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Metallized Gelled Monopropellants

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SUMMARY

Thermochemical calculations of seven metallized monopropellants were conducted to quantify theoretical specific impulse and density specific impulse performance. On the basis of theoretical performance, commercial availability of formulation constituents, and anticipated viscometric behavior, two metallized monopropellants were selected for formulation characterization: triethylene glycol dinitrate/ammonium perchlorate/aluminum and hydrogen peroxide/aluminum. Formulation goals were established, and monopropellant formulation compatibility and hazard sensitivity were experimentally determined. These experimental results indicate that the friction sensitivity, detonation susceptibility, and material handling difficulties of the evaluated monopropellant formulations and their constituents pose formidable barriers to their future application as metallized monopropellants.

INTRODUCTION

The Atlantic Research Corporation (ARC) was contracted by the NASA Lewis Research Center to address the performance advantages and technology issues of metallized gelled monopropellants. These monopropellants are known to possess the density specific impulse of solid propellants (i.e., greater than storable and cryogenic liquid propellants) and the throttling and on-off capability of liquid propellants. Feed system complexity is reduced with monopropellants since only one pumping system is required, and the oxidizer-to-fuel ratio remains constant. Also, the processing of metallized gelled monopropellants is less involved than that for solid propellants because no cure operation is needed, and monopropellants can be loaded into the rocket at the launch site. These features reduce launch costs. Under contract, ARC addressed theoretical sea level specific impulse I_{sp} performance, density specific impulse performance I_d (product of I_{sp} and monopropellant specific gravity), and monopropellant formulation compatibility and hazards sensitivity issues.

Atlantic Research Corporation Previous Work

The viability of developing a monopropellant for practical applications was demonstrated by ARC during 1958 to 1960. High-energy gelled monopropellants were formulated under contract to the United

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States Navy Bureau of Naval Weapons (refs. 1 and 2). This family of propellants became known as Arcogel. The most widely characterized Arcogel monopropellant was Arcogel APG-42. Its composition is nontoxic and noncorrosive, and consists of

Ammonium perchlorate	59.90 wt%	(solid monopropellant phase)
Aluminum	24.40 wt%	(solid metallic phase)
Dioctyl adipate	13.54 wt%	(liquid carrier, plasticizer)
Copper chromite	1.00 wt%	(solid burning rate catalyst)
Polyvinyl chloride	0.86 wt%	(liquid gellant)
Wetting agent	0.30 wt%	(liquid wetting agent for solids)

This monopropellant formulation has a density of 1.80 g/cm^3 and an I_{sp} of 261-lb_f-sec/lb_m, with the assumption that the equilibrium composition shifts from a 6.895-MN/m^2 (1000-psia) chamber pressure to a 0.101-MN/m^2 (14.7-psia) exit pressure. These values are comparable to the current space shuttle Space Transportation System (STS) polybutadiene-acrylic acid-acrylonitrile (PBAN) solid propellant of 1.77-g/cm^3 bulk density and 251.7-lb_f-sec/lb_m theoretical I_{sp}, with the assumption that the equilibrium composition shifts from 4.233-MN/m^2 (614-psia) chamber pressure and that the area ratio is 7.72 (ref. 3).

A fairly extensive characterization of Arcogel APG-42 was made, including rheological studies over a range of temperatures. Storage and handling stability were also evaluated, and a number of small motor firings were conducted. The polyvinyl chloride gelled the liquid dioctyl adipate for solids stability and produced a yield-point, shear-thinning rheology. The magnitude of the viscosity at low temperatures 219 K (-65 °F) was found to be unacceptably high. A 6-month storage life was demonstrated, and good stability was achieved under high-acceleration loading and vibration. Sensitivity tests indicated that the formulation was nondetonable and insensitive to ignition by friction and impact at the limits of the test equipment. Autoignition temperature was in excess of 533 K (500 °F). Stable combustion and a 10-to-1 throttling ratio on thrust were attained in a number of small motor tests.

Current Work

Recent emphasis on evaluating alternative propulsion systems to the present solid rocket boosters (SRB) on the STS led to the analytical and experimental study of liquid rocket boosters and advanced propellant options. Rocket boosters based on liquid chemical propellants were evaluated with respect to performance and booster size for the present STS. Metallized-storable and metallized-hydrocarbon fuels compared favorably to the existing PBAN solid propellant; and the liquid rocket boosters, sized for metallized propellant use, had minimal dimensional changes for the existing STS and launch pad structures (refs. 4 and 5). Implementation of metallized propellants for liquid rocket booster applications would require added technology and development.

NASA Lewis is conducting research on metallized fuels for space propulsion applications. Analytical studies have cited benefits for launch, upper-stage, lunar, and planetary applications (refs. 6 to 9). For example, if metallized $O_2/H_2/Al$ is used rather than conventional O_2/H_2 bipropellant, 20- to 33-percent additional payload can be delivered to the Mars surface on a piloted Mars mission. Experimental work has focused on metallized hydrocarbon rheology and combustion (refs. 10 and 11). Al/RP-1 metallized fuels have been formulated and physically characterized, and an Al/JP-10 metallized fuel has been combusted with gaseous oxygen with C^* efficiencies up to 93 percent.

To ensure a broad-based research program of metallized propellants, NASA Lewis contracted ARC to investigate metallized gelled monopropellants. The present investigation quantifies the theoretical specific impulse and I_d of metallized monopropellants by using a thermochemical equilibrium code. Monopropellants that were theoretically advantageous and had formulation constituents commercially available were experimentally formulated and characterized. Characterization included materials compatibility and hazards sensitivity testing.

RESULTS AND DISCUSSION

Metallized gelled monopropellant formulations were evaluated analytically and experimentally. The analytical evaluations focused on quantifying the theoretical specific impulse performance of a select number of monopropellants. I_{sp} values were subsequently combined with their respective monopropellant specific gravities to define I_d values. Those monopropellants that had commercially available formulation constituents and that demonstrated superior specific impulse and I_d and good predicted rheological behavior were selected for experimental evaluation. Experimental formulation goals were established that designated acceptable monopropellant performance, safety, stability, and flow characteristics. Formulation experimentation evaluated the selected monopropellants with respect to these formulation goals. Materials compatibility of the monopropellant stabilizers and monopropellant handling properties were assessed.

Thermochemical Calculations

Performance goals were defined for the formulations in terms of specific impulse and I_d. These values were determined by performing thermochemistry calculations for each formulation while parametrically varying the constituents of each formulation. The calculations were performed for an assumed chamber pressure of 6.895 MN/m^2 (1000 psia) and an exhaust pressure of 0.101 MN/m^2 (14.7 psia). Shifting equilibrium nozzle flow was assumed. The seven monopropellants identified as potential candidates were

- Triethylene glycol dinitrate/ammonium perchlorate/aluminum monopropellant: TEGDN/AP/Al (modified Arcogel)
- Hydrogen peroxide (wt% purity)/aluminum monopropellant: H_2O_2(wt%)/Al
- Triethylene glycol dinitrate/ammonium nitrate/aluminum monopropellant: TEGDN/AN/Al
- Trimethylol ethane trinitrate/ammonium nitrate/aluminum monopropellant: TMETN/AN/Al
- Triethylene glycol dinitrate/trimethylol ethane trinitrate/aluminum monopropellant: TEGDN/TMETN/Al
- Hydrazinium mononitrate/water/aluminum monopropellant: HN/$H_2$0/Al
- Ammonium nitrate/water/aluminum monopropellant: AN/$H_2$0/Al

The thermochemical calculations for these monopropellants considered only the major constituents listed here and in table I. Since stabilizing agents such as gelling and wetting agents compose only a small fraction of the overall composition, they were disregarded. A small reduction in monopropellant

theoretical performance is anticipated through the addition of stabilizing agents which, typically, have little chemical energy content.

Furthermore, the chemical composition of the H_2O_2 is documented as H_2O_2 within the text, tables (except table I), and graphs of this report for identification purposes; however, reduced-oxygen-content H_2O_2 chemical formulas and heats of formation were used in the thermochemical calculations to reflect reduced H_2O_2 purities. Reduced H_2O_2 purities reflect a decomposition of the H_2O_2 into water and oxygen according to the overall chemical reaction:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The H_2O_2 purities used in the present calculations reflect experimentally measured purities of ARC's stored H_2O_2 supply.

The I_{sp}, vacuum specific impulse I_{vac}, and I_d results for the latter five monopropellants mentioned are given in tables II to VI. The thermochemical calculations for these monopropellants were generally limited to 18-wt% Al. Solid propellant industry experience indicates that when Al concentrations exceed 18 wt% the combustion efficiency often suffers considerably because of two-phase flow losses. Furthermore, experience has shown that delivered specific impulse usually maximizes at Al levels of 18 wt% in typical solid propellant formulations (Personal communication, ARC, Feb. 1991).

Of these five systems, the $HN/H_2O/Al$ system looks very promising and gave the highest I_d values of all considered monopropellants at reasonable Al levels (i.e., 18 to 25 wt%). However, this system was not considered for experimental evaluations because of the limited commercial availability of HN. Furthermore, the $HN/H_2O/Al$ monopropellant would require temperature conditioning above 373 K (100 °C) to initiate HN decomposition prior to combustion chamber injection. This preconditioning of the monopropellant and the entire booster would be impractical. The TEGDN/AP/Al monopropellant and the H_2O_2/Al monopropellant proved to be the most beneficial on the basis of theoretical performance, commercial availability of the propellant constituents, anticipated rheology, and formulation and handling experience. These metallized monopropellants are described separately below.

Modified Arcogel (TEGDN/AP/Al) Monopropellant

Early formulation successes with Arcogel APG-42 were hampered by the formulation's low-temperature viscosity, which was exceedingly high for the applications under study. Energetic alternatives to the Arcogel APG-42 gelled liquid carrier, dioctyl adipate, were sought to minimize viscosity via an alternate liquid-gellant system. On the basis of ARC's solid propellant experience, the use of dinitrate esters (TEGDN, TMETN) was proposed. These dinitrate esters, or nitroplasticizers, in combination with a polymeric curing agent may be used as a solid propellant binder system.

The theoretical I_{sp} and I_d for the TEGDN/AP/Al monopropellant are given in figures 1 and 2, respectively. They are plotted as a function of Al loading with families of curves for selected values of TEGDN content. The AP fraction is defined by the requirement for the three constituents to total 100 wt%.

I_{sp} is a maximum for an Al content between 20 and 25 wt% and a TEGDN content between 40 and 50 wt%. I_d maximizes at 25- to 30-wt% Al and 25-wt% TEGDN.

In general, maximizing specific impulse and monopropellant density is advantageous in lowering propellant tank volumes and in increasing delivered payload mass. For example, figure 3 illustrates that

a 50/30/20-wt% TEGDN/AP/Al monopropellant liquid rocket booster (LRB), at 289.9-lb_f-sec/lb_m I_{vac} (264.8-lb_f-sec/lb_m I_{sp}) and 1.658-g/cm^3 monopropellant density, significantly reduces booster length at the present STS payload capacity and SRB diameter. In addition, large increases in payload mass may be achieved by increasing the LRB length while maintaining the LRB at the SRB's diameter. The desire to maximize specific impulse and monopropellant density tends to work in opposition to reducing viscosity, since viscosity generally increases with increasing solids loading (i.e., Al and AP) (personal communication, ARC, Feb. 1991). As a result, the TEGDN/AP/Al formulation selected by ARC for further experimental research is a compromise between good theoretical performance and good flow characteristics. This formulation contains 40-wt% TEGDN, 35-wt% AP, and 25-wt% Al and offers an I_{vac} of 289.4 lb_f-sec/lb_m (I_{sp} of 264.6 lb_f-sec/lb_m) and an I_d of 462.3 lb_f-sec/lb_m. Because of their typically low energy content, the addition of gelling agents and other chemicals will reduce these theoretical specific impulse values slightly. Also, delivered specific impulse may suffer slightly because of the higher Al content (25 wt%) than typically found in solid propellants.

After some initial sensitivity difficulties with the 40/35/25-wt% TEGDN/AP/Al formulation, discussed later in the Monopropellant Formulation Evaluation section, another series of thermochemical calculations were performed with the Al content held at 18 wt% while the TEGDN/AP ratio was changed. Again, the 18-wt% Al concentration was selected since solid propellant industry experience indicates that delivered specific impulse maximizes at this metal loading (personal communication, ARC, Feb. 1991). The results of these calculations are presented in table VII.

These data indicate a maximum I_d at 32-wt% TEGDN and 50-wt% AP. However, processing considerations mandate a minimum of 42-wt% TEGDN (with 40-wt% AP) (personal communication, ARC, Feb. 1991); consequently, a 42/40/18-wt% TEGDN/AP/Al formulation was also selected by ARC for further experimental study.

H_2O_2/Al Monopropellant

H_2O_2, alone, may serve as an energetic monopropellant or oxidizer; however, its practical utilization has always been limited by its susceptibility to decomposition due to material incompatibility. Proper control of H_2O_2 decomposition mechanisms would ensure the viability of H_2O_2 as a propellant; hence, ARC investigated the augmentation of H_2O_2's density and combustion energy with Al, because Al is H_2O_2-compatible and will not promote decomposition.

Performance values for the H_2O_2/Al gel were established by a number of thermochemistry calculations with varying Al loadings in H_2O_2. The purity assumed for the H_2O_2 was 88 wt%, which was a prior ARC experimental measurement of its supply of commercially available 90-wt% pure material. The difference between 100-wt% purity and the cited purity values represents liquid water. This purity difference was accounted for in the thermochemical calculations by utilizing a reduced H_2O_2 peroxide chemical formula and heat of formation as indicated in table I. The results of these calculations for theoretical I_{sp} and I_d are plotted in figures 4 and 5, respectively, as a function of Al loading. The maximum I_{sp} occurs at a metal loading between 29 and 33 wt%. The maximum I_d occurs at a metal loading of approximately 53 wt%.

The Al loading that produces the maximum I_d tends to decrease as the relative importance of I_{sp} compared with propellant density increases. For this reason, and in the interest of minimizing flow viscosity, the H_2O_2/Al monopropellant formulation selected by ARC for experimental I_{vac} of this formulation was 279.5 lb_f-sec/lb_m (an I_{sp} of 254.0 lb_f-sec/lb_m), and the I_d was 437.4 lb_f-sec/lb_m.

Again, the addition of gelling agents will cause a slight reduction in these values. The precise magnitude of performance benefits must be assessed on a mission-specific basis.

After some additional H_2O_2-purity testing of ARC's supply, the original 88-wt% purity was discovered to have further degraded to 76 wt%. Thus, the effect of a reduced H_2O_2-purity on theoretical performance was studied. Thermochemical calculations were performed for a H_2O_2/Al propellant with 76-wt% pure H_2O_2, and the performance values were compared with the 88-wt% pure H_2O_2 of figures 4 and 5. I_{sp} and I_d are shown plotted in figures 6 and 7 as a function of metal loading. I_d performance is affected more than I_{sp}, as expected; however, neither is affected significantly. ARC subsequently proceeded with a 60/40-wt% H_2O_2(76-wt%)/Al monopropellant experimental evaluation.

Monopropellant Formulation Evaluation

Formulation guidelines, or goals, were established to provide a definition of acceptable monopropellant physical, chemical, and thermal properties. These formulation goals were defined by ARC for rocket booster applications, such as the space transportation system. Tables VIII and IX document the desired values for theoretical performance, monopropellant sensitivity, solids stability, rheological behavior, and monopropellant processing and production costs for each formulation, TEGDN/AP/Al and H_2O_2/Al, respectively. As will be elaborated further below, the stability, rheology, and cost formulation goals were not demonstrated because of the handling and hazards sensitivity difficulties demonstrated by the initial monopropellant formulations.

Initial experimental evaluation focused on identifying gellants that were chemically compatible with the monopropellant's primary formulation constituents and that effectively imparted solids stability to prevent settling. Chemical compatibility was the primary issue addressed for the H_2O_2 system; gellant type and quantity were the primary issues addressed for the TEGDN system. Subsequent testing addressed the monopropellant formulation's hazards potential in terms of friction sensitivity and detonation susceptibility.

Initial hazard sensitivity studies involved the preparation of small "hand" mixes to obtain friction sensitivity and detonation susceptibility data. Although both of these data are important, the friction sensitivity data was considered most important since highly friction-sensitive formulations could not be used in the subscale or full-scale equipment necessary to produce larger quantities of each formulation. The friction sensitivity test simulates conditions occurring when the propellant is subjected to a friction force between moving objects such as during mixing and other material-handling operations.

The test apparatus used was a sliding friction apparatus equipped with a linear potentiometer to measure the velocity of the sliding anvil. The test apparatus, shown in figure 8, consists of a hardened steel anvil resting on roller bearings, a hardened steel stationary wheel, a constant weight pendulum that can be adjusted between 15° and 90° drop angles, and a hydraulic pressure source. A new contact surface between the stationary wheel and the anvil was used for each individual test. Contact surfaces were changed by built-in adjusting mechanisms.

The sample was placed on the anvil, and a known force was applied hydraulically through the stationary wheel, perpendicular to the test sample. The pendulum was released from the 90° drop angle, and the reaction to the force was recorded as either a "shot" or "no shot." A "shot" implies that the test material received sufficient mechanical energy to initiate an exothermic chemical reaction (i.e., a detonation). "Shots" were detected visually, and the response was recorded. Calibration tests show that at a 90° drop angle, the average anvil velocity was 7.6 ft/sec. ARC considers any formulation with a

positive response at a pendulum drop angle of 90° to be relatively insensitive to friction (personal communication, ARC, Feb. 1991). Formulations with a positive response, a shot, to a 60° drop angle are considered to be very sensitive, whereas those with positive responses at 45° or less are considered to be much too sensitive to work with using normal propellant processing equipment.

The second most important sensitivity parameter for monopropellants is detonation susceptibility, where the clear requirement is that the monopropellant be nondetonable. The monopropellants were tested with a standard card gap test using the apparatus depicted in figure 9. The steel witness plate was supported on two edges parallel to and approximately 6 in. above the ground surface. Four small pieces of plastic material, 1/16 by 1/2 in., were placed on the plate to support the tube containing the test sample and to maintain a 1/16-in. air gap, which did not overlap onto the monopropellant. (The air gap between the acceptor and witness plate should be free of solid material.) The test sample was located approximately in the center of the witness plate. A pentolite booster was then placed on top and in contact with the sample at the top of the tube, and the number 8 blasting cap was attached. The test sample and explosives booster were at a temperature of approximately 298±5 K (25±5 °C) at the time of the test. The arrangement of components for this test was similar to that shown in figure 9, except that the cellulose acetate cards and the cardboard tube were omitted in the first test.

Detonation was indicated when a clean hole was cut in the witness plate. If no detonation occurred in the first test, the test was repeated two more times. If detonation occurred, the test was repeated using eight cellulose acetate cards; if a detonation occurred again, the number of cards were doubled (i.e., 16 cards) for the second test. Doubling the number of cards continued in succeeding tests until no detonation occurred. When the number of cards was reached that prevented detonation, the next test was conducted with half the preceding number of cards. This procedure was followed until the point of 50-percent probability of detonation was obtained. The measure of charge sensitivity was the length of attenuation (gap length) at which there was a 50-percent probability of detonation according to this criterion. Charge sensitivity was expressed in terms of the number of 0.01-in. cards necessary for the 50-percent value between detonation and no detonation. Normally, a maximum of 12 tests was required to determine the 50-percent value.

Modified Arcogel (TEGDN/AP/Al) Monopropellant

A 100-g master batch of 40/35/25-wt% TEGDN/AP/Al monopropellant was formulated to evaluate the effects of different five gelling agents on the friction sensitivity. These included Cab-O-Sil (Cabot Corporation), AEROSIL R972 (Degussa Corporation), Carbopol 940 (The B.F. Goodrich Company), acetylene black, and Kevlar fiber (E.I. DuPont de Nemours & Company). Six smaller (approximately 10 g) mixes were then made, each containing a different stabilizer or level of stabilizer. The mixtures were thoroughly stirred by hand, then allowed to sit undisturbed at room temperature for 7 days. The physical state (homogeneity) was visually assessed and recorded. The samples were stored at room temperature for an additional 25 days and visually reexamined. The results of these studies are shown in table X.

Both Cab-O-Sil and acetylene black proved to be good stabilizers for the TEGDN/AP/Al monopropellant system. Cab-O-Sil is a particulate gellant composed of silicon dioxide (i.e., a nonenergetic material). Acetylene black is recommended for further study because it imparts fuel value to the monopropellant, hence, the I_{sp} would be affected less than for a system containing Cab-O-Sil.

Historically, nitrate-ester/AP combinations have proved to be friction sensitive (personal communication, ARC, Feb. 1991). Indeed, the 40/35/25-wt% TEGDN/AP/Al system was extremely friction sensitive, exhibiting a positive response with a load of 100 lb_m at a 45° drop angle. The particular mix tested contained 200-μm AP and 6-μm Al. The coarse AP, in combination with the fine Al, may have been responsible for the unusually high-friction sensitivity. Several combinations of various sizes of AP and Al were then evaluated for their friction sensitivity. The results of these evaluations are presented in table XI. None of the combinations improved the friction sensitivity to any great degree.

Three wetting agents (or surfactants) commonly used in solid propellants were added to try to eliminate or minimize the possible surface interactions between the AP and Al particles. As shown in table XI, these additives brought about some improvement, in that a 60° drop angle was necessary to produce a positive response. Further attempts to improve the friction sensitivity to the desired 90° drop angle with higher levels of surfactants were unsuccessful.

Another potential approach to reducing friction sensitivity was that of changing the ratio of AP to Al. After the additional theoretical thermochemical performance calculations, discussed earlier, a 42/40/18-wt% TEGDN/AP/Al system was tested for friction sensitivity. Polydiethylene glycol adipate (PGA) was added at a 2-wt% level in place of British detergent as a desensitizing agent. PGA is a polyester binder commonly used in high-energy nitrate ester propellant formulations, which typically display no unusual friction sensitivity (personal communication, ARC, Feb. 1991). The results of the friction tests on this system were very discouraging, with the monopropellant showing a positive response at a 45° drop angle. Analysis of the data acquired to this point led to the conclusion that the unusual friction sensitivity of this formulation was probably not due entirely to AP/Al solid particle interactions, but rather to the influence of the nitrate ester (TEGDN, TMETN) combination with these two materials. Work with the TEGDN/AP/Al system was discontinued.

To confirm the nitrate ester hypothesis, a 47/35/18-wt% TMETN/AN/Al system was selected for friction sensitivity characterization. A small-scale monopropellant mix containing 44-wt% TMETN, 35-wt% AN, 18-wt% Al, 2-wt% PGA, and 1-wt% acetylene black was prepared and tested. The friction sensitivity was within the acceptable range with a positive response; that is, a "shot," was elicited only when the drop angle reached 90°. The propellant was then prepared in a 600-g batch size in a Baker-Perkins vertical mixer for detonation characterization in the card gap apparatus. The TMETN/AN/Al monopropellant proved to be detonable at the zero-card level and was, therefore, deemed unacceptable for further experimental study.

H_2O_2/Al Monopropellant

Because of the large amounts of H_2O_2 required to passivate mixing and flow contact materials and because of the limited ARC H_2O_2 supply, the experimental testing addressed only the chemical compatibility of potential stabilizers and Al with 76-wt% purity H_2O_2. Approximately 1 ml of H_2O_2 was placed into each of seven glass sample dishes. One of these, to which no other ingredients were added, served as a control. Small amounts of potential monopropellant stabilizing ingredients and (separately) Al were added, and the presence or absence of a chemical reaction (as defined by gas evolution) was recorded. The results are shown in table XII.

H_2O_2 decomposition was not evidenced with Cab-O-Sil and calcined Al silicate, and therefore, this monopropellant deserves further study. Also, the observed reaction of the Al powder with the H_2O_2 must be further investigated since Al is recognized as being H_2O_2 compatible.

CONCLUDING REMARKS AND RECOMMENDATIONS

The Atlantic Research Corporation (ARC) was contracted by the NASA Lewis Research Center to perform the Metallized Gelled Monopropellants Program. The primary objective of this program was to identify and characterize metal-containing gelled monopropellants for future development for space propulsion applications. Several gelled monopropellant systems can indeed offer the performance of solid systems with the advantages of liquid systems (throttle and on-off capabilities) and the added simplicity of a single pumping system.

Theoretical performance calculations were made for seven monopropellant systems to permit identification of specific compositions for consideration. A TEGDN/AP/Al monopropellant and a H_2O_2/Al monopropellant were selected for experimental study based on theoretical specific impulse and I_d performance, commercial availability of the formulation constituents, and forecasted viscosity behavior. With the space transportation system (STS) as a mission model for boosters, a 50/30/20-wt% TEGDN/AP/Al monopropellant analytically demonstrated significant payload mass increases or, alternately, reduced booster lengths at constant payload mass, in comparison with the present solid rocket boosters. Performance goals (theoretical specific impulse, theoretical I_d, rheology, stability, hazard sensitivity, and cost) were established for the TEGDN/AP/Al and H_2O_2(88-wt% purity)/Al systems.

Experimental gelation and friction sensitivity studies were conducted for the TEGDN/AP/Al system and for another nitrate-ester-based monopropellant, the TMETN/AN/Al system. Although the nitrate-ester-based (TEGDN, TMETN) monopropellants offer superior performance, they exhibit unacceptable sensitivity to friction and detonation. Nitrate esters in combination with AP and Al are unusually sensitive to friction stimuli and, therefore, should be approached cautiously regardless of the application. Experimental evidence clearly indicates that TEGDN and TMETN cannot be used at high levels in gelled propellants where nondetonability is a requirement. These experimental results indicate that the friction sensitivity, detonation susceptibility, and material-handling difficulties of the evaluated monopropellant formulations and their constituents pose formidable barriers to their future application as metallized monopropellants.

Chemical compatibility of H_2O_2 and Al, and H_2O_2 and of potential H_2O_2/Al stabilizers was experimentally evaluated, and comparisons of theoretical specific impulse and density specific impulse were made for metallized monopropellants with different H_2O_2 purities. The H_2O_2/Al candidate offered superior performance; however, the handling requirements associated with high-purity H_2O_2 rendered this candidate impractical for extensive experimental evaluations. Preliminary evaluations were performed and potential stabilizers, ones that do not induce H_2O_2 decomposition, were identified. Although the H_2O_2/Al combination requires special, often meticulous handling procedures, its potential benefits far outweigh the inconvenience of working with high-purity H_2O_2. A monopropellant consisting of Al powder and H_2O_2 (in purities ranging from 75 to 95 wt%) merit further consideration.

Finally, monopropellants based on the combination of HN, H_2O, and Al offer a high I_d monopropellant for space propulsion applications. Their theoretical I_d was the highest of the seven systems evaluated (489.6 lb_f-sec/lb_m). To fully assess this propellant's practicality, several areas would have to be investigated. These areas include laboratory evaluations of hazard sensitivity, rheology, and stability, as well as evaluations of the complexity of the feed system with temperature preconditioning of the monopropellant for hydrazinium mononitrate decomposition. More extensive characterization is warranted only if the preliminary evaluations are promising. Lack of commercial availability of hydrazinium mononitrate precluded performing any propellant evaluations under the ARC contract. Though not commercially available, producing this propellant is not foreseen as a barrier.

SYMBOLS AND INITIALISMS

Al	aluminum
AN	ammonium nitrate
AP	ammonium perchlorate
ARC	Atlantic Research Corporation
H_2O	water
H_2O_2	hydrogen peroxide
HN	hydrazinium mononitrate
I_d	density specific impulse (lb_f-sec/lb_m)
I_{sp}	sea level specific impulse (lb_f-sec/lb_m)
I_{vac}	vacuum specific impulse (lb_f-sec/lb_m)
LRB	liquid rocket booster
NASA	National Aeronautics and Space Administration
PBAN	polybutadiene-acrylic acid-acrylonitrile
PGA	polydiethylene glycol adipate
SRB	solid rocket booster
STS	space transportation system
TEGDN	triethylene glycol dinitrate
TMETN	trimethylol ethane trinitrate
ρ	monopropellant density

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TABLE I.—THERMOCHEMICAL PROPERTIES FOR MONOPROPELLANT CONSTITUENTS AT 298.15 K

Constituent	Chemical formula	Density, g/cm^3	Heat of formation, kcal/mol	Fuel or oxidizer	Physical state
Aluminum	Al	2.700	0.000	Fuel	Solid
Ammonium nitrate (AN)	NH_4NO_3	1.725	−87.270	Oxidizer	↓
Ammonium perchlorate (AP)	NH_4ClO_4	1.950	−70.690	↓	↓
Hydrazinium nitrate (HN)	$N_2H_5NO_3$	1.685	−59.000	↓	↓
Hydrogen peroxide (H_2O_2)	$H_2O_{1.7952}$ (88 wt%)	1.387	−49.663	↓	Liquid
	$H_2O_{1.6263}$ (76 wt%)	1.317	−53.598	↓	↓
Triethylene glycol dinitrate (TEGDN)	$C_6H_{12}O_8N_2$	1.332	−155.000	↓	↓
Trimethylol ethane trinitrate (TMETN)	$C_5H_9O_9N_3$	1.488	−105.800	↓	↓
Water	H_2O	1.000	−68.317	↓	↓

TABLE II.—THERMOCHEMICAL CALCULATIONS FOR TEGDN/AN/Al SYSTEM

Constituent, wt%			Monopropellant density, g/cm^3	I_{sp}, lb_f-sec/lb_m	I_{vac}, lb_f-sec/lb_m	I_d, lb_f-sec/lb_m
TEGDN	AN	Al				
0	82	18	1.844	252.9	277.7	466.3
7	75	↓	1.805	256.3	281.5	462.6
12	70	↓	1.777	257.7	282.8	457.9
17	65	↓	1.749	258.6	283.5	452.3
22	60	↓	1.725	259.3	283.8	447.3
27	55	↓	1.700	259.7	283.9	441.5
32	50	↓	1.675	259.9	283.7	435.3
37	45	↓	1.650	259.9	283.4	428.8
42	40	↓	1.628	259.8	282.9	423.0
47	35	↓	1.605	259.5	282.3	416.5

TABLE III.—THERMOCHEMICAL CALCULATIONS FOR TMETN/AN/Al SYSTEM

Constituent, wt%			Monopropellant density, g/cm^3	I_{sp}, lb_f-sec/lb_m	I_{vac}, lb_f-sec/lb_m	I_d, lb_f-sec/lb_m
TMETN	AN	Al				
32	50	18	1.749	261.7	286.8	457.7
37	45	↓	1.736	262.7	287.9	456.0
42	40	↓	1.722	263.7	289.0	454.1
47	35	↓	1.708	264.6	290.1	451.9
52	30	↓	1.694	265.5	291.0	449.8
57	25	↓	1.680	266.4	291.8	447.6
62	20	↓	1.666	267.2	292.6	445.2
67	15	↓	1.655	268.1	293.4	443.7
72	10	↓	1.641	268.9	294.2	441.3
77	5	↓	1.630	269.7	294.9	439.6
82	0	↓	1.617	270.4	295.6	437.2

TABLE IV.—THERMOCHEMICAL CALCULATIONS
FOR TEGDN/TMETN/AN/Al SYSTEM

Constituent, wt%			Monopropellant density, g/cm^3	I_{sp}, lb_f-sec/lb_m	I_{vac}, lb_f-sec/lb_m	I_d, lb_f-sec/lb_m
TMETN	TEGDN	Al				
77	5	18	1.608	270.0	294.8	434.2
72	10	18	1.597	269.4	294.0	430.2
67	15	18	1.586	268.8	293.0	426.3

TABLE V.—THERMOCHEMICAL CALCULATIONS
FOR HN/H_2O/Al SYSTEM

Constituent, wt%			Monopropellant density, g/cm^3	I_{sp}, lb_f-sec/lb_m	I_{vac}, lb_f-sec/lb_m	I_d, lb_f-sec/lb_m
HN	H_2O	Al				
73.8	8.2	18	1.702	264.6	289.8	450.3
72.0	8.0	20	1.719	265.2	291.0	455.9
67.5	7.5	25	1.758	266.0	290.9	467.6
63.0	7.0	30	1.802	266.4	291.8	480.1
58.5	6.5	35	1.844	265.5	291.3	489.6
54.0	6.0	40	1.891	258.5	283.7	488.8

TABLE VI.—THERMOCHEMICAL CALCULATIONS FOR AN/H_2O/Al SYSTEM

Constituent, wt%			Monopropellant density, g/cm^3	I_{sp}, lb_f-sec/lb_m	I_{vac}, lb_f-sec/lb_m	I_d, lb_f-sec/lb_m
AN	H_2O	Al				
68.3	13.7	18	1.666	246.5	270.0	410.7
66.7	13.3	20	1.683	248.0	272.2	417.4
65.0	13.0	22	1.700	248.8	273.7	423.0
63.3	12.7	24	1.716	249.3	274.2	427.8
61.7	12.3	26	1.733	249.9	274.1	433.1
60.0	12.0	28	1.749	250.5	274.5	438.1
58.3	11.7	30	1.766	251.0	275.2	443.3

TABLE VII.—THERMOCHEMICAL CALCULATIONS FOR TEGDN/AP/Al SYSTEM

Constituent, wt%			Monopropellant density, g/cm^3	I_{sp}, lb_f-sec/lb_m	I_{vac}, lb_f-sec/lb_m	I_d, lb_f-sec/lb_m
TEGDN	AP	Al				
32	50	18	1.774	262.8	287.2	466.2
37	45	↓	1.738	263.4	287.6	457.8
42	40	↓	1.702	263.8	289.1	449.0
47	35	↓	1.669	264.1	289.0	440.8
52	30	↓	1.636	263.9	288.1	431.7
57	25	↓	1.605	263.2	286.7	422.4

TABLE VIII.—FORMULATION GOALS FOR TEGDN/AP/Al SYSTEM

Primary constituents (no additives), wt%	
Al	25
AP	35
TEGDN	40
Theoretical performance, lb_f-sec/lb_m	
Sea level specific impulse,[a] I_{sp}	264.6
Vacuum specific impulse, I_{vac}	289.4
Density specific impulse, I_d	462.3
Sensitivity	
Propellant class	Class 1.3 nondetonable
Impact	Negative at 300 kg-cm
Friction	Negative at 90° drop angle and 1800 psi
Electrostatic discharge	Negative at 6 J and 5 kV
Autoignition	Above 373 K (212 °F)
Stability	
Storage, days	14
Acceleration, g	5
Vibration, g	
at 0 to 20 Hz	13
at 400 to 600 Hz	5
at 1000 to 2000 Hz	3
Thermal stability, K (°F)	273 to 311 (32 to 100)
Chemical stability	No decomposition in 30 days
Rheology	
Viscosity versus shear rate, cP	500 at 100 sec^{-1} and 294 K
Viscosity versus temperature, cP	1000 maximum at 273 K
Maximum yield point, dynes/cm^2	100
Cost, \$/kg (\$/lb_m)	
Raw material cost,	11.75 (5.33)
Processing cost	1.65 (0.75)
Production cost goal	13.45 (6.10)

[a] $\frac{\text{chamber pressure (psia)}}{\text{exit pressure (psia)}} = \frac{1000}{14.7}$.

TABLE IX.—FORMULATION GOALS FOR H_2O_2/Al SYSTEM

Primary constituents (no additives), wt%	
H_2O_2 (88-wt% purity)	60
Al	40
Theoretical performance, lb_f-sec/lb_m	
Sea level specific impulse,[a] I_{sp}	254.0
Vacuum specific impulse, I_{vac}	279.5
Density specific impulse, I_d	437.4
Sensitivity	
Propellant class	Class 1.3 nondetonable
Impact	Negative at 300 kg-cm
Friction	Negative at 90° drop angle and 1800 psi
Electrostatic discharge	Negative at 6 J and 5 kV
Autoignition	Above 373 K (212 °F)
Stability	
Storage, days	14
Acceleration, g	5
Vibration, g	
at 0 to 20 Hz	13
at 400 to 600 Hz	5
at 1000 to 2000 Hz	3
Thermal stability, K (°F)	273 to 311 (32 to 100)
Chemical stability	No decomposition in 30 days
Rheology	
Viscosity versus shear rate, cP	500 at 100 sec^{-1} and 294 K
Viscosity versus temperature, cP	1000 maximum at 273 K
Maximum yield point, dynes/cm^2	100
Cost, \$/kg (\$/lb_m)	
Raw material cost,	4.06 (1.84)
Processing cost	1.65 (0.75)
Production cost goal	5.73 (2.60)

[a] $\frac{\text{chamber pressure (psia)}}{\text{exit pressure (psia)}} = \frac{1000}{14.7}$.

TABLE X.—GELLING AGENT STUDIES FOR THE TEGDN/AP/Al SYSTEM

Gelling agent	Concentration, wt%	Observations	
		After 7 days	After 32 days
Cab-O-Sil[a]	1.0	Subsided	Possible sedimentation, supernatant layer
Cab-O-Sil[a]	2.0	Intact, homogeneous	Intact, homogeneous
AEROSIL R972[b]		Some subsidence	Subsided
Carbopol 940[c]		Some subsidence	Subsided
Acetylene black[d]		Intact, homogeneous	Intact, homogeneous
Kevlar fiber[e]		High viscosity	No observation

[a]Cabot Corporation.
[b]Degussa Corporation.
[c]The B.F. Goodrich Company.
[d]Chevron Chemical Company.
[e]E.I. DuPont de Nemours & Company.

TABLE XI.—FRICTION SENSITIVITY TEST RESULTS FOR TEGDN/AP/Al SYSTEM

[All mixes contained 40-wt% TEGDN, 35-wt% AP, 25-wt% Al, and 1.0-wt% acetylene black gelling agent.]

Wetting agent	Size of AP particles, μm	Size of Al particles, μm	Positive friction sensitivity	
			Hydraulic force, lb	Drop angle, deg
None	7	40	500	45
None	7	6	100	
None	3	40	100	
None	3	6	200	
None	200	40	200	
None	200	6	100	
1.0 wt% British detergent	7	40	700	60
1.0 wt% lecithin	7	40	100	60
1.0 wt% DER 331	7	40	200	60

TABLE XII.—H_2O_2 COMPATIBILITY WITH PROPELLANT CONSTITUENTS

Mixture composition	Observations
H_2O_2	Some gassing after 30 min
H_2O_2/Al	No reaction initially; some gassing after 30 min
H_2O_2/Cab-O-Sil[a]	No reaction; wetted well
H_2O_2AEROSIL R972[b]	No reaction; did not wet well
H_2O_2Volclay[c]	Some gassing noted; did not wet well
H_2O_2/#80 calcined aluminum silicate[d]	No reaction; wetted well
H_2O_2/Gel B Attapulgite clay[e]	Some gassing after 5 min

[a]Cabot Corporation.
[b]Degussa Corporation.
[c]American Colloid Company.
[d]Burgess Pigment Company.
[e]Milwhite Company.

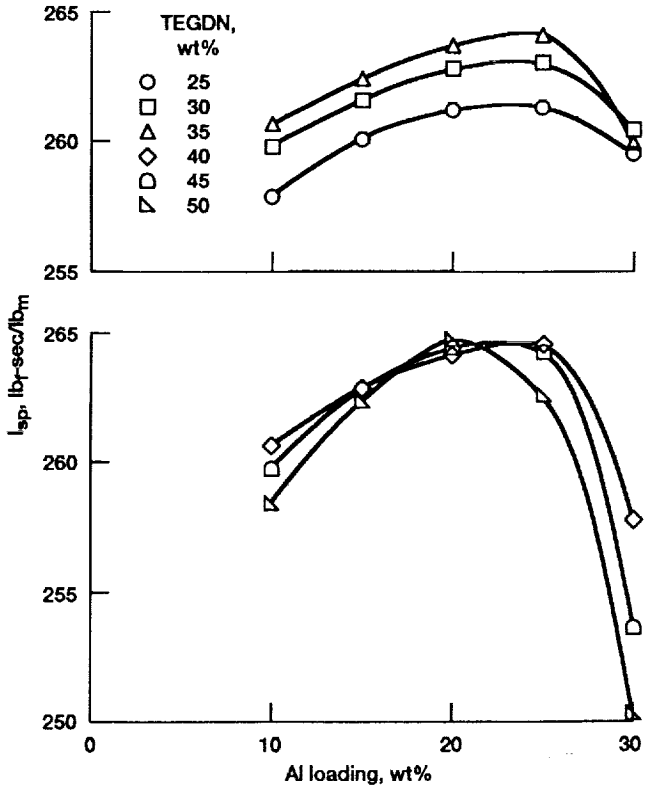

Figure 1.—Sea level specific impulse, I_{sp}, of TEGDN/AP/Al.

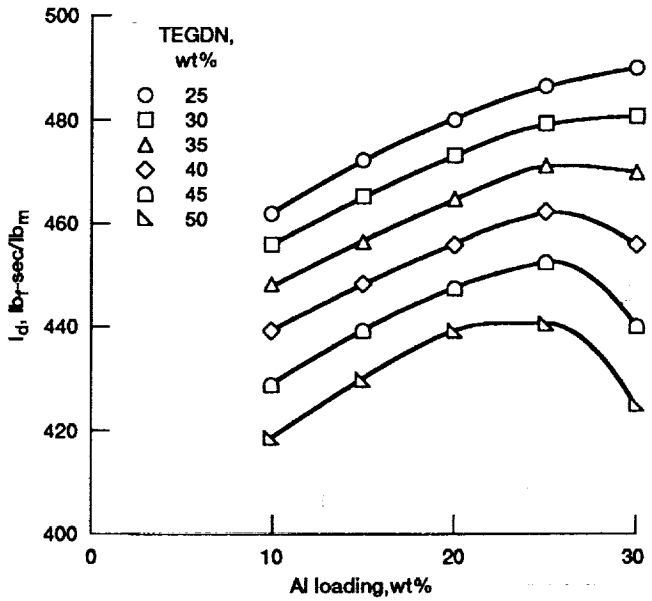

Figure 2.—Density specific impulse, I_d, of TEGDN/AP/Al.

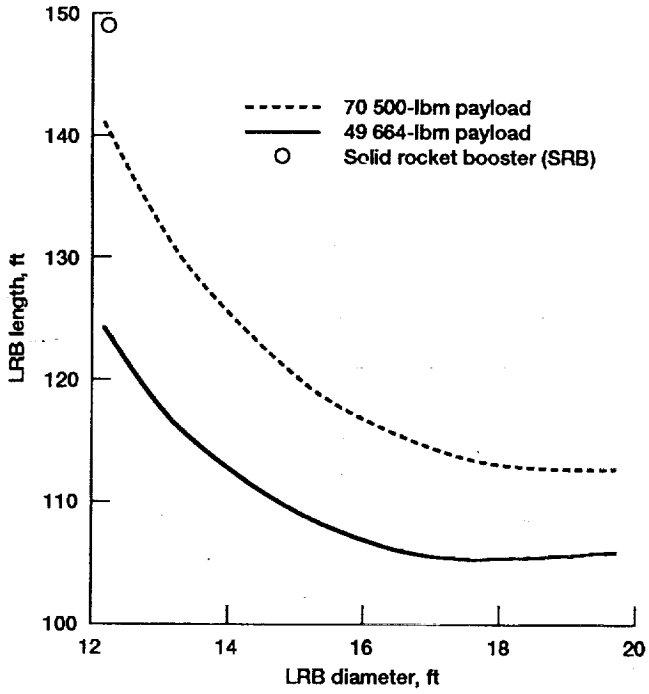

Figure 3.—Liquid rocket booster (LRB) analysis for a 50/30/20-wt% TEGDN/AP/Al monopropellant.

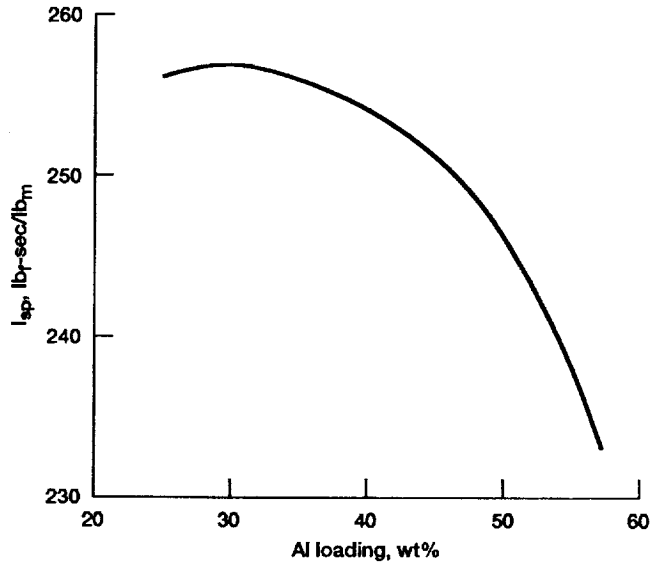

Figure 4.—Sea level specific impulse, I_{sp}, of H_2O_2 (88 wt%)/Al.

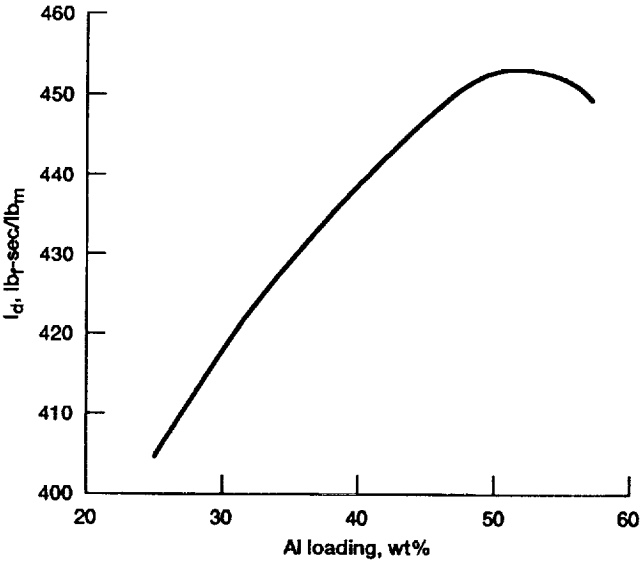

Figure 5.—Density specific impulse, I_d, of H_2O_2 (88 wt%)/Al.

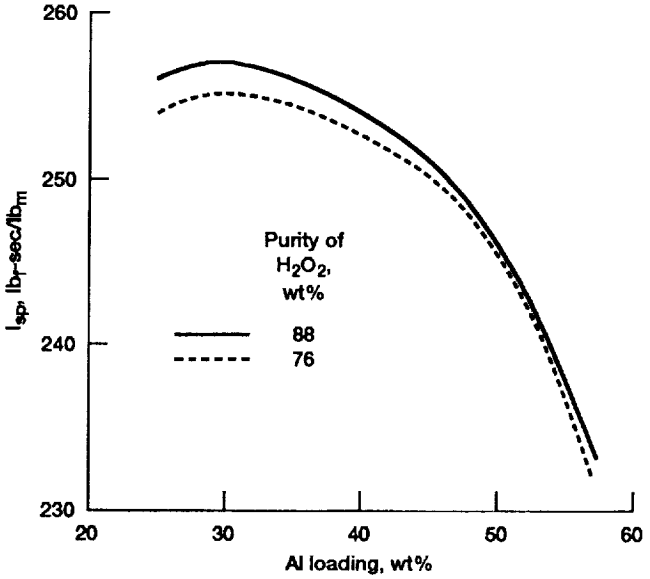

Figure 6.—Sea level specific impulse, I_{sp}, comparison of H_2O_2 (88 wt%)/Al and H_2O_2 (76 wt%)/Al monopropellants.

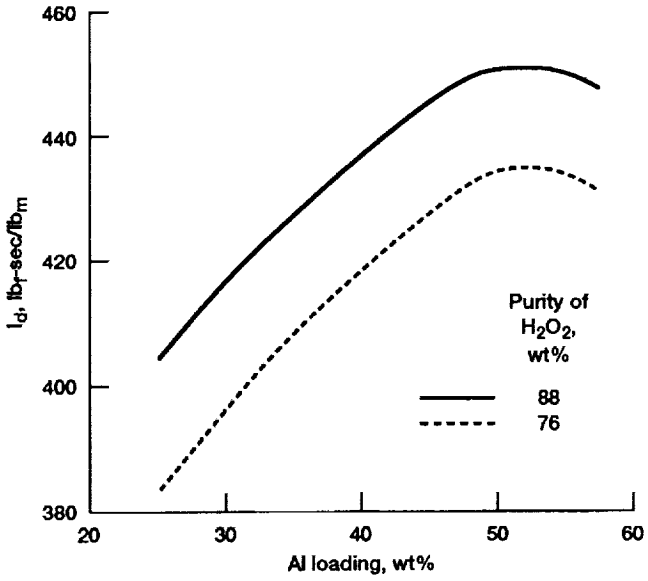

Figure 7.—Density specific impulse, I_d, comparison of H_2O_2 (88 wt%)/Al and H_2O_2 (76 wt%)/Al monopropellants.

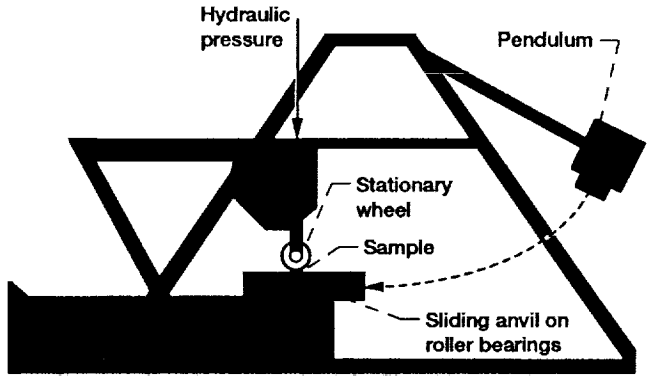

Figure 8.—Sliding friction sensitivity test apparatus.

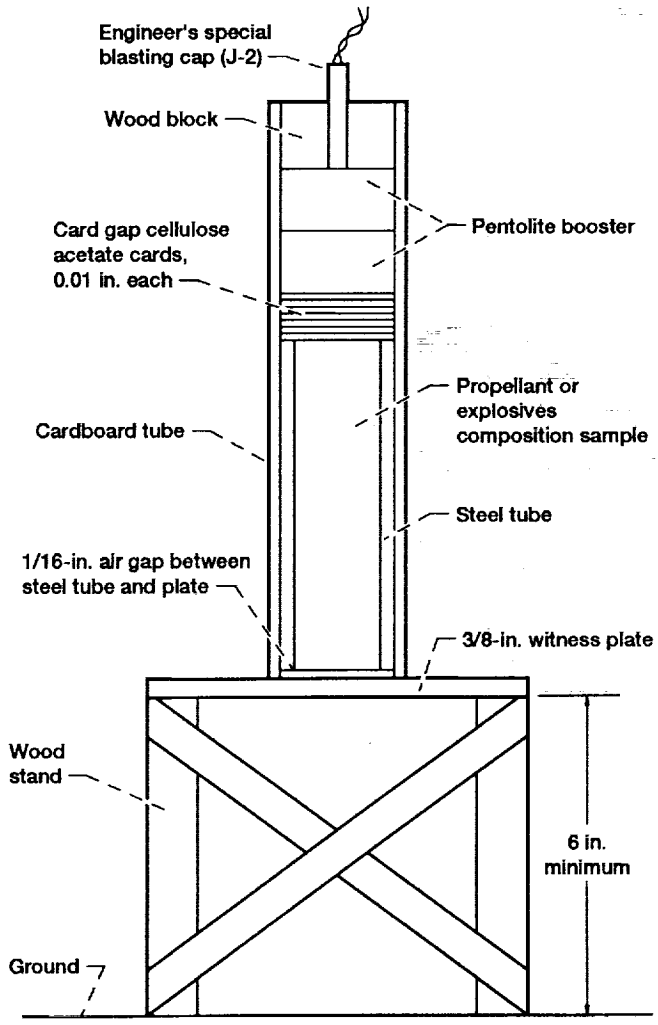

Figure 9.—Setup for card gap test.

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Thermochemical calculations of seven metallized monopropellants were conducted to quantify theoretical specific impulse and density specific impulse performance. On the basis of theoretical performance, commercial availability of formulation constituents, and anticipated viscometric behavior, two metallized monopropellants were selected for formulation characterization: triethylene glycol dinitrate/ammonium perchlorate/aluminum and hydrogen peroxide/aluminum. Formulation goals were established, and monopropellant formulation compatibility and hazard sensitivity were experimentally determined. These experimental results indicate that the friction sensitivity, detonation susceptibility, and material handling difficulties of the evaluated monopropellant formulations and their constituents pose formidable barriers to their future application as metallized monopropellants.

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