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Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1969

By Staff, Safety Research Center

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RESEARCH AND TECHNOLOGIC WORK ON EXPLOSIVES, EXPLOSIONS, AND FLAMES: FISCAL YEAR 1969

by

Staff, Safety Research Center[1]

INTRODUCTION

The principal activities of the Bureau of Mines Explosives Research Center during fiscal year 1969 (July 1, 1968, to June 30, 1969) are reviewed in part 1. Part 2 presents short abstracts of the publications issued during this period in the Bureau series and in the outside press. These publications are referenced in part 1 by underlined numbers in parentheses. Other publications, which are not abstracted, are cited in footnotes throughout the paper.

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PART 1.--SUMMARY OF EXPLOSIVES RESEARCH CENTER ACTIVITIES IN FISCAL YEAR 1969

As in previous years, the primary objectives of the Explosives Research Center were (1) to prevent loss of life and waste of material resources by identifying and eliminating the causes of accidental fires and explosions in the coal mining and other mineral industries and in aircraft and other flight vehicles; and (2) to develop safer and more effective procedures for the industrial and military utilization of fuels and explosives. The Center's activities were again divided into two main programs--Explosions, Flames, and Combustion Research and Explosives Research and Evaluation. These programs included a series of long-term experimental and theoretical studies aimed at a better understanding of the chemical and physical mechanisms involved in

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[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.

combustion and detonation processes. In addition, a number of short-term investigations were conducted; these were generally limited to an individual compound or class of compounds (fuels, blasting agents, hazardous chemicals, inertants, and extinguishants).

Research directed toward the prevention of coal mine fires and explosions again emphasized the special safety problems of underground mines that are both dusty and gassy. Extensive experiments were completed using rock dust to inhibit flame in mixtures of methane, coal dust, and air, and conditions were established for extending this line of investigation to other flame inhibitors. Aerodynamic studies yielded new information on the mechanism whereby coal dust deposits are eroded and dispersed into flammable clouds by weak methane explosions. A halogenated quenching agent (Halon 1301), which had proved exceptionally well suited as a fire extinguishant in space-vehicle compartments, was used experimentally against several types of coal fires.

In more fundamental research on the combustion of gases and dusts, evidence was obtained of an essential difference between the electric-spark ignition of flammable dust and that of flammable gas. Progress was also made in observing the reaction of individual coal particles exposed to intense radiation (laser beam) and the action of the irradiated particles toward methane-air atmospheres. Recently developed light-scattering techniques were evaluated as a preliminary to a study of molecular reactions associated with the thermal ignition of gases. Another phase of the Bureau's long campaign against environmental pollution caused by combustion processes was concluded with a study on possible catalytic effects of burner surfaces in the production of pollutants by gas flames.

Research in support of the manned space flights was again directed toward the problem of explosive ignition ("hard start") in Apollo attitude-control engines. Earlier flame-quenching experiments with Halon 1301 were extended to burning cotton sheeting. Small-scale firings in very high vacuum were continued to explore the feasibility of using conventional high explosives to exploit lunar mineral resources, and preparations were made for a large-scale study of the problem. An investigation to evaluate the hazards of disposing of waste hydrogen by flaring was completed.

In the long-term program to promote safety in conventional aircraft, a number of flame-arrester packings were evaluated for their effectiveness in preventing flame flashback into fuel tanks. The flammability characteristics of jet fuels and oils were again determined over a wide range of pressures and temperatures. In a closely related program, work was started to evaluate thickened (controlled-flammability) aircraft fuels as a potential means of minimizing postcrash fire hazards. Test procedures recently developed by the Bureau for this purpose were applied.

Condensed-phase explosives again were the subject of a number of fundamental studies ranging from their initiation by gas explosions to the molecular structure and reaction of their detonation products. Efforts were continued to devise new methods for the assessment of energy released from explosives and hazardous chemicals. Electrical phenomena associated with detonation were again explored as a means of characterizing the course of the detonation reaction. Low-velocity detonations and their transition to high-velocity detonation continued to be the subject of experimental and mathematical work that yielded considerable evidence in support of a theoretical model developed previously to describe events within the reaction zone.

In the field of mining explosives, four ammonium nitrate slurries developed experimentally by the Bureau met safety requirements specified by the Bureau for use in gassy mines. Two new commercial formulas were approved as permissible. The relative safety of a series of gelatinous and granular permissible explosives was evaluated in a flammable methane-coal dust environment. A study of the incendivity of electric blasting caps currently used in coal mines was conducted.

The Bureau continued to provide industry and Government agencies with information on the fire and explosion hazards of various materials submitted for evaluation. A major step-up in this activity was made possible by the development of a semiautomated apparatus for measuring the limits of flammability of liquid and gaseous fuels. Large-scale spill experiments were conducted to evaluate the hazards associated with marine transportation of liquid natural gas; techniques developed for this purpose will be applied in a new, similar study on liquid chlorine. An earlier study on the detonability of condensed-phase nitric oxide was extended to include the gas phase. The burning rates of nitromethane mixtures were determined as a function of pressure.

Assistance was given the Department of the Air Force in establishing the cause of an explosion in a jet fuel pumphouse, an in-flight fire and subsequent crash of an F-4 aircraft, and a hangar fire that destroyed two F-4 aircraft and killed three men. At the request of the Commonwealth of Puerto Rico, a field survey was made of a number of Puerto Rican gas and liquefied-gas industries; training and recommendations on related safe practices were also provided. Assistance was given the Indiana Public Service Commission in taking necessary measures to prevent accidents such as the gas explosion which occurred at Richmond, Ind., in April 1968.

Twenty-four papers were published in the Bureau series and other scientific publications during fiscal year 1969. Five papers were presented at meetings and conferences. Courses and lectures were given as needed to disseminate information on the storage, transport, and handling of explosives.

Explosion, Flame, and Combustion Research

Inhibition of Coal Dust-Methane Flames

Apparatus-related problems were identified and corrected by major modifications to existing equipment. Measurements were made to determine the rock dust/coal dust ratio and the rock dust/(coal dust + methane) ratio required to inhibit flame propagation in dust clouds of known concentrations (up to about 450 mg per liter) with nearly uniform radial and vertical concentration profiles. No preferential dispersion of coal dust over the heavier rock dust occurred during generation of dust clouds. Duct walls were heated electrically to avoid wall-quenching of the flame. With the duct walls heated up to about 250° C, flame speeds were about 100 to 275 cm/sec; coking of coal by the duct walls was minor. These experiments established that a 15-cm-id, 3.6-cm-long duct could be used to study the inhibition of coal dust flames by rock dust and other flame inhibitors. Quenching by the wall is not significant if the coal concentration is stoichiometric or more and the wall temperature is at least 100° C.

Aerodynamics of Formation of Clouds of Float Coal Dust

The aerodynamic characteristics of airflows in a small wind tunnel were investigated with a hot-wire anemometer (16). The air velocities and turbulence intensities computed from boundary layer theory were in agreement with measured values. High-speed movies were taken of dust as it was being dispersed; the minimum air velocities required for dispersion of variously shaped piles were measured. Dust beds were prepared from Pittsburgh seam coal, from rock dust, and from mixtures of the two; beds were also prepared from rock dust containing anticaking agents and from glass beads. A shear-force apparatus was used to obtain a second measure of the force required to disperse a dust pile. The empirical fits of wind-tunnel and shear-force data indicated that the minimum air velocities were functions of the bulk density, shear strength, and length of the pile in the direction of the airflow.[2]

A fast-response weight cell was used to measure the rates of dispersion of various dust piles. In fast dispersion, dust beds were fractured at the leading edge into relatively large masses that were lifted into the airstream. In slow dispersion, particles were lifted almost individually or in relatively small aggregates.

Heterogeneous Ignition by Intense Radiation (Laser Radiation)

A technique for measuring radiation-intensity contours in a laser beam was developed and used to determine the radiant energy required to ignite combustible particles suspended in various oxidizing atmospheres. Groups of approximately 100 coal particles with diameters of 60 to 80 microns, suspended in air in concentrations of about 50 mg per liter, ignited when the radiant energy exceeded 0.2 mj per particle. As against that, ignition of individual particles in this size range required approximately 8 mj per particle. This showed the pronounced cooperative effect associated with dust cloud ignitions. Streak photographs of the burning particles were used to measure particle lifetimes as a function of environment and particle conditions.

A distinct difference was noted in the ignition and combustion mechanisms of irradiated anthracite and bituminous coal particles. A 60-micron bituminous coal particle subjected to 50 j/cm^2 appeared to explode and burned completely in less than 1 msec. The same size anthracite coal particle disintegrated into a few large fragments that did not appear to burn

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[2] Singer, J. M., E. B. Cook, and J. Grumer. Dispersal of Dust Piles. Pres. at Internat. Conf. of Safety in Mines Research, Tokyo, Japan, November 1969, 19 pp. Preprinted for Conference.

appreciably. The minimum laser intensity required for ignition of these particles was found to vary approximately as the 5/2 power of the particle diameter. The energy requirements for the ignition of these particles were essentially the same in pure oxygen as in air, suggesting that the ignition process is not controlled by oxygen diffusion. The burning lifetime of the particles in air varied from 1/5 to 1/10 of the values previously recorded in low-temperature furnace experiments, indicating the pronounced effect of the laser radiation on their ignition and combustion.

When irradiated particles were used as ignition sources, the laser energy required to ignite stoichiometric methane-air mixtures decreased with increasing particle size; this is opposite to the results observed for particle ignition in air. The minimum radiation energy required to ignite a 25-micron-diameter magnesium particle in air was much less than the minimum energy that must be supplied to the same size particle for ignition of a stoichiometric methane-air mixture.

Practical Aspects of Inerting and Extinguishment

A short study was completed on the possible application of new chemical extinguishing agents to fires in culm banks and mines.[3] Bromotrifluoromethane (Halon 1301), which had been shown to be exceptionally well suited as a fire extinguishant in space-vehicle compartments,[4] was chosen as representative of the halogenated hydrocarbon extinguishants. It was used experimentally in the following combustion conditions: The "smoldering" of coal dust with a reaction zone temperature of 360° to 520° C; the burning of an individual charcoal briquet in an airstream (550° to 620° C); the burning of charcoal on a grate (fuel bed temperature, 700° to 850° C); and the burning of bituminous coal on a grate at bed temperatures approaching 1,000° C.

No critical (minimum) reaction zone temperature was found for the effectiveness of Halon 1301 with the experimental arrangements used. The dominant consideration was probably the diffusion of the extinguishant to the "seat" of the fire. In the grate fires, the addition of Halon 1301 inhibited the oxidation of CO to CO_2 but had little observable effect on the fuel bed temperature. In the burning of individual charcoal briquets with a directed airstream, extinguishment was achieved quickly at 2.0 percent Halon 1301 and more slowly with 0.8 to 1.0 percent Halon 1301. In the smoldering combustion of coal dusts, Halon 1301 was conspicuously more effective than nitrogen with one sample of dust but not with another sample.

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[3] Burgess, D. S., and J. N. Murphy. Some Experiments With the Application of Bromotrifluoromethane to Coal Beds. Pres. at Internat. Conf. of Safety in Mines Research, Tokyo, Japan, November 1969, 17 pp. Preprinted for Conference.

[4] Burgess, D. S., G. H. Martindill, J. N. Murphy, F. J. Perzak, J. M. Singer, and R. W. Van Dolah. Inerting and Extinguishment of Aerozine-50 With Water and/or CF_3 Br. J. Spacecraft, v. 6, No. 11, November 1969, pp. 1259-1268.

Thermal Ignition Processes in Gaseous Systems

A program was initiated to study the thermal ignition of gases at the molecular level; newly developed light-scattering techniques were used to establish the relevant physical and chemical processes. A preliminary survey of existing information indicated that, whereas considerable work has been done on the effect of physical perturbations on light-scattering, relatively little is known about the influence of chemical perturbations. These latter reactions will therefore be emphasized. Efforts were made to extend the linearized Rayleigh-Brillouin theory of light-scattering to include nonlinear effects.

Construction of an experimental facility was essentially completed. This includes a thermostatic flow reactor, a laser radiation source with a very narrow band width, and a low-level photon counter for measuring the intensity and frequency of the scattered radiation.

Minimum Energy for Dust Ignition

Spark ignition studies were extended to flammable dusts dispersed in air to obtain data for direct comparison with values obtained earlier for gas-air mixtures. Experimental investigations indicated that the electrical energy required for ignition of dust in air dispersions might be greater when the discharge was produced by a condenser charged to a high voltage than when a low-voltage condenser was discharged through the primary of a step-up transformer. The gas-ignition efficiencies of the high-voltage condenser discharge and of the low-voltage discharge through pulse transformers approached one another. Coal dust dispersions are ignited with smaller stored energy if the step-up transformer is designed for audiofrequency operation than if the pulse transformer is designed for radiofrequency use. Thus, the ignition mechanisms of flammable gas mixtures and dust dispersions in air appear quite different. In particular, dust ignition is quite sensitive to the duration and time spacing of the electrical discharges.

Electrical Initiation of Gas Detonations

A digital computer program applicable to gas detonations was written and checked. The program allowed for the possible presence of condensed species in the reaction products and permitted calculation of the shock produced by reflection of the detonation wave at a rigid wall. This was achieved with unexpected accuracy for gas mixtures that can be represented by the equation of state for ideal gases. At a 0.25-atmosphere initial pressure, the experimental and computed values of the reflected detonation wave pressure from a stoichiometric ethylene-oxygen mixture agreed to within 3 percent; agreement was not as good in the case of ethane, propane, and butane.

Other experimental efforts were directed toward the extremely complex problem of the minimum energy transition to detonation. Comparison of events associated with ignition at energies slightly above or below the minimum for initiation of detonation suggests that in the one case a second shock occurs that reinforces the first to produce a detonation.

Hydrogen Safety

Investigation of fire and explosion hazards in hydrogen-flaring was completed. Blowout and flame-lift limits of hydrogen diffusion flames were determined with and without added inert gases. The temperature, geometry, and burning rate of the neat flames were measured. The use of a reverse flow seal to prevent mixing of air with hydrogen in a flare stack was investigated. The blowout limit for a hydrogen diffusion flame was found to be 10^8 sec^{-1}; its average temperature was about 2,600° F, with spot instantaneous temperatures of about 3,600° F. These values may be compared to an adiabatic flame temperature of 3,812° F for a stoichiometric hydrogen-air flame and a computed diffusion flame temperature of about 3,000° F based on radiation measurement.

In connection with this investigation a computational procedure was developed for predicting mixing spread of buoyant and momentum-controlled hydrogen plumes. The method is also applicable to air pollutants exhausted into the open.[5]

Hypergolic Ignition and Combustion

Experiments were continued to determine the cause of "hard-start" ignitions in the Apollo 100-lb-thrust attitude-control engines in a space environment. An intensive study was made of the product spectrum for the gas-phase reactions involving hydrazine, monomethylhydrazine, unsymmetrical dimethylhydrazine, or Aerozine-50 with gaseous nitrogen tetroxide. A two-dimensional plastic rocket engine and a low-pressure gas-phase flow reactor were used in this work. Condensed-phase reaction products were analyzed by infrared spectrometry; gaseous products were analyzed by mass spectroscopy. Hydrazine azide, tetramethyl tetrazene, and hydrazine dinitrate, which had been identified as minor constituents of the reaction products, were prepared in the laboratory and evaluated for TNT equivalence and impact sensitivity.[6]

Initiation of condensed-phase hydrazine mononitrate by an ethylene-oxygen gas detonation indicated that granular hydrazine nitrate underwent an explosive reaction with a velocity of approximately 2 mm/ms, even with gas detonation shocks as low as 7,000 psi. A study of the explosibility of a hydrazine-hydrazine nitrate solution, containing 75 percent by weight hydrazine nitrate, showed that the mixture was initiated to detonation not by shock from the gas detonation but by the high-temperature product gases behind the gas detonation front. It was also shown that an intense shock propagating down a pipe coated internally with hydrazine or hydrazine nitrate solution took part in a detonative combustion process. Both these explosive mechanisms are believed to be relevant to the explosive ignition processes observed in the Apollo attitude-control engines.

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[5] Cook, E. B., and J. M. Singer. Predicted Air Entrainment by Subsonic Free Round Jets. J. Spacecraft, v. 6, No. 9, September 1969, pp. 1066-1070.

[6] The TNT equivalence values for the azide, tetramethyl tetrazene, and dinitrate were 144, 50, and 75, respectively. Thus, only the azide was more powerful than TNT in this test. The impact sensitivity of the azide and dinitrate were 815 kg-cm and 115 kg-cm, respectively. The impact sensitivity of the tetrazene was not determined.

Fire and Explosion Hazard Assessment and Prevention Techniques for Aircraft

Experiments were continued to evaluate the effectiveness of various materials for packing flame arresters. In small-scale experiments, randomly packed 3/4-inch-diameter hollow polyethylene spheres were less effective than 1-inch-diameter spheres with the same size perforations. Large-scale experiments indicated that higher than random packing densities (<65 percent) are required for the spheres to protect aircraft fuel tanks effectively against explosions. The spheres were less effective in suppressing vapor-phase explosions than the reticulated polyurethane foam with 10 pores per inch evaluated in earlier work (8).

Earlier research[7] on the flammability of fabrics in oxygen-rich atmospheres was extended in a series of large-scale fire experiments using cotton sheeting burning in air at atmospheric pressure to evaluate the effectiveness of Halon 1301 (bromotrifluoromethane) as an extinguishant for aircraft fires. At a combustible loading of 1 g/ft^3, a 6-percent-Halon concentration extinguished the cotton sheeting fires within about 2 seconds or less, depending upon the burning period and the Halon injection pressure. As expected, the concentration of toxic products (CO_2, CO, Br_2, HBr, HF) decreased greatly when the burning time decreased.

A study was initiated on the hot-surface ignition of aircraft combustible fluids, under stagnant and flow conditions, with nonuniform heating. Initial results indicated that when JP-4 and JP-8 fuels and MIL-L-7808 lubricating oil are injected onto a 2-inch-diameter heated target (9 inches long) their respective ignition temperatures are several hundred degrees higher than the corresponding autoignition temperatures measured in uniformly heated vessels. This apparent decrease in ignition hazard is observed even in stagnant air and at very low airflows (<1 ft/sec).

Controlled-Flammability Fuels

Nine thickened (gelled or emulsified) aircraft fuels were evaluated by the fire hazard rating system developed by the Bureau for the Federal Aviation Administration (10). The fuels were either new formulations or earlier formulations modified to give a higher yield stress. Increasing the yield stress of a thickened fuel improves its safety rating, but greater pumping difficulties can be expected with the more viscous fuels.

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[7] Kuchta, J. M., A. L. Furno, and G. H. Martindill. Flammability of Fabrics and Other Materials in Oxygen-Enriched Atmospheres. Part I. Ignition Temperatures and Flame Spread Rates. Fire Technol., v. 5, No. 3, August 1969, pp. 203-216.
Litchfield, E. L., and T. A. Kubala. Flammability of Fabrics and Other Materials in Oxygen-Enriched Atmospheres. Part II. Minimum Ignition Energies. Fire Technol., v. 5, No. 4, November 1969, pp. 341-345.

Flammability Hazards of Thickened Fuels

In preparation for a new investigation to evaluate the behavior of thickened fuels under postcrash conditions, construction was started on two new experimental facilities. The first is a drop system consisting of three 150-foot-high towers in which tanks with capacities up to 100 gallons can be impacted at velocities of up to 60 miles per hour. The impact angle can be varied at will by the three-tower system from vertical (straight drop) to horizontal. The second facility is a laboratory wind tunnel, 1- X 2-foot cross section, to be used for a mechanical study of atomization and breakup and the ignition and propagation characteristics of candidate fuels. High-speed cameras and thermal radiation sensors will be used to record the reactions of the fuels.

Vaporization and Ignition Hazards of Liquid Natural Gas Spilled on Sea Water

An investigation was completed of hazards associated with possible spillage of liquefied natural gas (LNG) during maritime transportation. Small-scale spills of LNG onto water were conducted in a 2-ft^3 aquarium. The new 200-ft-wide, 25-ft-deep pond at Bruceton, Pa., was used for large-scale experiments in which about 2,000 gallons of LNG were consumed.

The initial vaporization rate of LNG was found to be 0.037 $lb/ft^2/sec$. When the spill was confined, this vaporization rate was moderated after about 20 seconds by the growth of an ice layer on the water surface. With unconfined spills, no coherent ice floe was observed, and the vaporization rate was essentially independent of time. It was found that the maximum diameter of the spreading LNG pool could be expressed as $6.3\ W^{1/3}$, W being the weight of LNG in pounds. Downwind of a natural gas source, time-averaged methane concentrations were given in good approximation by standard air pollution equations; however, peak concentrations were as much as 20 times higher than average, adding an additional factor to hazard assessment. Layering of the cold, evaporating natural gas had about the same effect on its dispersion as a strong temperature inversion in the atmosphere.

Hazards of Liquid Chlorine in Marine Transport

A study was initiated to establish the extent and persistence of toxic clouds formed by the accidental release of chlorine (1 to 3,000 tons) in or under water. Parameters to be investigated are the water temperature, the chlorine feed rate, and the purity of the water. Apparatus was assembled for bubbling chlorine gas through water with flow control down to 3 cm^3/min.

Detonability of Gaseous Nitric Oxide

An earlier investigation on the detonability of condensed-phase nitric oxide (NO) was extended to include its behavior in the gas phase. NO decomposes exothermally (+0.72 kcal/g) and thus provides the possibility of introducing additional enthalpy into a heated airstream to achieve the high temperatures associated with Mach numbers 8 to 9.

A 7-inch-id by 12-foot-long chamber was evacuated and filled with nitric oxide to 1 atmosphere initial pressure. The ignition source was an explosive charge suspended at one end of the chamber and initiated by an electric blasting cap. Propagation rates were measured with shock-sensitive probes over a length of 50 cm at the downstream end of the chamber. Using PETN or Composition A-5, the go/no threshold is roughly defined as follows: A 60-gram-PETN charge initiates detonation of the nitric oxide at 1 atmosphere pressure; and a 40-gram-PETN charge does not initiate detonation. A deflagration-type reaction occurred with as little as 10 grams of PETN. Such shock-induced reactions have been observed previously in fuel-oxidant systems.

Experiments were also conducted at pressures near 350 psig. A 3.25-inch-id by 4-foot-long chamber was filled as before and the same type of velocity probes were employed. Results indicate that the NO charge detonated when initiated by 20 grams of PETN. Deflagration occurred when 9 grams of PETN or less was used as the initiator.

Monopropellant Consumption Rate of Nitromethane

Consumption rates as a function of pressure were determined for nitromethane (NM), neat and mixed with tetranitromethane (TNM), in nitrogen atmospheres. At pressures of 1,000 to 2,000 psig, neat NM gave laminar burning with rates of 0.056 to 0.125 inch per second. With 10 percent TNM, laminar burning rates of 0.015 to 0.17 inch per second were measured at nitrogen pressures from 200 to 1,600 psig. The burning changed from laminar to turbulent for NM mixed with 20, 30, and 40 percent TNM at 1,100, 500, and 350 psig, respectively. The laminar consumption rates were less than 0.2 inch per second, whereas the turbulent rates ranged from 0.6 to 20 inches per second. Consumption rates of NM in air were also determined. In 13-mm-id glass containers, NM burned in air at nearly the same rate as in 7-mm-id glass tubes in nitrogen. These rates went from 0.055 inch per second at 1,000 psig to 0.125 inch per second at 2,000 psig. At lower pressures, burning was not sustained.

Flame Characteristics Causing Air Pollution

Experiments to determine whether burner surfaces exert a catalytic action on reactions in flames involving air pollutants were concluded. Concentrations of oxides of nitrogen, carbon monoxide, and light hydrocarbons were lower in flame gases from a ceramic infrared burner than from metallic noninfrared burners. There was no evidence of a catalytic effect on the formation of nitrogen oxides caused by contact of the burner surface with lean and stoichiometric flames. Experiments did not allow a conclusion as to possible catalytic action of the burner surface on the formation of nitrogen oxides in rich flames.

Flammability Limits and Autoignition Temperature:
New Concepts and Experimental Methods

The new limit-of-flammability apparatus was modified to permit rapid determinations on single-composition mixtures of liquid fuel vapor or gas, oxidant, and diluent. Because of cost considerations, design changes were limited to semiautomated operation. Modifications or improvements included addition of a precision liquid-feed pump with a 10-turn potentiometer speed control, a liquid-feed monitoring transducer, and retractable ignition electrodes. A torque limiter and travel-limit switches were installed to protect the stem device that drives the porous gas piston into the flammability tube (6-inch-id). Initial flammability data for n-hexane vapor-air mixtures agreed well with published values.

Explosives Research and Evaluation

Evaluation of Permissible Explosives in Predispersed Coal Dust

Work continued in the long-term program to evaluate the effect of various physical and chemical characteristics on the relative safety of permissible explosives in dusty and/or gassy mines. Eighteen granular and four gelatinous permissible explosives were evaluated for incendivity in mixtures of coal dust, natural gas, and air. The charges were fired unstemmed from a cannon into a mixture of 4 percent natural gas and 0.2 ounce per cubic foot (200 mg/l) coal dust predispersed in air. The weight of explosive, for which there is 50 percent probability of igniting the coal dust-natural gas atmosphere (W_{CDG}), ranged from 257 to over 906 grams for the granular explosives and from 288 to 660 grams for the gelatinous explosives.

Explosive Characteristics of Ammonium Nitrate Slurries

Results of an earlier study on ammonium nitrate slurry explosives (24) were applied in the development of four slurries which met the safety standards required for permissible explosives with respect to gassy atmospheres and which can be stored for several months. Two of the slurries had low densities ($\rho = 0.65$). One was pumpable; the other was cross-linked to a semirigid form suitable for packaging. The remaining slurries were denser ($\rho = 1.0$) and contained more aluminum, which gave them greater strength; their ballistic mortar value was 104 percent TNT, as compared to 77 percent TNT for the low-density formulations.

It was shown experimentally that when a minimum of 4 percent leafing-grade aluminum was added to the slurry as sensitizer, much less expensive grades of aluminum could be used to make up a total of up to 12 percent aluminum, without affecting the cap-sensitivity of the slurry.[8] Fumes were determined for six formulations representative of those developed at this laboratory; the resulting values ranged from 0.05 to 0.125 cubic feet per pound.

Potential Explosives for Ultrahigh Detonation Pressures

An attempt was made to explore the feasibility of obtaining detonation pressures from 500 to 1,000 kilobars by means of new ultrahigh-density

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[8] Mason, C. M., E. C. Lisotto, T. C. Ruhe, and R. W. Van Dolah. Further Development of Nonincendive Water Gel Explosives. Pres. at Internat. Conf. of Safety in Mines Research, Tokyo, Japan, November 1969, 20 pp. Preprinted for Conference.

explosives. Several formulations containing tungsten, hafnium, or hydrazine azide with bromine pentafluoride, iodine heptafluoride, and/or ammonium perchlorate were selected. The plan was to initiate detonation in a 1-inch-diameter, heavily confined, pressed grain of the formulation considered at a temperature 30° C below its autoignition temperature. As no promising compositions resulted, this program was terminated.

Initiation of Condensed-Phase Detonation by Gas-Phase Detonations

Pressures, reaction velocities, and delay times were measured for condensed explosives (PETN, RDX, Composition A-5, tetryl) initiated by a gas detonation wave established in a stoichiometric ethylene-oxygen mixture. Under rigid confinement, flour PETN and small crystal RDX ran up to detonation with gas-charging pressures of 1 atm. Composition A-5 granules did not run up to detonation at gas-charging pressures below 8 atm; pelletized explosives required significantly higher gas-charging pressures.

A gas detonation computer program, which includes reflection of the detonation wave at a rigid surface, was written. The calculated values were used to evaluate the experimental data.

Behavior of Detonation Products of Condensed Explosives

A new fundamental study was initiated to investigate the equation of state and the gasdynamic-kinetic behavior of the detonation products of a condensed explosive. A theoretical analysis of the equilibrium concentrations of large clusters in the products was undertaken to determine their importance in the equation of state. The main problem was to deduce the normal vibration modes of a cluster containing up to about 100 molecules and to establish the vibration energy of each mode. The normal modes of clusters containing up to 14 molecules were calculated; inclusion of nonnearest neighbors was significant although the classical approach ignores them. The potential energy curves of the resulting modes generally were decidedly anharmonic; the energy levels are being analyzed.

An abridged version of the theoretical equations for the 1-D method of characteristics analysis of nonsteady-state gasdynamic-kinetic phenomena in and after an expansion fan was prepared and is being debugged.

Mathematical Models of Growth of Explosions in Condensed-Phase Explosive Systems

Attempts were made to develop a computer program for the one-dimensional model of transition from deflagration to detonation in granular explosives, especially the final stage of the process in which detonation develops from compression initially induced by the accumulated deflagration products. The problem is complicated by the necessity of dealing with a multiphase fluid having various components that obey different equations of state. The quadratic Hugoniot equation of state (in which the pressure is a quadratic function of the particle velocity and which fits most substances) was used for the reacted solid material. The polytropic gas equation was applied to the detonation products. The Nobel-Abel equation was used for the interstitial gas during the early stages of reaction. To calculate temperature rise, the thermal energy was computed as the difference between the work done by the compression wave and the sum of the increase in kinetic and compressional energies. Difficulties were encountered due in part to insufficient numerical stabilization. A simple technique was developed for improving the stability of finite difference calculations of the partial differential equations arising in shock hydrodynamic problems.

Energy Transfer Studies

Efforts were continued to establish a relation between the total energy released by a detonating explosive and the total work that it performs. The objective is to develop methods of maintaining and increasing the useful output of commercial explosives and blasting agents.

The kinetic energy transferred from a composite explosive charge to its casing was measured with a precision streak camera. Charges with 1.0-inch-diameter cores of inert and reactive materials, highly confined and centered in 1.5-inch-id copper tubes filled with nitromethane, were used. The unit casing energy per unit mass of nitromethane was used as a figure of merit in interpreting the experimental results. Highly compressible inert core materials seriously degraded the energy transfer. With reactive core materials such as pentaerythritol tetranitrate (PETN), ammonium nitrate-fuel oil (AN-FO), ammonium perchlorate, prilled ammonium nitrate, and a composite aluminum-ammonium perchlorate propellant, the energy transfer was considerably higher. This suggests a substantial contribution by the reactive materials. The technique used in these experiments may be applicable to the assessment of hazards from energetic substances not ordinarily considered to be explosives.

Multidisciplinary Research for Utilization of Extraterrestrial Resources

Studies were continued to develop information on the use of high explosives in a high vacuum, such as the moon's atmosphere. Firings were completed over the pressure range from 1.0 to 1.8 X 10^{-7} torr. Photographic observations were made of the charge profile and in some cases a 45° mirror was employed to view simultaneously the free end of the charge and the impact of the detonation products on the flask walls in the direction of detonation. The velocity of the fastest detectable ejecta was approximately 22 km/sec and was constant over the pressure range from 10^{-3} to 10^{-7} torr. This material was invisible against the background lighting. Its presence was indicated by a bright impact glow localized in the region on the wall of the flask on a line with the axis of detonation. An opaque products cloud, suggesting the presence of free carbon, traveled at approximately 8 km/sec in the direction of detonation, its velocity remaining sensibly constant between 10^{-3} and 10^{-7} torr. Below 10^{-3} torr there was no visual evidence of a shock wave. At 10^{-3} torr, the opaque products cloud was enveloped by a faint blue shock wave that advanced at approximately 22 km/sec, whereas the opaque products cloud maintained a velocity of about 8 km/sec in the direction of detonation. At 1 torr, the shock velocity had decayed to about 13.5 km/sec, while the opaque products cloud apparently maintained a velocity of about 8 km/sec. It was also noted that the self-luminosity of the detonating charge was very rapidly quenched at low pressures, apparently in less than the 1-μsec interframe time used in the experiment.

In preliminary experiments, a 1-inch-diameter by 1-inch-long pellet of Composition A-5 (RDX + 1 percent wax) was subjected to vacuums ranging from 5×10^{-7} to 5×10^{-8} torr for as long as 72 hours. The vapor pressure of Composition A-5 was less than 10^{-8} torr at ambient temperature.

The expansion of detonation products in a high vacuum was studied in 22-liter glass flasks with 2-inch-diameter spherical charges at 10^{-8} torr. The expanding products attained a velocity of 20 km/sec, which remained essentially constant until they impinged on some obstructing surface. Pressure measurements in the expanding products cloud from a detonating solid explosive showed that the peak stagnation pressure in a high vacuum is roughly one-half the reflected shock pressure in air at the same distance from the charge. The pressure rose rather gradually, taking 5.0 sec to reach a peak; the rise time appeared to increase with increasing distance from the charge.

In the course of this work, some extremely interesting luminous phenomena were observed when the expanding products impinged on the walls of the vacuum vessel. There was a wide variation in coloring suggesting a spatial separation of the chemical constituents of the products; these observations may lead to a more fundamental understanding of the structure of the detonation zone in high explosives.

Propellant Ingredient Safety

The complex wave phenomena accompanying low-velocity detonation were studied to determine the relative positions of the precursor wall waves and the reactive shock wave. The liquid explosive system was loaded into containers of various materials and shock-initiated; corresponding water-filled systems were used as controls. Nitroglycerin-ethylene glycol dinitrate (NG-EGDN) in plexiglass, aluminum, lead, polyethylene, and glass gave respective wall wave velocities of 2.2, 5.1, 1.2, 1.9, and 5.0 mm/μsec and reactive shock wave velocities of 1.4-2.0, 1.9, 1.7, 1.4, and 1.6 mm/μsec. In all but the lead container, low-velocity detonations were observed at essentially constant velocities below the wall wave velocities. In the lead container, where the elastic wall wave velocity was less than the reaction wave velocity, unstable pulsating detonations were observed. These results agree with the model for low-velocity detonation previously developed in this program, which postulates precavitation ahead of the reaction zone produced by precursor waves in the container wall (6).[9]

Minimum film thicknesses for propagation of detonation were determined by the wedge technique (14) for various mixtures of NG-EGDN and nitromethane (NM).

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[9] Watson, R. W. The Structure of Low-Velocity Detonation Waves. 12th Symp. (Internat.) on Combustion. The Combustion Institute, Pittsburgh, Pa., 1969, pp. 723-729.

NM does not exhibit a low-velocity detonation and is used to inhibit low-velocity detonation in NG-EGDN. Both high- and low-velocity detonations were measured in steel trays. Minimum film thicknesses for high-velocity detonation ranged from 0.18 to 0.2 inch for neat NM and neat NG-EGDN, respectively. Minimum film thicknesses for low-velocity detonation ranged from approximately 0.60 inch for 80 percent NM-20 percent NG-EGDN to ≤0.01 inch for neat NG-EGDN. Transitions from high- to low-velocity detonations were observed in mixtures with more than 25 percent NG-EGDN. No low-velocity detonations appeared in neat NM or in mixtures containing less than 20 percent NG-EGDN.

Minimum film thicknesses for a system consisting of NM and a commercially available desensitized nitroglycerin (NG_d) were established for both the high- and low-velocity regimes at various concentrations. For a high-velocity detonation, minimum film thicknesses ranged from 0.18 inch for neat NM to approximately 0.08 inch for neat NG_d. Minimum film thicknesses for low-velocity detonations ranged from approximately 0.61 inch for 50-50 NM/NG_d to 0.03 inch for neat NG_d. Transitions from high- to low-velocity detonations may occur in mixtures containing more than 53 percent NG_d. No low-velocity detonations were observed in mixtures containing less than 50 percent NG_d in NM.

Detonation Zone Structure and Reaction Kinetics

The report period was devoted primarily to investigating the buildup of detonation in condensed-phase secondary explosives as indicated by the growth of electrical conductivity and luminosity in shock-initiated liquid acceptors. Shock detectors and measuring circuits with a resolution of less than 10 nanoseconds were developed for this purpose. The growth of reaction in shock-initiated NM was measured over a wide range of diluent concentrations, shock inputs, and ambient temperatures. However, the great sensitivity of the induction time to even small perturbations in the shock amplitude resulted in considerable scatter of the experimental results. Attempts are being made to correct this by stimulating inhomogeneities in the charge caused by electronic probes and by placing stringent requirements on the performance of the donor charge.

Evaluation of Nonincendive Detonating Cord and Electric Blasting Caps

A systematic evaluation was made of a variety of electric blasting caps. Their incendivity was found to be substantially higher than in a corresponding investigation conducted many years ago. The increased incendivity is attributed to the change in the composition of the base charge from tetryl to PETN.

Testing of Explosives and Hazardous Materials

A number of potentially explosive compounds and mixtures were examined for their reaction to impact; the TNT equivalence was determined for two compounds (table 1). In addition, one material was tested for sensitivity to pendulum friction and for thermal stability; another was tested for gaseous detonation products.

TABLE 1. - Compounds examined during fiscal year 1969

Compound	Impact test, height,[1] cm (method 1)[2]	Ballistic mortar, strength of TNT, percent
Unsymmetrical dimethylhydrazine carboxylate	>330	-
Tritonal	126	-
H-6[3]	107	-
HBX-3[4]	136	-
Hydrazine dinitrate	23	75
Hydrazine azide	163	-
Tetramethyl tetrazene	-	50

[1] Height of drop of a 5-kg weight for 50 percent probability of ignition.

[2] 0.5-inch-diameter cup with a closely fitting striker pin.

[3] RDX--45 percent; TNT--30 percent; aluminum--20 percent; D-2 wax--5 percent; and calcium chloride--0.5 percent.

[4] RDX--31 percent; TNT--29 percent; aluminum--35 percent; D-2 wax--5 percent; and calcium chloride--0.5 percent.

Two new permissible explosives were submitted and approved in fiscal year 1969. These explosives, formulated with a very high (30-percent) sodium chloride content, are designed as a substitute for black powder. Thirteen field samples of permissible explosives met all schedule 1-H requirements. Two samples passed but were out of tolerance in rate of detonation; one passed but was out of tolerance in chemical analysis. Two field samples of one permissible explosive failed gallery test 7, and the corresponding lots were withdrawn by the manufacturer.

Investigation of Actual and Potential Disasters

At the request of the Commonwealth of Puerto Rico, the Bureau took part in a field survey of the gas and liquefied petroleum gas industries in San Juan and other cities of Puerto Rico. A report was prepared with recommendations for developing improved safety codes, and a 1-week training course was given to representatives of Government and industry on the explosion hazards and safe practices associated with gas or liquefied-gas systems.

At the request of the Air Force, the Bureau of Mines participated in the investigation of the following accidents: An explosion in a JP-4 fuel pumphouse at Plattsburgh Air Force Base, N.Y.; an in-flight fire and subsequent crash of an F-4 aircraft at Homestead Air Force Base, Fla.; and an aircraft hangar fire at the Fifth Air Force Base, South Korea, where two F-4 aircraft were destroyed and three ground crewmen lost their lives.

Assistance was given to various industries for the design and safe operation of systems involving combustible gases and liquid chemicals. A Bureau of Mines representative appeared at public hearings before the Indiana Public Service Commission to testify on the serious gas leakage problem uncovered in the City of Richmond, Ind. Based on the Bureau's subsequent recommendations, the Commission issued an interlocutory order to the responsible utility company outlining necessary repairs and safety measures.

Courses and Seminars

A course entitled "Explosions--Causes, Prevention and Protection," was presented in cooperation with the Manufacturing Chemists Association (Pittsburgh, Pa., Mar. 3-7, 1969). This was the fifth course in the series initiated in 1964. It was attended by 30 participants representing 22 member companies of the Manufacturing Chemists Association.

Storage, handling, and usage of explosives was the subject of several lectures and field sessions conducted for personnel of the Bartlesville Petroleum Research Center and the Twin Cities Mineral Research Center (Bruceton, Pa., Apr. 28-May 1, 1969). At the request of the National Park Service, a 2-day course on explosives was conducted for employees of Shenandoah National Park (Luray, Va., May 12-14, 1969). Monthly seminars and film presentations were continued throughout the year to keep Explosives Research Center personnel informed of developments within the Center and in related research conducted elsewhere.

Meetings and Conferences

Explosives Research Center personnel presented five papers at the following meetings:

Twelfth Symposium (International) on Combustion, Poitiers, France, July 1969: "The Structure of Low-Velocity Detonation Waves," by R. W. Watson. (Published in 12th Symp. (Internat.) on Combustion. The Combustion Institute, Pittsburgh, Pa., 1969, pp. 723-729.)

Tenth Liquid Propulsion Symposium, Las Vegas, Nev., Nov. 19-21, 1968: "Potential Application of Halon 1301 to Hypergolic Propellant Spills and Fires," by R. W. Van Dolah (22).

Society of Automotive Engineers Lightning and Static Electricity Conference, Miami, Fla., Dec. 3-5, 1968 and Society of Automotive Engineers National Air Transportation Meeting, New York, N.Y., Apr. 21-24, 1969: "Spark Ignition. Ignition of Flammable Mixtures as a Consequence of Gaseous Electronic Discharge," by E. L. Litchfield (13).

Sixty-fourth National Meeting of the American Institute of Chemical Engineers, New Orleans, La., Mar. 17-19, 1969: "Detonation Potential of Nitric Acid Systems," by R. W. Van Dolah. (Published in Proc. 1969 Loss Prevention Symp., "Loss Prevention," v. 3, AIChE, 1969, pp. 32-37.)

Sixth Space Congress, Cocoa Beach, Fla., Mar. 17-19, 1969: "Application of Halon 1301 to the Prevention of or Extinguishment of Aerozine-50 Fires," by R. W. Van Dolah and D. S. Burgess. (Unpublished to date.)

Other technical meetings attended by Explosives Research Center personnel included:

Intergovernment Maritime Consultative Organization Subcommittee on the Carriage of Hazardous Goods, Berlin, Germany, Sept. 2-4, 1968, and London, England, Nov. 4-8, 1968.

Armed Services Explosives Safety Board Tenth Annual Explosives Safety Seminar, Louisville, Ky., Aug. 13-15, 1968.

Army Research Office--Explosive Chemical Reactions Seminar, Durham, N.C., Oct. 21-23, 1968.

Symposium on Problems of the Fire Services, Washington, D.C., Oct. 30-31, 1968.

Society of Automotive Engineers A-6C Fluids Panel, Palm Springs, Calif., Sept. 30-Oct. 2, 1968.

Aviation Fuel Safety Group, Coordinating Research Council, Los Angeles, Calif., Oct. 9-10, 1968.

Western Pennsylvania Safety Engineering Conference, Pittsburgh, Pa., Apr. 8, 1969.

Conference on Transportation of Hazardous Materials, Warrington, Va., May 7-8, 1969.

American Gas Association Operating Section Conference, Philadelphia, Pa., May 12-14, 1969.

In addition, Center staff members served on committees of the National Fire Protection Association; the American Chemical Society; the American National Standards Institute; and the American Society for Testing and Materials; and participated in meetings of various Government agencies and private research groups.

PART 2.--PUBLICATIONS DURING FISCAL YEAR 1969[10]

1. 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.

The characteristics of gas-phase detonations were observed in 20 instrumented firings in earthen tunnels, in 100 such detonations in a 24-in-diam by 163-ft-long steel pipe, and in about 200 smaller scale firings. Most of the fuels studied were representative hydrocarbons--acetylene, propane, gasoline, and a roughly equimolar mixture of methylacetylene, propadiene, and propane.

In a pipe with both ends closed, the detonable limits were demonstrated to be very nearly the same as reported limits of flammability. The side-on impulses (pressures integrated over 200-msec intervals) were shown to be the same function of concentration regardless of whether deflagration or detonation had occurred.

In a pipe with only the initiation end closed, the impulses of all fuel-air systems tended toward the same level when averaged over comparable ranges of fuel concentration; the lower pressures with saturated hydrocarbons were nearly compensated by longer durations of pressure transient. In all fuel-air systems, unexpectedly high impulses were obtained with slightly lean mixtures.

In earthen confining structures, the impulse of the explosive was efficiently converted into momentum of the failing wall. In the configurations studied, an earth velocity of about 20 fps was critical to overcome the soil's resistance to shear. The destructive effect was determined by gas pressure rather than by total energy release.

The assignment of a "TNT equivalent" to an explosive gas mixture is discussed in terms of the confinement of the mixture.

2. Cooper, J. C., and D. R. Forshey. Explosive Sensitivity of N-Chlorodimethylamine and N, N-Dichloromethylamine and N, N-Dibromomethylamine. Explosivstoffe, No. 6, June 1969, pp. 129-130.

Determination of the sensitivity of N-chlorodimethylamine, N, N-dichloromethylamine, and N, N-dibromomethylamine to initiation by mechanical impact or to initiation of detonation by shock showed that the dihalo compounds appear to present a greater explosion hazard than N-chlorodimethylamine. Bromine desensitized the dihalo compounds when used in a 3-to-2 ratio with N, N-dibromomethylamine.

3. Forshey, D. R., J. C. Cooper, G. H. Martindill, and J. M. Kuchta. Potential Hazards of Propargyl Halides and Allene. Fire Technol., v. 5, No. 5, May 1969, pp. 100-111.

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[10] Publications are listed alphabetically according to senior author.

The combustion characteristics and detonability of propargyl bromide, propargyl chloride, and allene were investigated as a means to evaluate their hazard in storage, use, and transportation. Susceptibility to compression heating was evaluated by drop-weight impact and detonability by a version of the gap test. Monopropellant consumption rates were measured in the liquid state, and vapor-phase flammability limits were determined as a function of pressure. Propargyl bromide was observed to be readily ignited by impact; propargyl chloride was much less readily ignited. None of the three materials was detonable under the conditions used in the testing. All three materials undergo monopropellant burning. Ignitability and tendency toward monopropellant burning were reduced by dilution with toluene. Propargyl halide vapors form decomposition flames at 1 atmosphere and down to 0.03 psia, although flame propagation is prevented by 30 percent toluene in the vapor.

4. Forshey, D. R., J. C. Cooper, and W. J. Doyak. Detonability of the Nitromethane-Hydrazine-Methanol System. Explosivstoffe, No. 6, June 1969, pp. 125-129.

A study of the detonability of binary and ternary mixtures of nitromethane, hydrazine, and methanol revealed that hydrazine strongly sensitizes nitromethane and nitromethane-methanol mixtures to detonation. However, the binary and ternary mixtures were insensitive in the drop-weight impact test. Hydrazine was found to increase 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 yielded reasonable estimates of the energy content of the mixtures.

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

The recent occurrence of fatal accidents in copper mines, presumably caused by premature ignition of loaded holes by the heat from reacting ammonium nitrate-fuel oil (AN-FO) and pyrite-bearing ores, has led to an examination of this reaction. The reactivity of prilled AN-FO mixtures with pyrite-bearing ores and the effects of water, dilute sulfuric acid, and potential inhibitors on reactivity of the mixtures were evaluated. Initiation of an exothermic reaction was observed as low as 150° F with acid in the absence of inhibitors. Low concentrations of urea, calcium carbonate, zinc oxide, and magnesium oxide were effective in inhibiting the reactivity of the mixtures. The temperatures produced during the reaction of mixtures of AN-FO and pyrite-bearing ores, in the absence of inhibitors, always exceeded the temperature at which electric blasting caps are thermally initiated.

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[11] Also published in slightly shortened form in Min. Cong. J., v. 55, No. 1, January 1969, pp. 34-35.

6. Hay, J. E., and R. W. Watson. Mechanisms Relevant to the Initiation of Low-Velocity Detonations. Ann. N.Y. Acad. Sci., v. 152, art. 1, October 1968, pp. 621-635.

Low-velocity detonation of liquid explosives has been shown to result from liquid breakup through cavitation. The initiation phase of low-velocity detonations has been modeled in experiments in which bubbles formed by pre-induced cavitation or by gas injection are subjected to shocks of controlled amplitude. The results of this study indicate that while impact of microjets can cause initiation when the jets are generated by strong shocks, the primary mechanism for initiation by weak shocks is compression of the gas or vapor in the bubble with microjetting possibly playing an auxiliary role. It is doubtful whether direct shock-heating of the liquid phase or heating by viscous interaction in cavity collapse can be significant at the shock strengths usually associated with low-velocity detonation.

Related studies show that the propagation of low-velocity detonations requires that the effective consumption rate of the explosive at a pressure of a few kilobars be of the order of 10^4 $cm^3/sec/cm^2$ of bubble surface. In liquid-strand burning experiments, which were conducted to verify the possibility of attaining consumption rates of this magnitude, values in excess of 10^3 $cm^3/sec/cm^2$ of the strand cross section were indicated at pressures of a few tenths of a kilobar.

7. Kuchta, J. M., and R. J. Cato. Ignition and Flammability Properties of Lubricants. SAE Trans., v. 77, 1968, pp. 1008-1020.

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

8. Kuchta, J. M., R. J. Cato, W. H. Gilbert, and I. Spolan. Fuel Tank Explosion Protection. BuMines ERC Rept. 4073, March 1969, 31 pp.; ASTIA, AD 849701.

Small-scale and large-scale experiments were conducted to determine the flame-arrester effectiveness of three types of hollow, perforated polyethylene spheres proposed for fuel tank fire and explosion protection. In small-scale experiments, the flame-quenching effectiveness of the spheres decreased with an increase in initial pressure and flame runup distance (ignition void length) and with a decrease in sphere size and packing density. Randomly packed beds of sphere types A (1-inch-diameter, 0.1-inch perforations) and B (1-inch-diameter, 0.05-inch perforations) prevented flame propagation at pressures up to 5 and 0 psig, respectively, whereas sphere type C (3/4-inch-diameter, 0.10-inch perforations) failed at 0 psig. With uniformly packed beds, none of the spheres failed at 0 psig. All three sphere types were noticeably less effective than reticulated polyurethane foam with 10 pores per inch. Results from most of the large-scale gun-firing experiments with randomly packed spheres revealed that the spheres were not effective in arresting flames at 0 psig in a 74-gallon, modified fuel tank. Other data obtained in pressure drop experiments at various air velocities indicated that the flow resistance is slightly greater for sphere type C than for A or B. Empirical relationships are presented for predicting the pressure drop gradients across dry and wet beds of the spheres at air velocities from 5 to 25 ft/sec.

9. Kuchta, J. M., A. L. Furno, A. Bartkowiak, and G. H. Martindill. Effect of Pressure and Temperature of Flammability Limits of Chlorinated Hydrocarbons in Oxygen-Nitrogen and Nitrogen Tetroxide-Nitrogen Atmospheres. J. Chem. Eng. Data, v. 13, No. 3, July 1968, pp. 421-428.

Limit-of-flammability data were obtained in oxygen and nitrogen tetroxide atmospheres for several chlorinated hydrocarbons that are currently of interest as solvents in rocket and space flight applications. Flammability diagrams that define the complete range of flammable mixtures that can occur with the combustibles are presented for various mixture temperatures (25° to 200° C) and pressures (760 to 50 mm Hg). Generally, the range of flammable compositions does not vary greatly with temperature or pressure if the vapor pressure of the combustible is not a limiting factor. The range of flammable mixtures for the combustibles is usually greater in oxygen-nitrogen than in nitrogen tetroxide-nitrogen atmospheres. Also, the minimum oxidant concentrations required for flame propagation are much less in the atmospheres containing oxygen.

10. Kuchta, J. M., A. L. Furno, G. H. Martindill, and A. C. Imhoff. Crash Fire Hazard Rating System for Controlled Flammability Fuels.[12] BuMines Rept. NA-69-17, March 1969, 20 pp.; ASTIA, AD 684089.

The use of thickened aircraft fuels may provide a significant reduction in the crash fire hazard. Accordingly, a method for rating the potential crash fire hazard of gelled and emulsified hydrocarbon fuels was developed by the Bureau of Mines at the request of the Federal Aviation Administration. The rating system is designed primarily for screening candidate thickened fuels with respect to their overall flammability hazard under laboratory-scale conditions. The fuel properties included in the rating system are minimum autoignition temperature, flash point, volatility rate, self-spread rate,

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[12] Reprinted as Nat. Fire Protect. Assoc. Aviation Bull. 365, August 1969, 23 pp.

regression or burning rate, flame-spread rate, and fire ball size under impact condition. Methods for determining these fuel properties are described in this report. Experimental data are presented for JP-4 and JP-5 or Jet A thickened fuels that were formulated with an emulsifying agent or with one of three different gelling agents submitted for evaluation. The results of these determinations and the numerical rating derived for each fuel composition are discussed.

11. Liebman, I., J. Corry, and H. E. Perlee. Timing Mark Counter. Rev. Sci. Instr., v. 39, No. 10, October 1968, pp. 1591-1593.

A simple optical device has been developed for automatically counting time marks on motion picture film at a maximum rate of 300 counts/min while observing the film in the field of a microscope. This device enables one to scan the contents of extensive film records quickly without having to manually count and record the timing marks during the process. Although this device was designed for use with 16-mm film, it could readily accomodate larger film with only a few modifications.

12. Liebman, I., J. Corry, and H. E. Perlee. Rupture Mechanism of a Liquid Film. Science, July 26, 1968, v. 161, pp. 373-375.

An investigation was conducted to determine the rupturing mechanism of liquid lamella in an initial effort to study the flame propagation characteristics of flammable foams. The films were prepared on wire frames, and the physical changes occurring in these films during collapse were observed by high-speed motion photography, flash interferometry, and flash photography. During rupture, the film's free edge was observed to thicken as it moved into the film, continually generating drops approximately 50 microns in radius. The film-rupturing velocity was inversely proportional to the square root of the film thickness, 620 to 880 cm/sec for film thicknesses ranging from 1.16 to 0.58 microns. The kinetic energy of the rupturing film edge was found to be constant and independent of film thickness. It appears to depend only on the surface tension and density of the liquid.

13. Litchfield, E. L. Spark Ignition--Ignition of Flammable Mixtures as a Consequence of Gaseous Electronic Discharge. SAE Preprint 690438, April 1969, 5 pp.

The concept of minimum energy for spark ignition is summarized and applied to the question of ignition hazard for triboelectrified fluids. It is shown that if certain auxiliary conditions are satisfied, assurance of safety can be given if, and only if, the electric field strength is maintained below the dielectric breakdown strength of the flammable air-vapor mixture.

14. Ribovich, J. A Wedge Technique for Evaluation of Detonation Hazards of Liquid Explosives. Ann. N.Y. Acad. Sci., v. 152, art. 1, October 1968, pp. 766-772.

A wedge technique has been developed to determine film thicknesses at which detonations fail in liquid explosive systems. This technique makes it possible to rank detonable liquids according to hazards associated with thin films. It has been applied to evaluating the effectiveness of desensitizing additives as inhibitors for both high- and low-velocity detonations. Information relating to transitions between the two detonation regimes was also obtained.

The initiation source is an explosive-generated shock analogous to that used in the card-gap test. Continuous detonation velocity measurements are obtained. In some cases the results were substantiated by pressure measurements.

Compositions studied include nitroglycerin-ethylene glycol dinitrate (NG-EGDN) containing up to 25 percent triacetin (TA), mixtures of nitromethane and tetranitromethane, and several mixtures of NG-EGDN with miscible organic compounds, as well as other liquid explosive systems.

15. Ribovich, J., R. W. Watson, and F. C. Gibson. Instrumented Card-Gap Test. Am. Inst. Aeronautics and Astronautics J., v. 6, July 1962, pp. 1260-1263.

The card-gap test is a widely used method for evaluating the sensitivity to detonation of explosives and hazardous chemicals. Recent work at the Bureau of Mines has led to modifications of this test which have reduced some of the ambiguities in the interpretation of results using earlier versions. The knowledge gained has led to a reassessment of some of the criteria previously used in establishing the shock sensitivity of liquid explosives. Modifications consist of the addition of an expendable pressure gage to provide a qualitative measure of off-end peak pressures and a probe system capable of continuous determination of detonation velocities (fig. 1). Charge arrangements, construction details, and interpretation of results are given.

16. Singer, J. M., N. B. Greninger, and J. Grumer. Some Aspects of the Aerodynamics of Formation of Float Coal Dust Clouds. BuMines Rept. of Inv. 7252, 1969, 26 pp.

The Bureau of Mines investigated the threshold of dispersal of monolayers and piles of rock dust, anthracite, and Pittsburgh seam coal dust in a small wind tunnel that simulated a coal mine gallery, with the objective of preventing or limiting the formation of flammable dust clouds. The effect of selected variables on entrainment velocity was examined. Mode of entrainment and flow processes in the wake region of dust configurations were investigated by means of high-speed motion pictures. Significant results were as follows: (1) Local minimum air velocities required for dispersal were only slightly

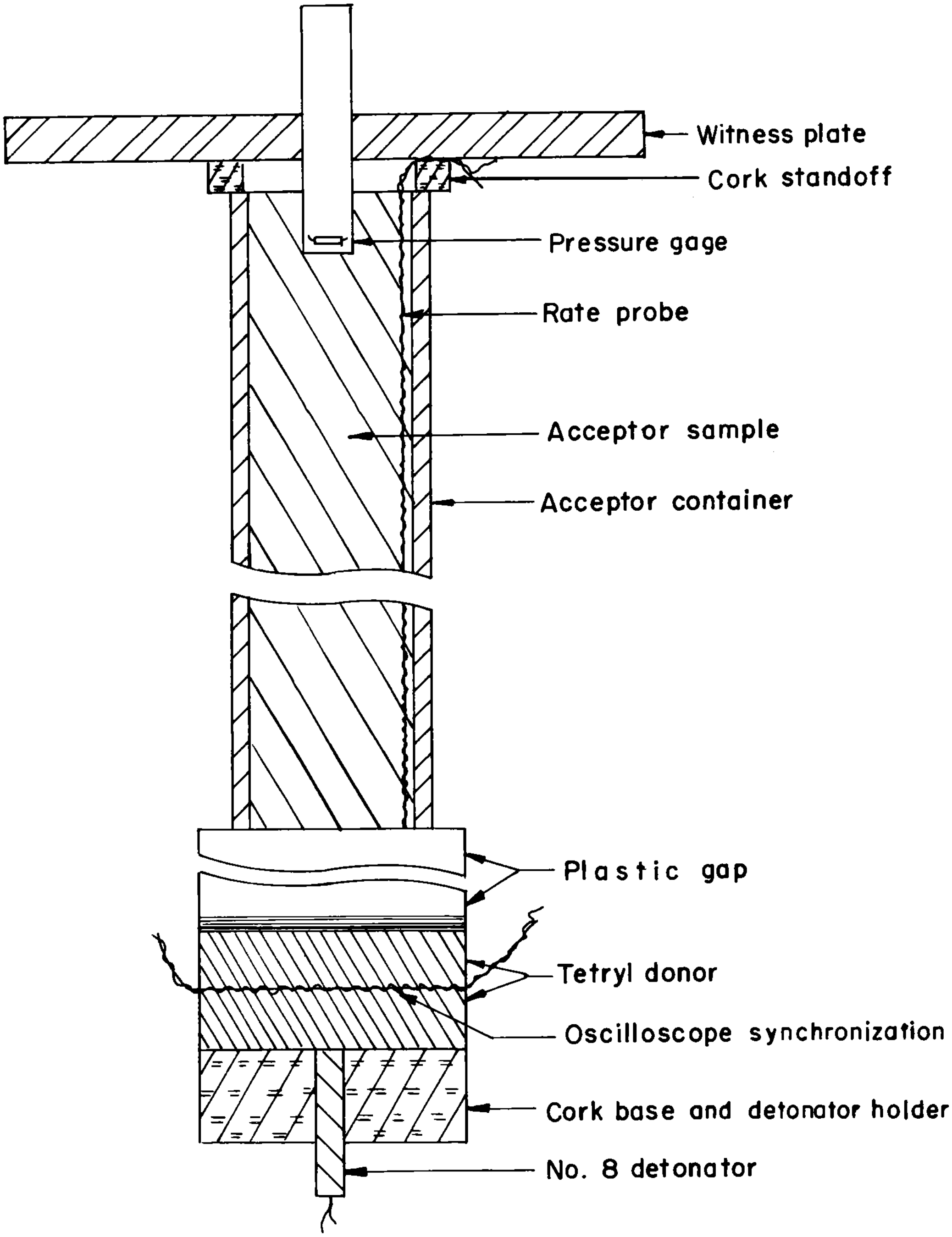

FIGURE 1. - Details of Instrumented Card-Gap Arrangement.

higher for shallow dust ridges than for dust particles; (2) minimum velocities for entrainment of dust particles from smooth glass and coal surfaces increased in the order rock dust, anthracite, Pittsburgh seam coal; and (3) the mechanism for dispersal of dust piles depended significantly on dust pile geometry, cohesiveness of dust, bulk density and compaction of dust, adhesive surface, and vibrations perturbing the supporting surface.

17. Singer, J. M., and I. Liebman. Spherical Flames of Spark-Ignited Dust Clouds. Combustion and Flame, v. 12, No. 5, October 1968, pp. 506-509. (Letter to the editors.)

Streak-film photographs of spark-ignited combustible dust and of combustible dust and combustible gas mixtures were used to study the mechanism of flame propagation, burnout time of particles, and burning velocities. Spherical flames developed symmetrically from a capacitance spark (about 0.2 j) in a cylindrical vessel (15.2 cm in diameter and 33 cm high) equipped with a grid-type open top.

Flame records obtained with dust or with hybrid fuel mixtures indicate that the flame speed increases as the flame front moves away from the ignition source. For spherical flames of gas mixtures without combustible dust, flame acceleration was negligible in our experiments.

In some instances, the growing coal dust-methane-air flame definitely appeared to separate into distinct zones near the lower ignition limit. Such flame separation had been observed previously for flat burner flames of aluminum-methane-air but not for coal dust-methane-air flames.

18. Staff, Explosives Research Center. Research and Technologic Work on Explosives, Explosions, and Flames: Fiscal Year 1967. BuMines Inf. Circ. 8387, 1968, 24 pp.

The principal activities of the Bureau of Mines Explosives Research Center during fiscal year 1967 (July 1, 1966, to June 30, 1967) 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 shock initiation of hydrogen peroxide not destined for publication elsewhere.

19. Van Dolah, R. W. Fire and Explosion Hazards of Cryogenic Liquids. Ch. in Applications of Cryogenic Technology, ed. by R. W. Vance and H. Weinstock. Tinnon-Brown, Los Angeles, Calif., 1969, pp. 227-247.

Physical and physiological hazards of all cryogenic liquids are reviewed, but the fire and explosion problems associated with storage and handling are emphasized. Liquid hydrogen and liquid methane are the fuels considered with hydrogen receiving the most emphasis. Problems considered are detection, ease of ignition, explosion pressures, pool burning, and large-volume disposal by means of vent stacks or burn ponds. Several approaches to the question of separation distances for large-volume storage are examined. Liquid oxidizers such as oxygen, fluorine, nitric oxide, and nitrogen tetroxide present severe fire problems if they are spilled because of increased burning rates of combustibles in the oxidant-enriched atmosphere and the possibility of mixing with liquid fuels to produce condensed-phase explosives. Fluorine presents unique hazards because of its extreme reactivity with nearly all materials it may contact and nitric oxide has an unanticipated sensitivity toward detonation.

20. Van Dolah, R. W. Gas Explosion Hazards. Fire J., v. 62, No. 6, November 1968, p. 119. (Letter to the Association.)

The article "Gas Explosion, Recreation Center, Atlanta, Georgia," in the July 1968 Fire Journal contains a statement that that incident, an explosion presumably involving methane from decaying refuse, was the first of its kind to come to the attention of the NFPA. The Bureau of Mines Report of Investigations 6127, Biological Formation of Flammable Atmospheres, by M. G. Zabetakis, lists six related investigations conducted by the Bureau in recent years. Only one of the investigations was associated with an explosion; the other cases concerned explosion hazards. However, the problem may increase in magnitude as sanitary landfills become widespread and developers build on the property that usually results upon completion of a site.

21. Van Dolah, R. W. Large-Scale Investigations of Sympathetic Detonation. Ann. N.Y. Acad. Sci., v. 152, art. 1, October 1968, pp. 792-801.

The widespread use of ammonium nitrate-fuel oil (AN-FO) as a commercial blasting agent and its common association with very large stocks of raw ammonium nitrate stimulated an investigation into the problem of sympathetic detonation of these materials. Earlier investigations on sympathetic detonation had frequently suffered from the choice of small acceptor charger, with only the donor charges being scaled. Concern over the effect of acceptor scale, coupled with the knowledge that only large-diameter ammonium nitrate charges would detonate at all, required the use of quite large charges in this investigation. AN-FO donors weighing between 200 and 5,400 pounds were fired against acceptor charges weighing about 1,600 and 5,000 pounds. The donors had either light plastic or sheet metal faces aimed at the acceptors which were mostly AN-FO and AN, although dynamite was included to provide comparative data. The "up-and-down" experimental design with scaled charges was chosen to maximize the information with the small number of shots in each series that could be afforded. Contrary to expectations, based on the ready failure of small-diameter AN-FO charges to propagate over an air gap, the large charges were sympathetically initiated over air gaps as large as 4 to 8 charge diameters for AN and as large as about 30 charge diameters for AN-FO. Substantially larger separation distances were obtained when the metal-faced donors were employed. The efficacy of simple sand-filled barricades was investigated; they were found to reduce the sympathetic detonation distances by a factor of about seven. Collateral information on air blast from AN-FO, large-diameter detonation velocities, and fragment velocities were obtained. The data developed in this program will be used in the development of tables of safe separation distances for AN and AN-FO.

22. Van Dolah, R. W. Potential Application of Halon 1301 to Hypergolic Propellant Spills and Fires. Proc. 10th Liquid Propulsion Symp., Chem. Propulsion Inf. Agency Pub. 176, v. 2, October 1968, pp. 579-593.

An investigation was conducted into the possibility of using Halon 1301 (bromotrifluoromethane) to inert enclosed, personnel-occupied spaces where spills of Aerozine-50 or nitrogen tetroxide might occur. The effectiveness of this agent in extinguishing Aerozine-50 fires and plastic materials burning in nitrogen tetroxide-enriched atmospheres was also investigated. The concentrations of Halon 1301 required to inert Aerozine-50 vapor-air mixtures depended upon the vapor concentration; except at very high fuel concentration, the amount required was always less than that for nitrogen.

High concentrations of Halon 1301 are required to extinguish Aerozine-50 fires, and extinguishment appears possible only during the early stages of burning, before the monopropellant combustion phase commences in hydrazine-enriched mixtures. Extinguishment of Aerozine-50 fires presents additional difficulties by virtue of the dense cloud of smoke that is produced and the anticipated toxicity of the combustion products. The burning rate of polyethylene film increased dramatically with nitrogen tetroxide enrichment of the atmosphere, but Halon 1301 proved effective in preventing fire spread in these enriched atmospheres.

23. Van Dolah, R. W. Threat of Sonic Booms to Explosive Facilities. Am. Soc. Safety Eng. J., v. 13, No. 9, September 1968, pp. 12-14.

Aircraft flying at supersonic speeds can generate air shocks with pressures that are in the range of 1 to perhaps 100 pounds per square foot, depending upon airspeed and altitude (or slant range distance). Direct initiation of even very sensitive materials, such as initiating explosives and nitroglycerin, is not possible with the shock pressures associated with sonic booms. Windows may be broken by shock overpressures as low as a few pounds per square foot, and falling glass or glass translated by air shocks could initiate impact-sensitive explosives. Repetitive sonic booms may cause bottles to walk to the edge of shelves and fall. Startle reactions engendered in individuals handling explosives could cause them to drop the explosives; however, individuals quickly adapt to repetitive sonic booms, and experience in explosive plants does not suggest that the startle reaction is a serious problem.

24. 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.

The feasibility of formulating cap-sensitive slurry explosives for use in underground mines with potentially flammable gas atmospheres was examined. Formulations containing aluminum metal as sensitizer and sodium chloride to reduce incendivity were prepared; some were cap-sensitive and had adequate air-gap sensitivity. Flaked aluminum metal rather than atomized aluminum proved to be the more effective sensitizing agent in the formulations tested for incendivity at the large gallery of the Bureau of Mines. Some formulations were found to be suitably nonincendive.

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