JOURNAL OF PROPULSION AND POWER
Vol. 20, No. 1, January–February 2004

Novel High Nitrogen Propellant Use in Solid Fuel Micropropulsion

A. N. Ali,* S. F. Son,† M. A. Hiskey,‡ and D. L. Naud§
Los Alamos National Laboratory, Los Alamos, New Mexico 87544

The use of two novel materials, 3,6–bis(1*H*–1,2,3,4–tetrazol–5–ylamino)–s–tetrazine (BTATz) and mixed N–oxides of 3,3′–azo–bis(6–amino–1,2,4,5–tetrazine) (DAATO3.5, where the 3.5 indicates the average oxide content), as solid fuels in micropropulsion systems is investigated. These materials were selected due to their ease of ignition, relatively good safety characteristics, long-term storage capability, low combustion temperature, noncorrosive combustion products, and reasonable projected material cost. Material safety data including impact, friction, differential scanning calorimetry, and electrostatic sensitivity are reported and compared to the previously implemented micropropulsion fuels, lead styphnate, glycidyl azide polymer (GAP) and 3,6–diamino–1,2,4,5–tetrazine–1,4–dioxide. Burn rate data are also reported for both materials. Whereas BTATz and DAATO3.5 have very high burn rates, DAATO3.5 is believed to have the highest burn rate of any known stable organic solid. Additionally, DAATO3.5 has a very desirable pressure exponent of 0.28. Test stand results using a quartz microthruster are reported for these materials. Estimated chamber pressures reached 18 atm with peak thrust levels around 0.1 N. Measured specific impulses of approximately 14% of the theoretical specific impulse (218 s for BTATz and 228 s for DAATO3.5) were obtained. This level of inefficiency is believed to be acceptable for micropropulsion systems and is comparable to other, independent work.

Introduction

IN recent years, an interest in micropropulsion systems has developed due to the unique propulsion requirements of microspacecraft and the need for precise attitude control of newly emerging applications, such as satellite interferometry.[1] This research area is still quite young and many technological hurdles remain. Microspacecraft have been categorized into three major classes, where class 1 microspacecraft are defined as being less than 10 kg, class 2 microspacecraft are 1–5 kg, and class 3 microspacecraft are less than 1 kg (Ref. 1). There are significant power, weight, size, and thrust limitations for all three classes. Reduced power-generating capabilities of microspacecraft result in the need for microthrusters that can operate on as little as 1 W. Reduced spacecraft mass results in the need for low minimum thrust levels, or impulse bits, to achieve acceptable attitude control precision. It is generally desirable for the impulse bit to be less than 10^{-4} N for class 1 microspacecraft.[1] Thrust levels high enough to perform rapid slew maneuvers must also be attainable.

The miniaturization of thrusters to achieve the outlined parameters lends itself to the most simplistic of designs. A successful design must withstand the rigors of the space environment and operate after long periods of quiescence without loss of function. It is also desirable to use thruster propellant materials that will not contaminate or damage the entire spacecraft should they fail.

One of the more promising designs is that of solid-fuel digital micropropulsion systems, where many individual thrusters containing a solid propellant are etched into a single silicon chip or other microstructure. The impulse bit is then predetermined by the thrust capabilities of a single chamber. Activating multiple chambers simultaneously will increase the thrust level as needed. There have been several different solid-fuel digital micropropulsion array designs in recent years.[2–4] In each of these designs, ignition of an individual thruster is accomplished by either a resistive igniter (a thin wire contacting the propellant) or a diode laser. All designs have a small size and low-power usage, depending on the ignition method and the specific propellant's ignitability. The long-term storage capability, contamination potential, and performance of a given system also depend on the specific propellant selected.

Propellants that have been previously considered for solid-fuel digital microthrusters include the energetic binder, glycidyl azide polymer (GAP)[4]; the class 1.1 primary explosive, lead styphnate[3]; and the insensitive, gas-generating solid, 3,6–diamino–1,2,4,5–tetrazine–1,4–dioxide (LAX–112) (Ref. 2). LAX–112 was very promising, theoretically, but failed to perform experimentally. LAX–112 was chosen because of its excellent safety and environmental characteristics, low combustion temperature (less thermal stress imposed on the thruster chamber and better combustion stability) and competitive specific impulse I_{sp} (Ref. 2). However, because of the incomplete combustion characteristics of LAX–112, upstream filters were required to prevent solid particulates from clogging the nozzle. Compounding the problem was the slow burn rate of LAX–112, which necessitated a small nozzle throat to attain sufficiently high chamber pressures for stable combustion. LAX–112 also proved to have nonrepeatable ignition temperatures and was unable to be easily and repeatedly ignited by the chosen diode laser. Because of these problems, LAX–112 was considered to be a poor propellant choice for the decomposing solid thruster concept.[2]

LAX–112 was part of the family of heterocyclic high nitrogen materials developed in the late 1980s.[5] Since then, many advancements and additional material discoveries have occurred in this family.[6–10] The current high nitrogen, solid gas-generating materials that appear the most promising for use in microthrusters are 3,6–bis(1*H*–1,2,3,4–tetrazol–5–ylamino)–s–tetrazine (BTATz) (Ref. 11) (Fig. 1a), and mixed N–oxides of 3,3′–azobis(6–amino–1,2,4,5–tetrazine) (DAATO3.5) (Ref. 12) (Fig. 1b). DAATO3.5 is the newest and possibly the most interesting of these materials. DAATO3.5 has the highest burn rate of any known organic solid, although BTATz has a fairly high burn rate as well. (Burn rate data

Received 25 June 2002; revision received 15 July 2003; accepted for publication 16 July 2003.

*Staff Member, High Explosives Science and Technology, Mail Stop C 920.
†Staff Member, High Explosives Science and Technology, Mail Stop C 920; son@lanl.gov.
‡Staff Member, High Explosives Science and Technology, Mail Stop C 920.
§Staff Member, High Explosives Science and Technology, Mail Stop C 920.

are reported for the first time in this paper.) High burn rates allow for larger nozzles and, thus, reduce the chance of nozzle clogging. DAATO3.5 also has an exceptionally low-pressure exponent. Both materials are easily ignited by resistive wire heaters or laser, but retain a high degree of insensitivity to impact and thermal stimuli. Whereas the long-term stability of BTATz and DAATO3.5 in harsh spacelike environments has not been investigated, they have been observed to retain complete function with no decomposition after years of storage at ambient conditions. The materials and their combustion products are also environmentally benign and noncorrosive. This paper experimentally investigates the use of these high nitrogen materials in microthrusters and reports preliminary microthrust stand results with material, combustion, and ignition property data.

Experimental Setup

Material Safety Data

Standardized tests at Los Alamos have been used to characterize various material properties that are deemed important to safety. Those safety tests include impact sensitivity, differential scanning calorimetry (DSC), friction sensitivity, spark sensitivity, and vacuum thermal stability. Generalized descriptions and techniques for these tests have been published previously.[13–18] Specific equipment for the impact sensitivity test included using a 2.5-kg impact weight and 40-mg energetic material samples on 40-grit sandpaper. The DSC is used to test materials by thermal analysis for endothermic and exothermic behavior as a function of temperature. DSC uses a very small sample (1 mg) and is a first screening tool for new materials to determine safety for handling. In addition, the onset of exothermic behavior is a sensitive indicator of decomposition in energetic materials removed from storage. The friction sensitivity test used a Bundesanstalt für Material-prüfungen (BAM) friction machine, Julius Peters K. G. Model Berlin 21 with loading weights ranging from 0.5 to 36 kg. The DSC used a TA Instruments Model 2920 with a 1-mg energetic material sample contained within a hermetically sealed aluminum holder with 0.2-mm hole in the lid for pressure equalization. The spark sensitivity test used a custom built apparatus to deliver a 0.36-J electrostatic charge to a 40-mg sample of the energetic material.

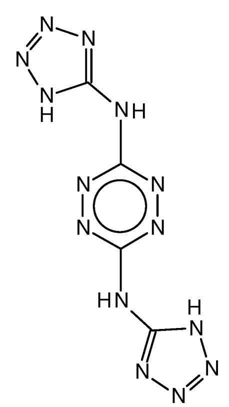
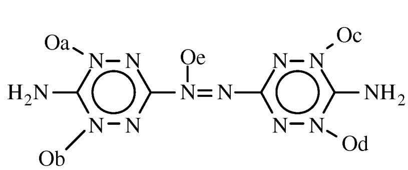


Fig. 1a Molecular structure of BTATz.



a+b+c+d+e=3.5

Fig. 1b Molecular structure of DAATO3.5.

Burn Rate Measurements

Existing techniques and apparatus were used to measure the burn rates of BTATz and DAATO3.5 formulations. High-speed video imaging was employed to record the surface regression of the pressed energetic material pellets. (The burn rate pellets were significantly larger in size than those used in the microthruster test stand.) These techniques and burn rate measurements for BTATz have been previously published.[10] Additional BTATz formulations and DAATO3.5 burn rate data are presented in this paper for the first time.

Electric Match Ignition Tests

The ignitability of DAATO3.5 and BTATz was tested using commercially available bare electric match heads (U.S. supplier Firefox, Inc.). These electric match heads had a 51 gauge nickel–chromium (NiChrome) bridge wire soldered onto the end of a silicon chip. The manufacturer states that the match head requires a minimum of 1.5 V and 0.5 A (0.75 W) to ignite. With this small amount of power, the bridge wire heats and glows white hot before it breaks. The entire heating process occurs within 2 ms. This commercial product was chosen because the stated power requirements are well within the capabilities of a class 3 microspacecraft,[1] and the basic use of a small-diameter NiChrome wire could be easily incorporated into existing silicon digital microthruster designs. Testing involved securing the match head against powder samples of pure high nitrogen material. The match head was then ignited using a 1.5-V AA battery and recorded as a go if reaction of all of the powder occurred.

Microthruster Test Stand

The specific impulse and other thrust properties of DAATO3.5 and BTATz were tested using a pendulum-type microthrust stand in which a quartz microthruster was suspended by strings and placed in contact with a horizontally mounted force transducer (Figs. 2 and 3). As shown in Fig. 2, a variety of nozzle throat sizes and exit sizes were used; the chamber size and length were fixed. The quartz microthruster was held in place with a screw-type aluminum clamp (Fig. 3). The open end of the quartz thruster was sealed with an O-ring and backplate. The thruster was suspended by four nylon strings. A force transducer was placed between the backplate and a secured, vertical mount. The thruster was arranged such that the exit plume would be directed horizontally and opposite the force transducer. Quartz was chosen as the thruster material because of its low thermal conductivity (1.4 W/m K) and thermal expansion properties (5.5×10^{-7} K^{-1}). It was hoped that the low thermal conductivity would increase the efficiency of the microthruster by allowing more of the heat energy to be converted to kinetic energy

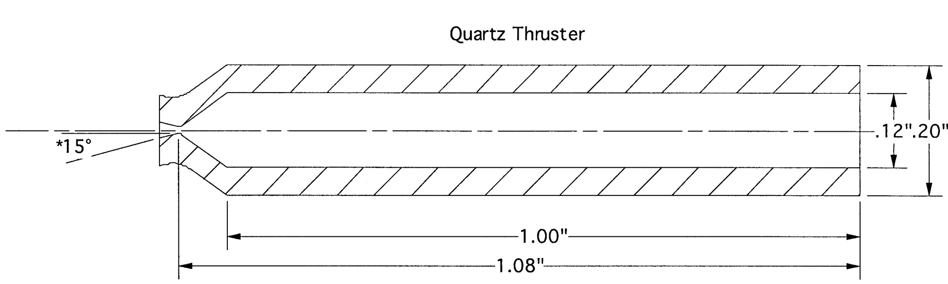


Fig. 2 Schematic of the quartz microthruster used in the test stand.

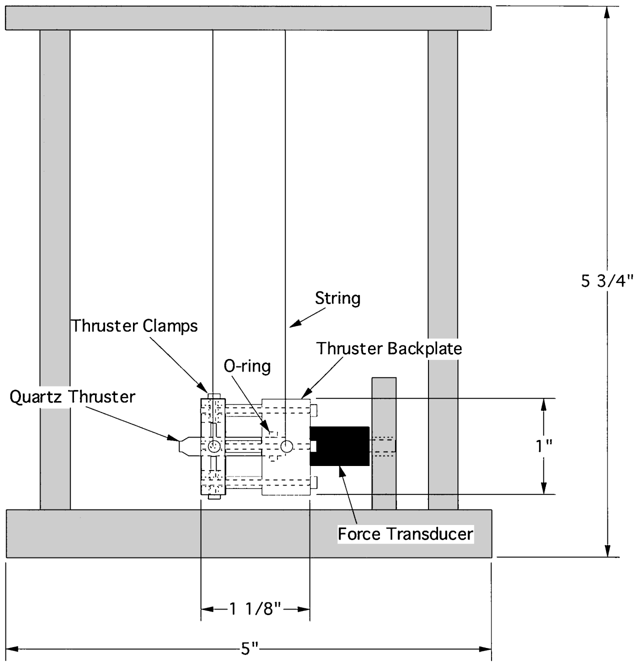


Fig. 3 Schematic of the entire microthruster test stand.

within the nozzle. Although the softening point of quartz is only 1500–1670°C, which is less than 2277°C, the approximate theoretical chamber combustion temperature of the high nitrogen materials at 68.03 atm (as calculated using the equilibrium code CHEETAH 3.0), this was not anticipated to be a problem due to the short burn times of the thruster. Measurements before and after firings revealed no erosion of the nozzle throat. The machining and creation of pure quartz thrusters of such small size proved exceedingly difficult. As a result, there was a large range in the nozzle tolerances of the quartz thrusters used. As seen in the results section, this resulted in significant experimental uncertainty.

Pressed 3-mm-diam pellets of pure DAATO3.5 and BTATz mixed with 3% Hytemp™ 4051CG (Zeon Chemicals, Inc.) binder were inserted through the back of the quartz thruster. Each pellet weighed between 60 and 75 mg and had an approximate density of 1.3 g/cm^3. The quartz thruster was then inserted into a screw-type aluminum clamp with an O-ring sealed backplate and suspended by strings. Ignition of the high nitrogen material was via a Nd:Yag laser (Quanta Ray Model DCR1, 10 Hz, 400 mJ/pulse, and 10-ns pulse length). The ignition event was recorded with a 1000 frame per second high-speed camera (Redlake Motionscope Model 8000 S) and a 30 frame per second digital video camera (Canon Model XL1). The force transducer (Kistler Model 9205) used to measure the resulting thrust had a published natural frequency of greater than 10 kHz, a threshold of 5×10^{-4} N, and a sensitivity of −115 pC/N. A digital oscilloscope recorded the voltage output from the transducer amplifier.

Results and Discussion

Material Safety Data

The use of a safe, insensitive propellant in microthruster systems is important to protect both personnel and the actual spacecraft. It is desirable to have a relatively insensitive, yet workable (easily ignitable) propellant. Lead styphnate (lead 2,4,6–trinitroresorcinate), although easily ignitable, has very poor safety characteristics.[19] As seen in Table 1, lead styphnate has the lowest impact score out of all of the energetic materials considered. It is also remarkably sensitive to electrostatic discharge (0.0009 J) (Ref. 19). Lead styphnate is so sensitive that it is classified as a 1.1 primary explosive, and its routine use is prohibited at the authors' federal research institution.

GAP, however, has relatively good safety properties. Although not as insensitive as BTATz/3% polyethyl acrylate (PEA), it has a relatively insensitive impact score and is generally classified as a 1.3 hazardous material.[20] As seen in Table 1, GAP also has acceptable

Table 1 Material sensitivity test data

Material	Impact sensitivity H_{50}, kg · cm	DSC onset, °C	Friction sensitivity, kg	Vacuum stability (100°C)
Lead styphnate, normal	17[a]	N/A	N/A	N/A
MMW-GAP	200[b]	240[c]	32.4[b]	≥3 ml/g (uncured)[b]
Pure BTATz	80	264	>36	0.22 ml/g
BTATz/ 3% PEA	250	255	22	0.11 ml/g
Pure DAATO3.5	50	177	2–14	N/A
DAATO3.5/ 5% PVA/ 1%TEG	80	169	17.4	15.5 ml/g
PETN[d]	30–35	N/A	9	N/A
HMX	57.5	N/A	N/A	0.08 ml/g

[a]Ref. 19. [b]Ref. 20. [c]Ref. 21. [d]Pentaerythrital tetranitrate.

DSC and friction sensitivity measures.[21] Note that the data in Table 1 are for medium molecular weight GAP (MMW-GAP) and polymerization details are unknown. The sensitivity of GAP is highly dependent on the type and degree of polymerization.[21] Although GAP is a relatively insensitive propellant, previously reported problems include "... less than desirable low-temperature mechanical properties, an undesirably high friction sensitivity associated with the mixing cycle of ammonium perchlorate/nitrate ester/GAP propellants, and less than desirable thermal stability/aging characteristics. ..."[20] The latter of these issues may prove to be the most significant concerning long-term space flight.

BTATz and DAATO3.5, also regarded as 1.3 hazardous materials, are also relatively insensitive to impact and have favorable DSC and friction measures. A problematic area of BTATz and especially DAATO3.5 is the high sensitivity to electrostatic discharge. Pure BTATz ignited 11 out of 13 times when subjected to a 0.36-J spark. Pure DAATO3.5 ignited 13 out of 13 times when subjected to the same level of spark. This high sensitivity to spark, though considered somewhat undesirable, allows for easy ignition by commercial electric match or laser, which is key to fielding a functional system. When a small amount of inert binder (3% PEA) is added to BTATz, the spark sensitivity is reduced to 3/13 ignitions with a 0.36-J spark. DAATO3.5 electrostatic sensitivity is likewise reduced to 0/13 ignitions with the addition of 5% polyvinyl alcohol (PVA) and 1% triethylene glycol (TEG). This favorable reduction in spark sensitivity with the addition of a small amount of inert binder allows these materials to be easily tuned to the needs of a given system. This flexibility allows for a balance to be struck between ignitability and safety, such that the specific needs of different thruster systems may be met.

Burn Rate Results

BTATz burn rate measurements are shown in Fig. 4 and compared with that of octahydro–1,3,5,7–tetranitro–1,3,5,7–tetrazocine (HMX), a common high-performance propellant ingredient. It is seen that the burn rate of BTATz is significantly higher than that of HMX, and that the addition of the inert binders PEA and Kel-F™ 800 (3M Corporation, chlorotrifluroethylene/vinylidine fluoride copolymer) result in nearly the same burn rate profile. The pressure exponent of these BTATz formulations is 0.49, which is acceptable, but not as good as some existing propellants. The addition of 55% ammonium perchlorate (AP), an oxidizer commonly used in composite propellants, results in a significant reduction in burn rate and without a corresponding improvement in the pressure exponent. It is generally desirable to use a propellant that has a pressure exponent as low as possible to reduce combustion instabilities that may result in unreliable performance or even complete rocket failure. A high burn rate propellant is advantageous in many rocket applications because it allows for a simplification of grain design. To achieve the required burn rate (and, thus, chamber pressure), low

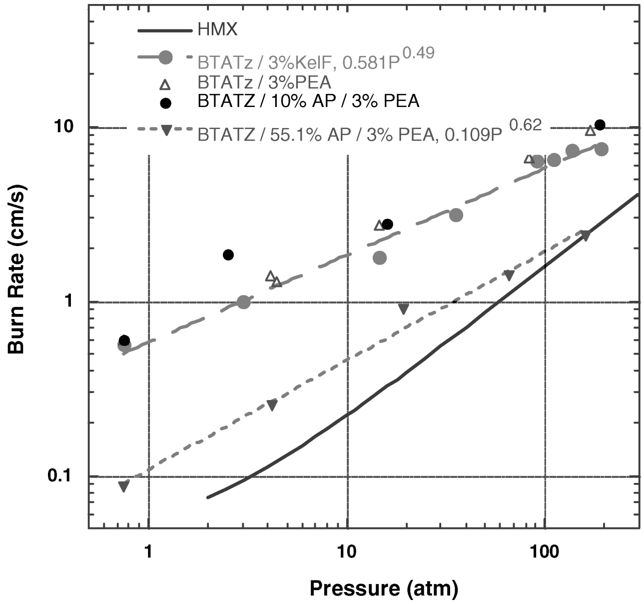


Fig. 4 Burn rate data for BTATz formulations containing the inert binders PEA and Kel-F™ 800 and the propellant oxidizer AP compared with the standard high-performance propellant ingredient, HMX.

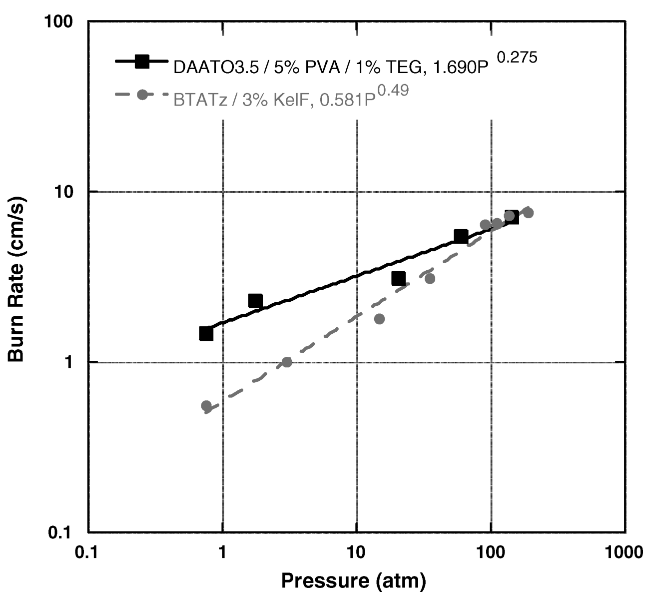


Fig. 5 Burn rate data for a DAATO3.5 formulation containing 5% PVA and 1% TEG.

burn rate propellants need to be configured into a complex geometry grain design with a large surface area. High burn rate propellants reduce the need for complex geometry grain designs. In solid-fuel microthruster applications, high burn rates also allow a larger throat for a given chamber pressure, thus reducing the possibility of clogging due to the expulsion of solid decomposition products.

Though BTATz has a relatively high burn rate, it has the disadvantage of a moderately high-pressure exponent. However, as seen in Fig. 5, DAATO3.5/5%PVA/1%TEG (6.35-mm-diam, 300-mg, 1.52-g/cm^3 pressed pellet) has a higher burn rate than BTATz combined with an extremely low-pressure exponent (0.28). With these unique combustion properties, DAATO3.5 has the foundation to be a highly valuable propellant ingredient. In Fig. 6, DAATO3.5/5%PVA/1%TEG is compared with various types of standardized propellants.[22] It is seen that the burn rate of DAATO3.5/5%PVA/1%TEG is higher than the standard high burn rate composite. In fact, DAATO3.5 is believed to have the highest burn rate of any known organic solid. (This assertion has been

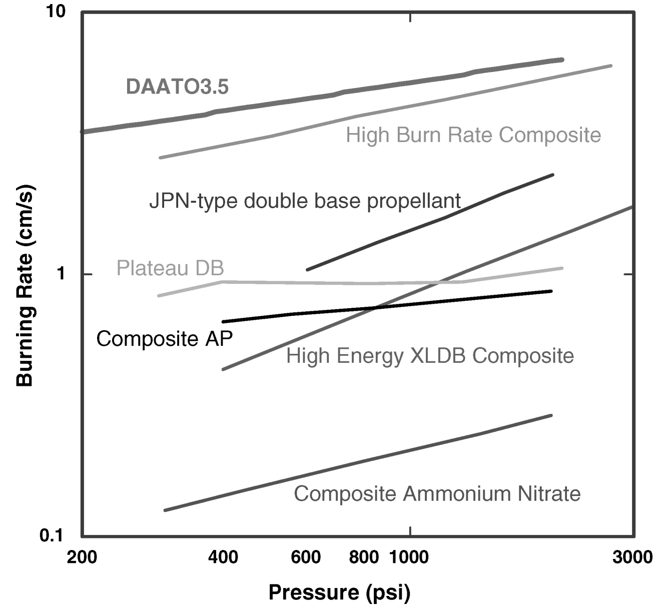


Fig. 6 DAATO3.5/5% PVA/1% TEG compared with various propellant standards.[22]

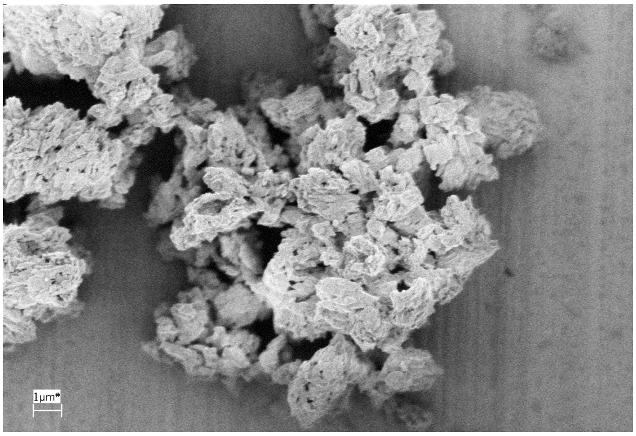


Fig. 7 SEM of DAATO3.5.

presented at several conferences and has not yet been successfully challenged.) From Fig. 6, it is seen that DAATO3.5/5%PVA/1%TEG has one of the lowest pressure exponents (shallow slope). Figure 7 is a scanning electron micrograph (SEM) of pure DAATO3.5, where the most striking feature of the macrostructure is its unusual level of porosity. The extremely fast burn rates of DAATO3.5 could be attributed to its high porosity. The authors also have had difficulty pressing pellets to the theoretical maximum density of 1.9 g/cm^3, and again, this may be due to the high porosity of DAATO3.5. Because it was not possible to press neat DAATO3.5 without a binder, and because binders generally suppress burn rates, it may be expected that the burn rate of pure DAATO3.5 is higher than that published here. In the design of a rocket system, it has been common practice to trade combustion stability (low-pressure exponent) for high performance (high burn rate) or vice versa. That may no longer be necessary with the introduction of DAATO3.5, which provides both an uncommonly low-pressure exponent and an extremely high burn rate.

Electric Match Ignition Tests

BTATz and DAATO3.5 powder samples ranging from 6 to 28 mg had a commercially available bare electric match placed in the sample. Each material had 8 trials in which the pure materials ignited 100% of the time. These results are believed to be related to the relatively high spark sensitivity of BTATz and DAATO3.5. It may, therefore, be expected that the addition of binder would reduce the ignition capability by electric match; however, that has yet to be demonstrated. As already explained, the size and power consumption of the NiChrome bridge wire used in these electric matches fit within the design requirements of digital microthrusters.

Microthruster Test Stand Results

The quartz microthruster test stand was used to measure the thrust and I_{sp} of DAATO3.5 and BTATz. The chosen grain configuration was an endburner, which was created by inhibiting the sides of the pressed material pellet with adhesive. The use of an endburner resulted in a lower peak thrust, but a neutral thrust profile. An example experimental force transducer trace is shown in Fig. 8. A fast Fourier transform analysis of the force traces revealed minor 60-Hz noise in some of the data. Occasionally, the adhesive did not completely inhibit the burn, and the flame would spread down the sides. As the sides regressed, the pellet was reduced in diameter as well as length. This reduction in overall surface burning area resulted in a regressive thrust profile. An example of such an occurrence is shown in Fig. 9.

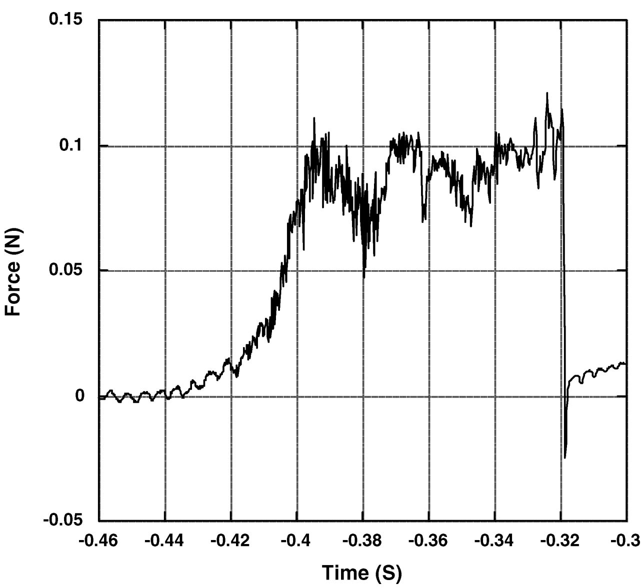


Fig. 8 Force trace from a quartz microthruster with a 0.053-in. throat diameter containing pure DAATO3.5 in an endburner grain configuration.

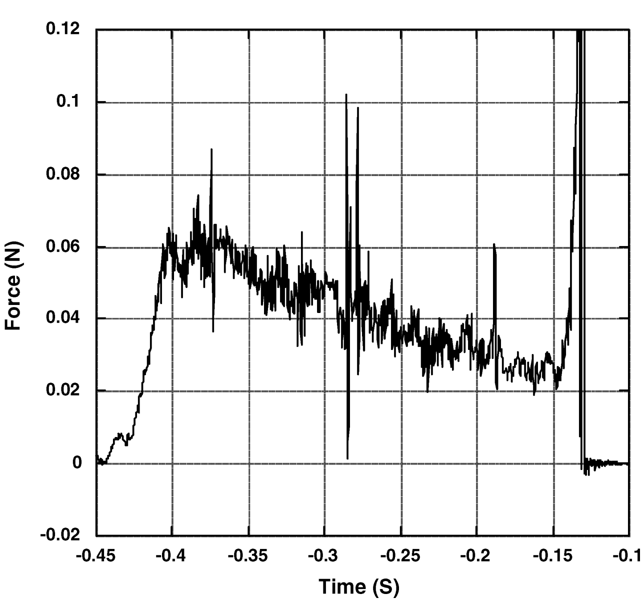


Fig. 9 Force trace from a quartz microthruster with a 0.062-in. throat diameter containing pure DAATO3.5 in an endburner grain configuration.

Figure 9 shows that the larger nozzle size relative to that shown earlier generates a lower thrust but of longer duration. The regressive thrust profile is believed to be due to the flame spreading down the sides of the grain configuration and thus reducing the grain diameter. This grain diameter eventually reached a small enough size to fit through the nozzle throat. Also seen in Fig. 9 is a thrust spike toward the end of the burn. This is most likely due to the recoil force caused by the expulsion of the pellet once its diameter was small enough to fit through the nozzle. To avoid this, the pellet was glued to the front of the thruster. (The recoil was not included in the integration of the force curve to calculate the I_{sp}.)

Another problem that arose was the cracking of the quartz thruster. The quartz proved quite resistant to the thermal shock of the propellant burn and did not crack due to the elevated combustion temperatures. However, to secure the thruster, screw-type clamps were used around the thruster. Occasionally, the clamps were overtightened and cracked the thruster. This resulted in the use of several different thrusters with nozzle throat diameters ranging from 0.050 to 0.068 in. (The manufacturing tolerance of the throats was not very high as already explained.)

The test data for DAATO3.5 and BTATz are shown in Table 2. The time-averaged (over burn duration) specific impulse I_{sp} was calculated by integrating the force trace F with respect to time t to yield the impulse. The impulse is then divided by the propellant weight W, such that

$$I_{sp} = \frac{\int F\,\mathrm{d}t}{W} \tag{1}$$

The propellant weight W is defined as

$$W = mg \tag{2}$$

where m is the propellant mass in kilograms and g is the gravitational acceleration (9.8 m/s^2). It is seen that the measured I_{sp} is fairly low. This is due, in part, to the low chamber pressures. To account for the reduction in I_{sp}, chamber pressures were estimated using the burn rate and pressure data provided in this paper. The burn rates were estimated from the known initial pellet length and from the burn time provided by the force trace. From these estimated burn rates, the chamber pressures were calculated and reported in Table 2. Note that these pressures are just estimates to illustrate the severe inefficiencies of such a small-scale thruster system. Accurately measuring the burn rates of such small pellets is virtually impossible due to the large effect of any minor combustion anomaly. As a result, the chamber pressures, estimated from the burn rates, are not expected to be of any statistical significance other than as an extremely rough gauge of the pressure scale in these experiments. Burn rates for the BTATz tests were not obtained due to incomplete pellet decomposition.

Theoretical I_{sp} at the estimated microthruster chamber pressures (listed in Table 2) were obtained from the CHEETAH 3.0 equilibrium code using 883 kJ/mol and 1.74 g/cm^3 for the heat of formation and density, respectively, of BTATz ($C_4H_4N_{14}$) and 550 kJ/mol and 1.9 g/cm^3 for DAATO3.5 (mixture of 50% $C_4H_4N_{12}O_3$ and 50% $C_4H_4N_{12}O_4$). As a comparison, the theoretical I_{sp} with a chamber pressure of 68.03 atm is 218 s for BTATz and 228 s for DAATO3.5. As a measure of overall efficiency and as an attempt to compare test results from different nozzle sizes, the theoretical I_{sp} for each estimated chamber pressure was divided by the measured I_{sp} and presented as a percentile in the last column of Table 2. The average efficiency for DAATO3.5 is only 14%; however, this was expected due to the extremely small size of the thruster system. Small rocket systems, in general, have inherently poor efficiency due to excessive heat and flow losses (relative to larger systems that have longer burn times and more ideal flow characteristics). The results of our experiments are comparable with previously published results from other research groups. For example, Lewis et al. reported that only 10% of the propellant produced thrust in their digital microthruster design using lead styphnate.[3] Additionally, de Groot et al. reported to see only about half the original propellant mass decompose within the their thruster system.[2]

Table 2 Quartz microthruster experimental test stand results[a]

Material	Impulse, N · s	Measured I_{sp}, s	Estimated chamber pressure,[b] atm	Theory I_{sp}, s	Measure/theory I_{sp}, %
DAATO3.5	0.008	12.8	N/A	N/A	N/A
DAATO3.5	0.018	30.5	18.7	216	14
DAATO3.5	0.020	33.6	18.1	214	16
DAATO3.5	0.014	21.1	2.2	138	15
DAATO3.5	0.014	21.5	2.4	145	15
DAATO3.5	0.011	18.0	3.3	159	11
DAATO3.5	0.011	18.8	3.1	156	12
DAATO3.5/3%Hytemp	0.023	36.0	N/A	N/A	N/A
BTATz	0.003	6.0	N/A	N/A	N/A
BTATz/3%Hytemp	0.007	10.5	N/A	N/A	N/A
BTATz/3%Hytemp	0.007	9.1	N/A	N/A	N/A
BTATz/3%Hytemp	0.009	12.5	N/A	N/A	N/A
BTATz/3%Hytemp	0.010	14.6	N/A	N/A	N/A

[a]Propellant grain masses 55–75 mg; different nozzle sizes used due to frequent cracking of the quartz.
[b]Not available for some tests due to immeasurable burn rates.

It is clear that high I_{sp} (approaching the theoretical I_{sp}) will not be obtainable in any digital solid-fuel microthruster system as they are in large-scale rockets, nor are they critical to microthrusters. Digital solid-fuel microthrusters are completely different from known propellant systems and require highly unique propellant properties. Whereas measures such as specific impulse, propellant density, and peak thrust-to-weight ratio are of prime importance to large-scale rocket systems, in the world of digital micropropulsion, functionality is valued over performance. Issues such as repeatability, ease of ignition, safety, long-term storage, low combustion temperature, noncorrosive combustion products, and inexpensive materials are the determining factors for the selection of the future's micropropulsion propellants.

Future Work

The high nitrogen materials introduced in this paper hold significant promise as microthruster propellants. The propellants will be evaluated at a range of pressures, both higher and lower than those reported here. A clear weakness in the experiments performed is the large variation in the performance data due mostly to the manufacturing tolerances of the quartz thrusters. An attempt was made to eliminate the effect of nozzle variation in the data by trying to estimate chamber pressure from estimated pellet burn rates. This was met with very limited success. Clearly the next step must be the implementation of a microthrust test stand design that has much higher manufacturing tolerances. When more precisely manufactured thrusters and nozzles are used, an acceptable level of performance and measurement reproducibility should be achieved. It is anticipated that increased performance, I_{sp}, will be seen at higher pressures (theoretical I_{sp} increases with pressure). However, due to the extremely small thruster size, it is unclear if an increase in overall efficiency (experimental I_{sp} compared to theoretical I_{sp}) will be seen without a significantly different microthruster test stand design. Plans have already been formulated to use a microthruster test stand design that more closely resembles actual digital micropropulsion systems. The new design will allow higher pressures and incorporate resistive heating ignition, in addition to laser ignition. Integration of the propellants into one of the existing digital micropropulsion systems will be also pursued.

Conclusions

This work evaluated two novel high nitrogen materials, BTATz and DAATO3.5, for use as propellants in micropropulsion systems and compared them with the previously implemented propellants, lead styphnate, GAP, and LAX-112. Material safety data were obtained for BTATz, DAATO3.5, GAP, and lead styphnate. Lead styphnate proved extremely sensitive to impact and spark, which supports its classification as a 1.1 primary explosive. BTATz and DAATO3.5 were relatively insensitive to impact and friction and had a high DSC onset. However, the pure forms of BTATz and DAATO3.5 were very sensitive to electrostatic discharge. The addition of 3–6% binder greatly reduced this spark sensitivity. It is hoped that the strong dependence of BTATz and DAATO3.5 spark sensitivity to binder would allow propellant formulations to be tailored to the specific ignition and safety requirements of a given system. Data were cited that indicated GAP was comparable in impact and friction sensitivity to BTATz and DAATO3.5.

Burn rate data for certain BTATz formulations and DAATO3.5 were presented for the first time. BTATz had a pressure exponent of 0.49 and proved to have an unusually fast burn rate that was significantly faster than HMX for all pressures. DAATO3.5 is believed to be the fastest burning organic solid known with a very low and desirable pressure exponent of 0.28. The pressed density of DAATO3.5 was 1.52 g/cm^3, which was 80% of the TMD of 1.9 g/cm^3. SEM indicated a high degree of porosity in DAATO3.5.

Commercially available electric matches were used as another measure of ignitability. The small size of the wire and minimal power usage (1.5-V AA battery) fits within the design requirements of existing digital micropropulsion systems. BTATz and DAATO3.5 powder both successfully ignited 100% of the time with the bare electric matches.

A quartz microthruster and test stand was used to measure the thrust and specific impulse of BTATz and DAATO3.5 formulations. The propellant was ignited within the thruster with a Nd:YAG laser. Measured specific impulses were highly variable due mostly to the imprecise manufacturing tolerance of the quartz thrusters. The specific impulse values were between 13 and 30 s for DAATO3.5. This represented only 14% of the estimated theoretical specific impulse, which ranged from 156 to 216 s at chamber pressures from 3 to 18 atm. This level of inefficiency is believed to be acceptable for small thruster systems and is comparable to other, independent work. It is anticipated that higher and much more repeatable specific impulse measurements will be seen with higher chamber pressures (theoretical specific impulse increases with pressure) and new, more precise thruster test stand designs. Possible explanations for the low overall efficiency (measured specific impulse compared to theoretical) include heat losses, flow losses, and/or propellant combustion losses due to the specific thruster design chosen. The importance of propellant specific impulse is considered secondary to such functionality issues as repeatability, ease of ignition, safety, long-term storage, low combustion temperature, noncorrosive combustion products, and inexpensive materials. The highly unique properties of BTATz, and especially DAATO3.5 make these materials ideal candidates for use on existing digital micropropulsion designs. The continued evaluation of these materials as microthruster propellants in new, higher pressure microthruster test stand designs and incorporation into existing digital micropropulsion systems is planned.

Acknowledgments

We acknowledge the support of Los Alamos National Laboratory, under contract W-7405-ENG-36. In particular, we acknowledge the support of the Laboratory Directed Research and Development Program of Los Alamos National Laboratory.

References

[1]Mueller, J., "Thruster Options for Microspacecraft: A Review and Evaluation of State-of-the-Art and Emerging Technologies," *Micropropulsion for Small Spacecraft*, edited by M. M. Micci and A. D. Ketsdever, AIAA, Reston, VA, 2000, pp. 45–126.

[2]de Groot, W. A., Reed, B. D., and Brenizer, M., "Preliminary Results of Solid Gas Generator Micropropulsion," AIAA 34th Joint Propulsion Conf., 1998.

[3]Lewis, D. H. J., Janson, S. W., Cohen, R. B., and Antonsson, E. K., "Digital Micropropulsion," *Sensors and Actuators*, Vol. 80, No. 2, 2000, pp. 143–145.

[4]Rossi, C., Rouhani, M. D., and Esteve, D., "Prediction of the Performance of a Si-micromachined Microthruster by Computing the Subsonic Gas Flow Inside the Thruster," *Sensors and Actuators*, Vol. 87, No. 1–2, 2000, pp. 96–104.

[5]Coburn, M. D., Hiskey, M. A., and Lee, K. Y., "Oxidations of 3,6–Diamino–1,2,4,5–tetrazine and 3,6–Bis(S,S–dimethylsulfilimino)–1,2,4,5–Tetrazine," *Journal of Heterocyclic Chemistry*, Vol. 30, No. 6, 1993, pp. 1593–1595.

[6]Cramer, R. J., Sitzmann, M., Devendorf, T., and Peters, S., "Dihydrazinotetrazine: A New Energetic Material for Advanced Gun Propellant Formulations," Indian Head Division, U.S. Naval Surface Warfare Center, Indian Head, MD, IHTR 2226, 15 Oct. 1999.

[7]Chavez, D. E., Hiskey, M. A., and Gilardi, R. D., "3,3′–Azobis(6–amino–1,2,4,5–tetrazine): A Novel High-Nitrogen Energetic Material," *Angewandte Chemie International Edition*, Vol. 39, No. 10, 2000, pp. 1791–1793.

[8]Hiskey, M. A., Chavez, D. E., Naud, D. L., Son, S. F., Berghout, H. L., and Bolme, C. A., "Progress in High-Nitrogen Chemistry in Explosives, Propellants, and Pyrotechnics," *Proceedings of the International Pyrotechnics Seminar*, International Pyrotechnics Seminars USA, Inc., Chicago, IL, 2000, pp. 3–14.

[9]Chavez, D. E., and Hiskey, M. A., "1,2,4,5–Tetrazine-Based Energetic Materials," *Journal of Energetic Materials*, Vol. 17, No. 4, 1999, pp. 357–377.

[10]Son, S. F., Berghout, H. L., Bolme, C. A., Chavez, D. E., Naud, D., and Hiskey, M. A., "Burn Rate Measurements of HMX, TATB, DHT, DAAF and BTATz," *Proceedings of the Combustion Institute*, Vol. 28, Pt. 1, 2000, pp. 919–924.

[11]Hiskey, M. A., Chavez, D. E., and Naud, D., "Propellant Containing 3,6–Bis(1H–1,2,3,4–Tetrazol–5–ylamino)–1,2,4,5–Tetrazine and Salts Thereof," U.S Patent 6,458,227, 1 Oct. 2002.

[12]Hiskey, M. A., Chavez, D. E., and Naud, D., "Preparation of 3,3′–azobis(6–amino–1,2,4,5–tetrazine)," U.S. Patent 6,342,589, 29 Jan. 2002.

[13]Metzner, A. P., and Coffey, C. S., "Hot Spot Initiation of Plastic-Bonded Explosives during the Rapid Flow Phase of the Drop Weight Impact Test," *10th Detonation Symposium*, Office of Naval Research, Arlington, VA, 1993, pp. 219–223.

[14]Larson, T. E., Dimas, P., and Hannaford, C. E., "Electrostatic Sensitivity Testing of Explosives at Los Alamos," *9th Detonation Symposium*, Office of the Chief of Naval Research, Arlington, VA, 1989, pp. 1076–1083.

[15]Coley, G. D., "The Growth of Reaction in Secondary Explosives Under Transient Confinement," *6th Detonation Symposium*, Naval Surface Weapons Center, White Oak, MD, 1976, pp. 290–298.

[16]Stinecipher, M. M., and Stretz, L. A., "Sensitivity and Performance Characterization of Dingu", *8th Detonation Symposium*, Naval Surface Weapons Center, White Oak, Silver Spring, MD, 1985, pp. 351–356.

[17]Dyer, A. S., and Taylor, J. W., "Initiation of Detonation by Friction on a High Explosive Charge," *5th Detonation Symposium*, Office of Naval Research, Arlington, VA, 1970, pp. 291–300.

[18]Whitbread, E. G., "Sensitiveness Testing and Its Relation to the Properties of Explosives," *3rd Detonation Symposium*, Office of Naval Research, Arlington, VA, 1960, pp. 659–670.

[19]Fedoroff, B., and Sheffield, O. E., Encyclopedia of Explosives and Related Items, Vol. 5, Picatinny Arsenal, Dover, NJ, 1972, pp. 1278–1281.

[20]Frankel, M. B., Grant, L. R., and Flanagan, J. E., "Historical Development of Glycidyl Azide Polymer," *Journal of Propulsion and Power*, Vol. 8, No. 3, 1992, pp. 560–563.

[21]Provatas, A., "Energetic Polymer and Plasticisers for Explosive Formulations—A Review of Recent Advances," Aeronautical and Maritime Research Lab. Melbourne, VIC, Australia, DSTO-TR-0966, April 2000, p. 37.

[22]Sutton, G. P., and Biblarz, O., Rocket Propulsion Elements, 7th ed., Wiley, New York, 2001, p. 429.