TECHNICAL NOTE

MINUTES OF THE THIRD REVIEW OF THE ROCKET PROPELLANT SUPPORTING RESEARCH

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SOLID BIPROPELLANT
Ordnance Project TB3-0110

The objective of the task, Solid Bipropellants, is to devise a combustion scheme which will permit the use of high-energy fuels and oxidizers which are too reactive to incorporate into a propellant by conventional propellant techniques. In the solid bipropellant the fuel components and the oxidant components are not incorporated into the same matrix or grain, but are made and affixed in the motor in two separate and distinct packages, a solid bipropellant. Experimental static firings have been made in a two-inch motor using ammonium perchlorate and a binder as the oxidant and magnesium and a binder as the fuel. A comparison of the firing results of this solid bipropellant and its comparable monopropellant has shown the efficient combustion can be achieved.

Since it has been demonstrated that the solid bipropellant can achieve efficient combustion with a conventional-type propellant, this technique then shows a way to formulate high-energy propellants ($I_{sp} < 275$ sec.) which cannot be made by the conventional techniques. A high-energy propellant which is being investigated consists of an "oxidizer propellant" and polyethylene-coated lithium aluminum hydride. Theoretical performance results for this solid bipropellant predicts a specific impulse of 275-279 seconds for fuel-to-oxidizer ratios over the range of 25/75 to 35/65.

HEXCEL ENCAPSULATION
ARPA Project No. 126-61

The objective is to determine the feasibility of separating otherwise incompatible propellant ingredients by incorporating them in the cells of aluminum honeycomb. The oxidizer, for example, would be in one cell, or one row of cells, and the fuel would be in an adjacent cell or row of cells. The first year's work, on a laboratory scale, has demonstrated that such separation can be made, and combustion caused to occur, using such fuels as jelled JP-4 or hydrazine and ammonium perchlorate-based oxidizers.

The aluminum foil which forms the honeycomb is consumed in the combustion process, at least in the range of foil thickness 1/2 - 5 mils. The apparent burning rate of the propellant is increased by the honeycomb (in the same fashion that wires do) and the increase in rate is proportional to the thickness of foil. For a constant foil thickness the increase in rate is inversely proportional to the cell size of the honeycomb. Materials which would not be considered solids, such as viscous slurries and gels, can be handled as solids once incorporated into the honeycomb -- in analogous fashion to that of honey in a wax comb. Small (2-inch) motor firings have been conducted and as end burners combustion of the honeycomb grain was smooth and reproducible. Large (6-inch) motor firings will be conducted using both end burners and central conduit grains.

HYPERVELOCITY STUDIES
Ordnance Project TB3-0116

One of the serious problems in space vehicle or ballistic missile design is that of resisting the impact of hypervelocity fragments. These fragments moving at velocities ranging from 7 to 40 miles per second, may be either meteors or particles from exploding anti-missile warheads. To study the resistance of missile structures to hypervelocity fragments under laboratory conditions, it is necessary to build projectors capable of accelerating fragments of known mass to hypervelocities. Of the numerous devices used to accelerate these fragments, two devices are being studied at the Interior Ballistics Laboratory. One device is the adiabatic compressor type of light gas gun and the other is the traveling charge gun.

In the adiabatic compressor type of light gas gun, the burning of a conventional solid propellant in a chamber accelerates a heavy piston in a gun bore. This piston compresses a light gas (either hydrogen or helium) to high (100,000 - 500,000 p.s.i.) pressures. At a pressure somewhat less than maximum pressure a fragment is sheared out of a shear disc and driven down a launcher barrel at hypervelocities. In the Interior Ballistics Laboratory experimental and theoretical interior ballistic studies are being made on a small light gas gun capable of accelerating a 5-gram projectile to 15,000 f/s. Experimental data from the firing of this gun will be used to design a gun capable of accelerating 5-gram fragments to velocities in excess of 20,000 f/s.

In the traveling charge gun a cylinder of fast-burning propellant is attached to the projectile being accelerated. The impulse from the burning of the propellant accelerates the projectile to hypervelocities in a manner analogous to the propulsion of a rocket. Theoretical studies have indicated that given a propellant of the desired burning characteristics and a launching tube of sufficient length, one should be capable of accelerating a projectile to velocities in excess of 20,000 f/s. Studies at the Interior Ballistics Laboratory have concentrated on the development of a propellant for the gun which would meet the desired characteristics. One such propellant, now under investigation, is a porous propellant compound of felted nitrocellulose. Experimental firings in a .625 cal. traveling charge gun using this propellant will determine if the propellant will accelerate the projectile to high velocities and give reproducible breech pressures and muzzle velocities.

MECHANICAL PROPERTIES OF SOLID PROPELLANTS
Ordnance Project TB5-20

The Applied Mechanics Branch, Interior Ballistics Laboratory, is engaged in a theoretical and experimental study of the mechanical and physical properties of solid propellants for rockets. The theoretical work has been concerned largely with the study of stress analysis problems within the framework of linear visco-elastic theory. The problems are being formulated in terms of the Laplace transform following the work of E. H. Lee, who is a consultant to the Army in this field, and also in terms of linear integral equations. The latter approach appears to be more powerful. The stress distribution in a rocket motor with a case-bonded grain is being investigated by both methods. The calculated stresses will be compared with experimental values obtained under carefully controlled conditions.

The experimental program is concerned largely with the measurement of the mechanical properties over a wide range of temperatures. A high-speed universal testing machine with associated temperature control equipment will be used for obtaining relaxation data in shear and tension. The bulk modulus can be measured with a pressurizing device developed at the Ballistic Research Laboratories. Preliminary results show a significant difference between the isothermal and adiabatic bulk moduli, indicating that thermodynamic variables should also be considered.

In the future, more attention will be given to thermodynamic variables in both the theoretical and experimental work. The theory of finite deformations will also be considered.

COMBUSTION INSTABILITY
Ordnance Project TB 5-20

Combustion instability in solid rocket propellants is being approached experimentally by IBL in an attempt to discover the basic mechanisms behind this phenomena.

In one project, a series of composite formulations are being studied which contain various percentages and particle sizes of aluminum. Slabs of these propellants are burned under rocket chamber pressures in a windowed cavity which can be pulsed with a siren. Motion pictures are taken of the combustion process. Globules of aluminum and aluminum oxide have been observed on the burning surface and some of these molten spheres have been traced in their subsequent travel into the hotter flame zones. The data obtained is being treated in light of evaporation or burning rate of droplets in a flowing medium similar to data treatment in a liquid propellant system. Periodic vibrations of the molten spheres also correlate quite well with the low frequency bands observed in some aluminized rocket propellant motor firings at other installations.

Another project is concerned with measuring the specific acoustic admittance of the burning zone-product gas boundary of solid propellants. Experiments are being conducted in which propellant samples are burned in a Helmholtz cavity. The resultant pressure variations from this self-excited system are then studied in search of logarithmic increments or decrements which would indicate amplification or attenuation. Amplification would result if the acoustic gains exceeded the losses and attenuation would result if the losses exceeded the gains. So far indications of the latter have been observed.

As an outgrowth of our studies on combustion instability, we are also observing the effects of a magnetic field on the burning rate of solid propellants. Variations in the burning rate at 1 atmosphere and below have been measured which indicate that there is an effect and further studies will be made.

REACTION OF BORON HYDRIDES WITH N-F COMPOUNDS
ARPA Project 126-61

The object of this work is to determine the products of the reaction between high energy fuels, such as the boron hydrides, with high energy oxidizers such as NF_3 and N_2F_4 and to gain an understanding of the reaction mechanism. When equimolecular amounts of B_2H_6 and N_2F_4 are heated at temperatures below 100°C, the diborane decomposes to yield higher boron hydrides and H_2, while the N_2F_4 remains unchanged, indicating that at these temperatures N_2F_4 is unreactive toward both boron hydrides and H_2. At 140°C, reaction occurs in which 75% by weight of the product is gaseous and 25% is solid. The gaseous product has been found to consist of H_2, N_2, and BF_3. The solid product has not yet been identified, but it appears to contain no BN. Rate studies of the reaction are in progress. The reaction has been found to be very sensitive to catalysis by certain metals. In the presence of $CuCl_2$ a violent explosion occurs. In the presence of $MnCl_2$, reaction without explosion occurs at room temperature. The products of the catalyzed reactions have not yet been determined.

NF_3	-	nitrogen trifluoride
N_2F_4	-	tetrafluorohydrazine
B_2H_6	-	diborane
BF_3	-	boron trifluoride
$CuCl_2$	-	copper (II) chloride
$MnCl_2$	-	manganous chloride
BN	-	boron nitride

HIGH-TEMPERATURE GAS REACTION KINETICS
Ordnance Project TB3-0110

It is the aim of this continuing research program to elucidate the rates and mechanism of reactions occurring in the flame zone of burning propellants and in other high-temperature processes.

The reactions are studied in a static system under closely controlled conditions of temperature and composition of reactants.

Premixed gas mixtures are admitted to a quartz reaction vessel placed in a high-temperature furnace and the concentration of a reactant or product of the reaction is recorded continuously by means of a logarithmic photometer. A collimated light beam traverses the reaction vessel, passes through a quartz monochromator, and falls on a photomultiplier tube whose applied voltage is changed in such a way as to hold constant its photocurrent. The change in voltage is recorded and it is closely related to the concentration of the absorbing gaseous species.

In the present study the rates and mechanism of the NO-H_2, NO-D_2, and NO-CO reactions are under investigation. The concentration of NO is measured by the absorption of the 0,0 band of its γ-system ($A^2\Sigma^+ - X^2\pi$). Results at temperatures of 950 to 1200° C have indicated that the NO-H_2 reaction is a complex, many-step process whose mechanism seems to involve the HNO radical and the formation of N_2O as an intermediate which rapidly reacts further to form N_2. The NO-CO reaction, however, seems to be explainable as the slow, rate-controlling decomposition of NO followed by the much faster CO-O_2 reaction. Small amounts of H_2 or H_2O exert a strong and continuing catalytic effect via the NO-H_2 reaction with the continuous regeneration of H_2 from H_2O by the water gas reaction as long as CO is still present.

A SHOCK TUBE TECHNIQUE FOR STUDYING THE KINETICS
OF HIGHLY EXOTHERMIC SYSTEMS
ARPA Project 126-61

A shock tube technique using reflected shock wave heating has been developed to determine the over-all kinetics of highly exothermic reactions. The shock and reflected shock are observed on a strip film (x-t) schlieren photograph and at some later time an adiabatic explosion occurs behind the reflected shock due to rapid exothermic reaction. Delays are measured as a function of temperature, pressure, concentration and the presence of sensitizing gases. The technique has been used to study the hydrogen-oxygen reaction, hydrazine decomposition and the decomposition reactions of pure diborane and diborane with added nitrogen, nitric oxide or oxygen. Data taken in the hydrogen-oxygen system check with the data of Schott and Kinsey and indicate the usefulness of the technique.

Initial results in the diborane system indicate that the decomposition reaction is half-order in diborane and has an activation energy of 18 Kcal over the temperature range of 750° K to 1200° K. Nitrogen addition has no effect on the reaction rate but nitric oxide causes an increase in the rate and some evidence for boron nitride has been found in the solid products of the reaction when nitric oxide is present.

SMALL SCALE ROCKET TESTING
Ordnance Project TB 3-0110

The objective of this study is to determine the usefulness of small size static rockets in predicting the ballistic performance of propellants in larger motors. The advantages of this concept are the saving of time and money, during the development phase, manufacture, acceptance, and surveillance of propellants.

Experimental work performed in the past year included static firing in 2" and 4-1/2" motors with constant K, but varying the amount of insulation on the walls of the motor. As much as 20% difference in performance was measured and attributed to heat loss. A series of firings in 1" and 2" motors were conducted using different propellants and the results indicated 5-10% lower results in the smaller motor. However, difficulty was encountered in measuring the nozzle throat area and igniting the smaller motors. During these firings, one propellant consistently showed an oscillation of 15-20 cycles per second on both the pressure and thrust traces. At present the cause of this cannot be explained; however, this propellant appears to be quite porous. Testing will continue, increasing the size of the motors to six inches.

The effect of the oxygen balance in the ratio of experimental to theoretical specific impulse will be investigated.

Many reports mentioning small scale firings and their correlation to large motor results have been published. However, there is a great need for combining these results and giving this information to the propellant industry.

PREPARATION OF NEW PROPELLANTS

Ordnance Project TB 3-0110

The object of this work is to prepare solid propellants having an I_{sp} of about 260 seconds at 1000 psi characterized by improved mechanical properties and ease of fabrication. The propellants being worked on are of the composite double base type in which the binder consists of cellulose nitrate, glycerine trinitrate, and a polymerizable system which is compatible with the cellulose nitrate and which renders the mixture liquid before curing and solid after curing. Our previous work in this field resulted in the invention of the BRL-1 propellant in which the polymeric portion of the binder was a polyurethane. This material, like all propellants containing polyurethane, suffers from the disadvantage of having to be made in the absence of moisture and all mixing and casting operations must be done in a vacuum system to prevent the formation of gas bubbles which arise from the reaction of isocyanate with moisture.

Two approaches are being used. The first involves the utilization of commercially available polymerizable materials. Very promising results have been obtained in which the binder consists of a diepoxide, Unox 201, manufactured by Union Carbide, dodecyl succinic anhydride, and the nitrate esters. The epoxide and the succinic anhydride react to yield a polyester of high molecular weight. Samples of propellant were displayed which showed the strong rubbery character of the binder and the complete absence of any gas bubbles although the mixing and curing operations were carried out without any effort to exclude moisture or without the use of vacuum equipment. Work is continuing to optimize the composition and to get data on physical, mechanical, and ballistic properties of these propellants.

The second approach involves the synthesis of new polymerizable materials which are not commercially available. Ketenes react with alcohols to yield esters.

$$R_2C{=}C{=}O + ROH \quad = \quad R_2C.CO_2R$$

We are attempting to make polyesters by reacting molecules containing two ketene functions, bisketenes, with diols. Since bisketenes represent a new class of compounds efforts are being made to synthesize them. Known methods of synthesizing monoketenes have been found to be unsatisfactory and a new and improved method has been developed. The utility of this new method is demonstrated by the synthesis of a number of monoketenes. This work will be written up for publication and the new method will be applied to the synthesis of bisketenes.

FAST FREE RADICAL REACTIONS BY ABSORPTION SPECTROSCOPY
AROD Project TN2-1242

It is the aim of this research project to determine the rates and mechanism of fast recombinations and reactions of simple free radicals such as OH, NH_2, CN, as well as to clarify the formation of free atomic and radical species in electrical discharges.

The experiments are carried out in a fast flow system, the high-energy species are formed in a powerful high-frequency discharge, they are mixed with other diluent or reactant gases, and are pumped rapidly through a quartz observation tube of 150-cm length and 3-cm inside diameter. The concentration of OH radicals is determined across the quartz tube by spectrometric methods. A discharge in flowing Ar-H_2O serves as the light source of OH radiation. The absorption of a particular rotational line of the OH emission spectrum thus measures the concentration of OH in a particular electronic-vibration-rotation state. Under steady-state flow conditions the OH concentration is determined at many positions along the observation tube and this space variation is transformed into a time variation of (OH) by the known flowrate and pressure. The rotational temperature of the absorbing OH is determined by measuring the absorption of several different rotational lines.

Several interesting results have so far been obtained on the formation of OH in H_2O discharges and on the decay of OH. H_2O discharges have been found to be good sources of H-atoms, but poor sources of OH. The reaction of H-atoms with O_2 added downstream of the discharge produces OH, presumably by the steps $H + O_2 + M \rightarrow HO_2 + M$ and $H + HO_2 \rightarrow 2OH$. When OH is produced by the reaction $H + NO_2 \rightarrow OH + NO$ (in great dilution with He), much larger concentrations of OH are obtained, but OH then decays very rapidly, apparently by the bimolecular reaction $2OH \rightarrow H_2O + O$. The lifetime of OH is about two orders of magnitude shorter than that reported by Oldenberg et al by u-v spectroscopy and by Townes et al by microwave spectroscopy. The reason is that these investigators were studying the products of H_2O discharges where OH is continuously formed throughout from H and O_2.

GAS EXPLOSION KINETICS
AROD Project No. TB2-0001

It is the aim of this research investigation to study the detailed course of thermal explosions of gases through experimental measurement; to test the theories of thermal explosions and to improve them where necessary; and to apply these improved experimental and theoretical methods to the explosive decomposition of hydrazine.

The apparatus consists of a quartz reaction vessel in a furnace to which the potentially explosive gas mixture is rapidly admitted from a heated, magnetically stirred reservoir. Admission times of 20 to 40 milliseconds are achieved by rapidly turning the stopcock connecting reservoir and reaction vessel from the closed through the open to the closed position. The pressure of the isolated, exploding gas is recording continuously by means of fast, sensitive pressure transducers whose electrical output is amplified, presented on a cathode ray oscilloscope, and photographed with a Polaroid Land camera. These records clearly show the pressure and temperature equilibration of the reactant gas, the slow pre-explosion reaction and induction period, the sharp explosion, and the final cooling of the explosion products. From pressure-time records of various inert gases information was obtained on the rate of approach to thermal equilibrium and its dependence on pressure, temperature, and composition. Hydrazine explosions were then studied in two different reaction vessels, from about 500 to 800° C, and in mixtures with various inert gases. Agreement with the simple thermal theory has been notably lacking, i.e., theoretical predictions of the temperature dependence of the explosion limit, of the effect of changing the thermal conductivity of the reactant, and of the extent of reaction during the induction period are not well substantiated. Experiments have now been under way to record the local temperature history in the exploding gas by means of fine, coated thermocouples. Initial results indicate maximum temperature rises at the center of spherical reaction vessel of almost 100° C before the explosion occurs. The apparatus has been further modified to permit the simultaneous measurement of pressure, gas temperature at the center and near the wall of the vessel. This represents a considerable advance in the experimental study of thermal explosions and will clarify their detailed mechanism.

REACTIONS OF NITRIC OXIDE
Ordnance Project TB5-20

Because nitric oxide is an important intermediate in the combustion and decomposition of propellants based on C, H, O, and N, and because many of the reactions of nitric oxide are not well understood, the chemistry of this compound is of particular interest to the ordnance chemist. We have, therefore, a continuing program of research devoted to a study of the reactions of nitric oxide. Two reactions which have recently been discovered here are being investigated. The first is the reaction between nitric oxide and trialkyl boranes. The reaction occurs at room temperature and yields a solid and a liquid product. The solid product yields on hydrolysis the dialkylborinic acid and dialkylhydroxylamine, and so we believe that it has the structure

$$R_2BONR_2$$

We tentatively believe that the reaction may be represented by the equation

$$2R_3B + 2NO \longrightarrow R_2BONR_2 + RBONR$$

Both of these products represent new classes of organic boron compounds. Further studies are in progress to establish the identity of these compounds.

The second new reaction is that between nitric oxide and diazopropane which yields nitrogen and an unstable liquid product which may be a mixture of several substances. Work on the identification of the liquid product is under way.

THERMODYNAMIC CALCULATIONS
Ordnance Project TB 5-20

The objective of the task, Thermodynamic Calculations, is, as the name implies, to perform thermodynamic calculations for the complete theoretical evaluation of a solid propellant rocket system, from propellant performance to flight trajectory. A number of programs are available for use on BRL's high speed digital computers, ORDVAC and EDVAC.

A program called The Propellant Thermodynamic Performance Program is used for the thermodynamic evaluation of possible solid rocket propellants. The program on the ORDVAC will handle up to 19 elements, 70 combustion products, and 1 condensed phase. A second program on the EDVAC will handle more than one condensed phase, and no initial estimates are required for convergence.

Results of the Propellant Thermodynamic Performance program are used as part of the input for a second program on the ORDVAC. This program computes the interior ballistics of a solid propellant rocket motor. The interior ballistics program predicts the pressure-time, thrust-time, and other parameters of interest for a given propellant grain design and rocket motor design.

Results of the interior ballistics program are used as part of the input for a third program on the ORDVAC. This program computes the flight trajectory of a solid propellant rocket, assuming the rocket to be a simple mass point.

To summarize, the task, Thermodynamic Calculations, makes available programs on BRL's computers, EDVAC and ORDVAC, for the complete theoretical evaluation of a solid propellant rocket system from the thermodynamic performance of the propellant to the flight trajectory of the rocket.