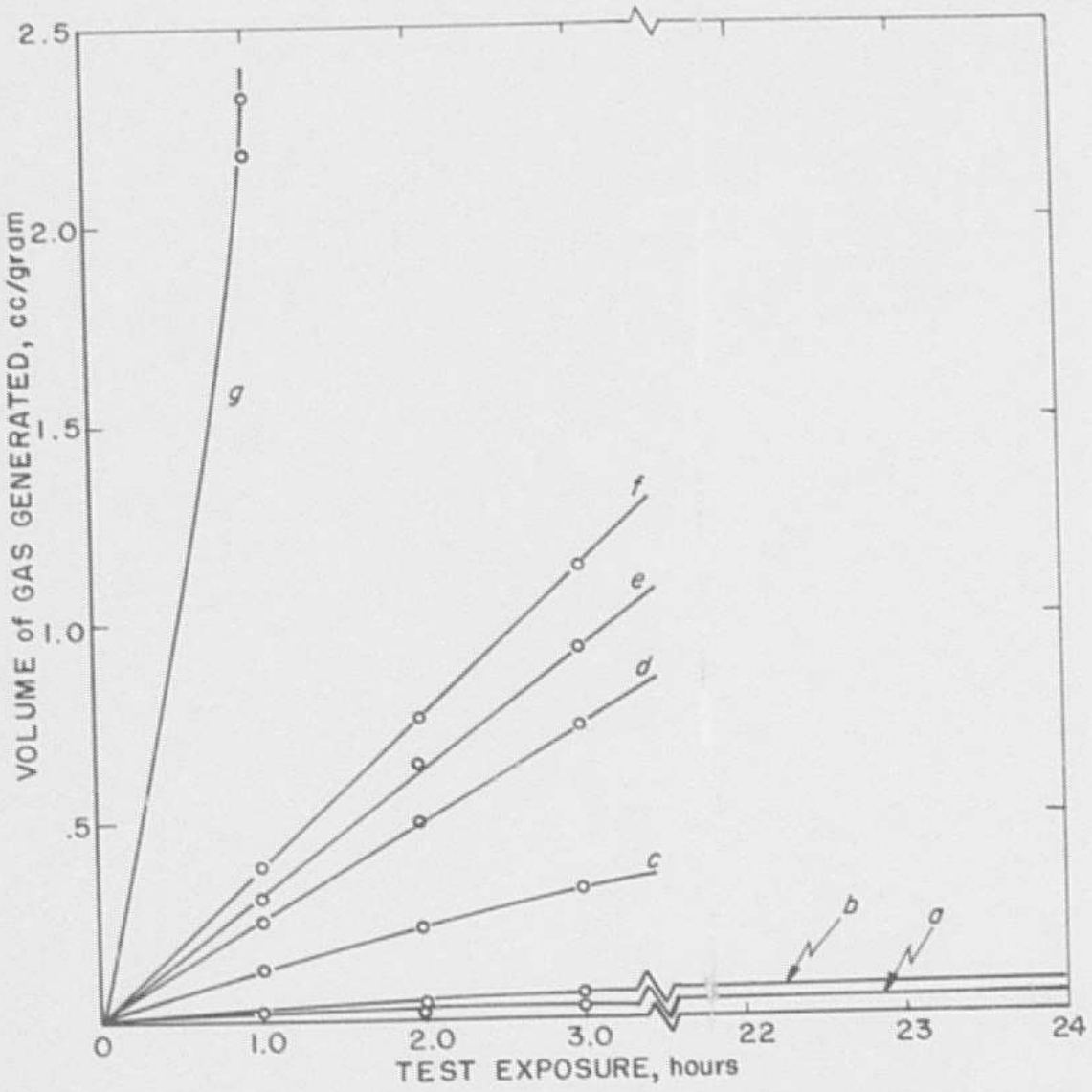

FIGURE 3. - Taliani Results for RDX at Various Temperatures: *a* - 225° F, *b* - 295° F, *c* - 320° F, *d* - 338° F, *e* - 356° F, *f* - 363° F, *g* - 375° and 383° F.

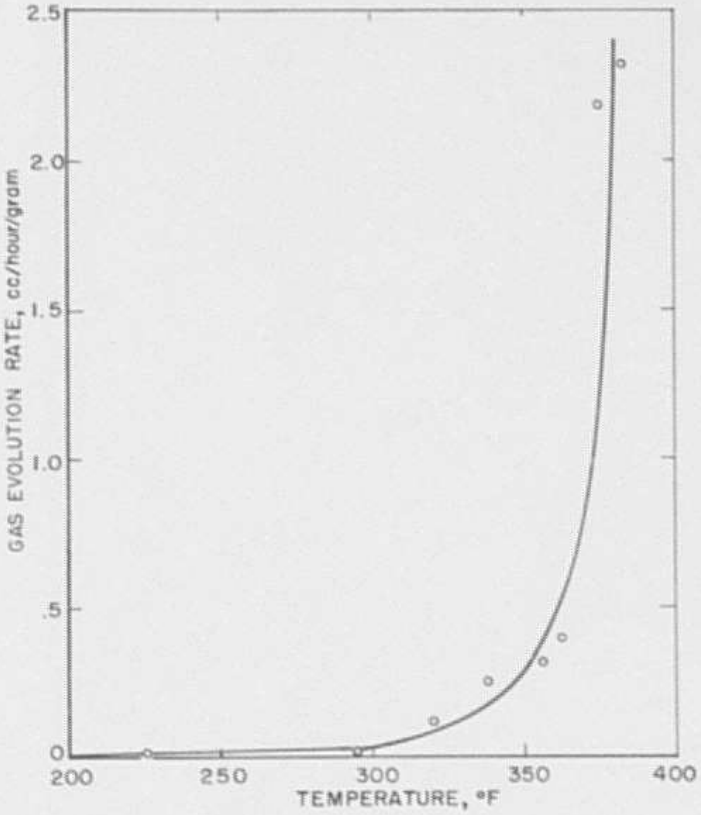

FIGURE 4. - Gas Evolution Rate of RDX as a Function of Temperature.

temperatures was studied by the Taliani procedure.[19] Both compounds were obtained from the Holston Defense Corporation.

Figure 3 shows the Taliani results for RDX (Holston Lot No. HOL-20-1, 99.8 percent pure) from 225° to 383° F. The rate of gas evolution increased from 0.01 to 2.32 cubic centimeters per hour per gram over this temperature range. The gas evolution rate of RDX as a function of temperature is shown in figure 4.

Gas evolution from HMX (Holston Lot No. HOL-700-7, 99.7 percent pure) increased from 0.02 cubic centimeter per hour per gram at 254° F to 2.10 cubic centimeter per hour per gram at 410° F (fig. 5). A plot of the evolution of gas from HMX as a function of temperature is shown in figure 6.

The gas evolution rate of RDX is low from room temperature to about 300° F. It increases progressively from 300° F to the melting point. The rate of gas evolution from HMX increases slowly to about 350° F and more rapidly above this temperature. HMX shows a marked increase in thermal decomposition about 50° F higher than RDX (350° F for HMX, 300° F for RDX).

[19]Boyars, C., and W. G. Gough. Test for Establishing Residual Safe Life of Stabilized Solid Propellants. Anal. Chem., v. 27, 1955, pp. 957-961.
Taliani, M. Quantitative Stability Test Toward Heat for Explosives Containing Nitroglycerin. Gazz. chim. ital. 51 (I), 1921, pp. 184-193.

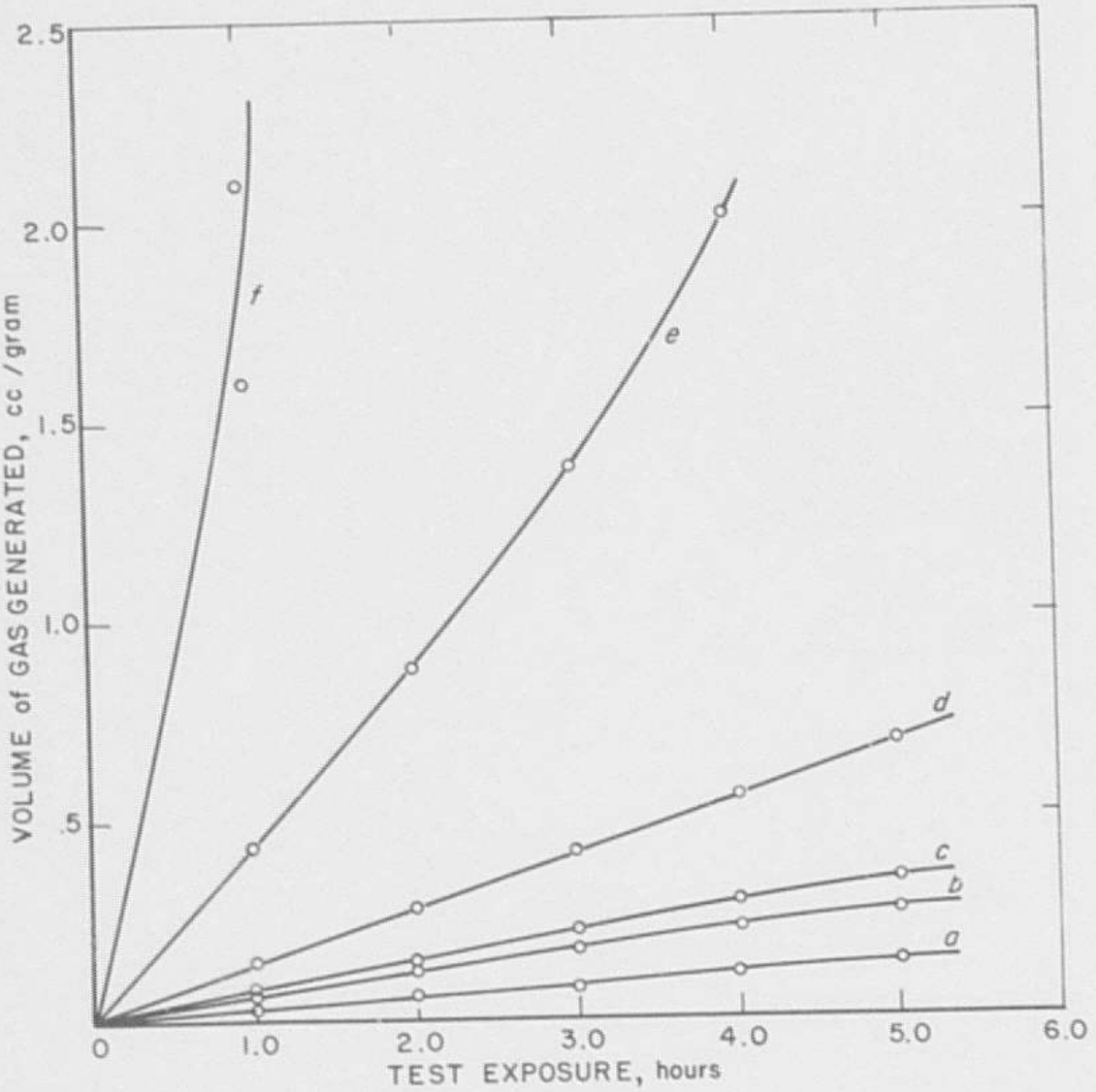

FIGURE 5. - Taliani Results for HMX at Various Temperatures: *a* - 254° and 270° F, *b* - 309° F, *c* - 348° F, *d* - 363° F, *e* - 386° F, *f* - 406° and 410° F.

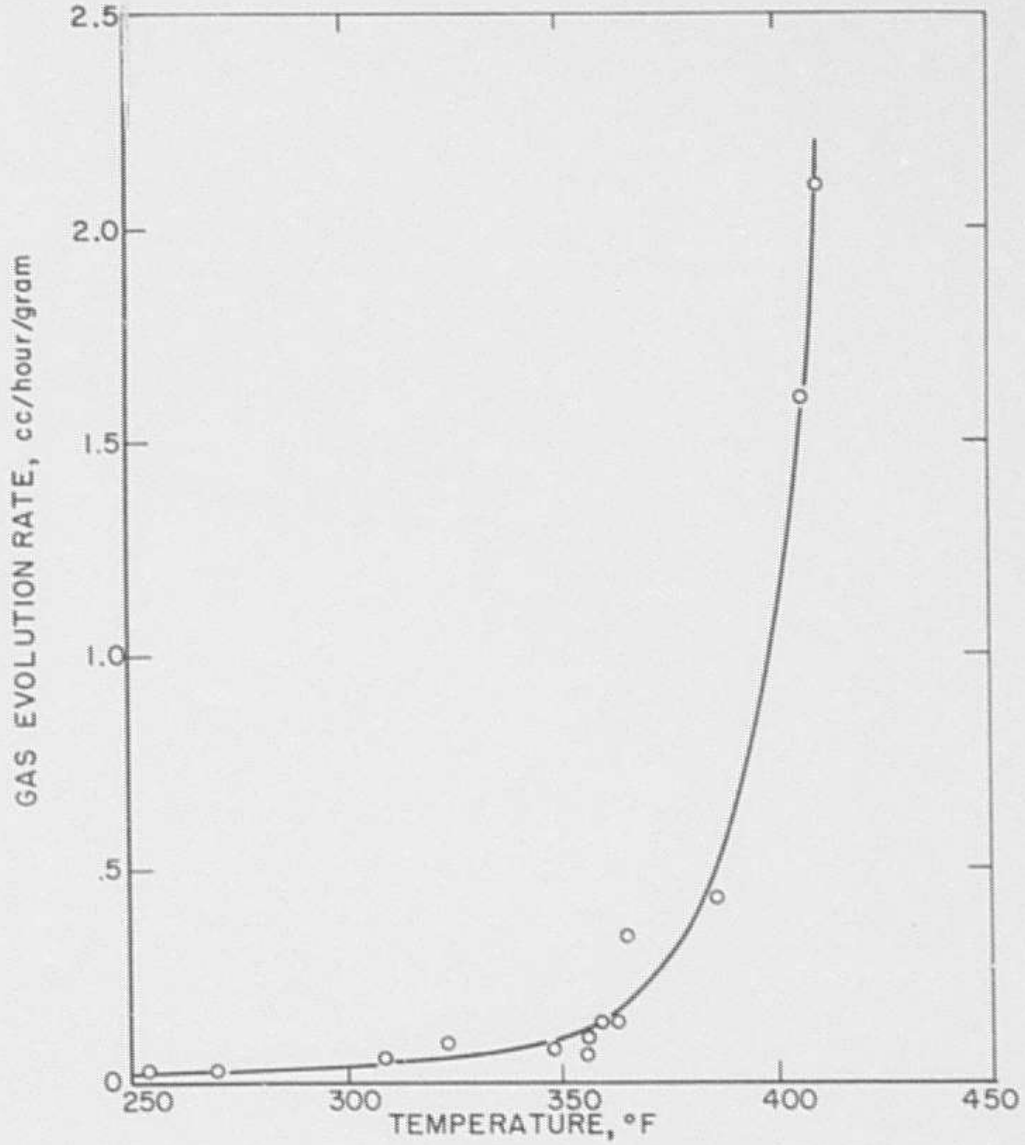

FIGURE 6. - Gas Evolution Rate of HMX as a Function of Temperature.

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